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Effect of Dissolution and Refaceting on Growth Rate Dispersion of Sodium Chlorate and Potassium Dihydrogen Phosphate Crystals

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ABSTRACT: Effects of partial dissolution and refaceting on growth rates of sodium chlorate and potassium dihydrogen phosphate (KDP) crystals are presented. Under the same external conditions, crystals of sodium chlorate and KDP exhibit growth rate dispersion (GRD), prior to dissolution and after refaceting. These GRDs were described by multiple normal distributions. Dissolution and refaceting reduce the GRD. A number of growth rates pertained to higher order maxima decreases, whereas a number of those pertained to lower order increases, that is, crystals continue to grow at leveled rates. Maxima positions are related to the activity of dominant dislocation groups emerging on the crystal surface. Many nongrowing {100} faces of sodium chlorate and KDP crystals, as well as the nongrowing roofs of KDP crystals, were also noticed before dissolution and after refaceting, which is related to a lattice strain effect.

INTRODUCTION

Under the same solution and external conditions, different crystals of the same material grow at different rates. This phenomenon, termed as the growth rate dispersion (GRD), which occurs for a number of inorganic and organic crystals generated by primary or secondary nucleation, is still not understood well.[1−4] Also, it was shown that under the same external macroscopic conditions, specific crystal faces grow at different rates, that is, a GRD of crystal faces occurred.[5,6]

Recently it was shown that in the first few hours of the growth period, the majority of the crystal growth rates decreased, and did not change significantly later.[7] Leveling of the growth rates during the growth occurred as well.

The growth rate dispersion affects the crystal size distribution, and hence the industrial crystallizers product quality. Changing the growth temperature or the solution supersaturation is the usual way of altering the crystal growth rate (or size) distribution. Another way is to change the parameters influencing GRD at a specific temperature and supersturation. Therefore, studying the crystal growth rate distributions under the same external conditions is important, especially the ways that they affect them. It is shown that partial dissolution of crystals, and the subsequent resumption of their growth, changes these distributions.[6,8] Effects of the growth rate history on current growth rate was studied through the changes in the supersaturation,[9,10] and crystal dissolution and refaceting.[8]

As is shown, GRD of sodium chlorate crystals in the ⟨100⟩ direction can be described by multiple normal distributions.[11] Recently we have shown that after the dissolution and refaceting, fast growing faces disappeared.[6] All faces either grow at rates that correspond to one GRD maximum, or they did not grow at all. These considerable changes in the growth rate distributions might be significant for the quality of products in industrial crystallizers. We test whether the same conclusion is valid for different supersaturations of sodium chlorate and potassium dihydrogen phosphate (KDP) solutions, and the results are presented in this paper.

Distribution changes are correlated with the activity of the dominant dislocation group emerging on the crystal faces.

EXPERIMENTAL SECTION

The purpose of our experiments was to investigate the growth rate of small sodium chlorate (SC) and KDP crystals from aqueous solutions. The analar grade of these systems (99% purity) was used. The relative solution supersaturation, expressed in mass %, was calculated as $\sigma = (C - C_0)/C_0$, where C and C_0 are saturation concentrations at the saturation temperature of the solution (actual concentration) and at the growth temperature, respectively. Concentrations are calculated on the basis of the empirical formulas $C = 0.226T(°C) + 44.38$ (g NaClO$_3$/100 g solution),[12] for sodium chlorate and $C = 0.0000743T^2(°C)^2 + 0.00102T(°C) + 0.17554$ (kg KDP/kg solute)[13] for KDP.

The solutions were prepared by equilibrating an excess of crystals with distilled water for 3 days at a saturation temperature. The number of growth rates measured, N, the saturation temperature of solution, T_0, the crystal growth temperatures, T, the corresponding relative supersaturations, σ, the range of initial crystal sizes, l_0, and the range of crystal sizes after refaceting, L_0, are listed in Table 1.

Crystals were nucleated in the cell by introducing air bubbles through a needle into the cell. The nucleation of crystals was performed at the growth temperature in order to reduce the risk of uncontrolled growth conditions changes. The experimental setup as well as the procedure of nucleation is previously described in detail.[7] Crystal dimensions were measured by digital optical microscope Nikon SMZ800 supplied by camera Luminera, Infinity 1, using a transmitted light. Crystal growth over time was then recorded for the preselected crystals. Between 20 and 33 crystal nuclei,

Table 1. Experimental Conditions

crystal	direction	N	T_0 [°C]	T [°C]	σ (mass %)	l_0 [mm]	L_0 [mm]
SC	$\langle 100 \rangle$	292	30.0	28.0	0.9	0.018−0.288	0.171−0.884
	$\langle 100 \rangle$	155				0.018−0.257	0.126−0.918
KDP	[001]	128	31.0	26.0	10.4	0.023−0.433	0.193−1.368

sufficiently distant to avoid intergrowth during the growth, were chosen for growth rate measurements during each growth run.

The performed experiments consisted of three parts. In the first part the crystals were nucleated and grown for about 4 h at a temperature T. In the second part the dissolution and refaceting of crystals were performed. The temperature of the solution was increased to $T_d = (34.0 \pm 0.1)$ °C with a heating rate of about 0.5 °C/min. The solution was kept at this temperature for about 25 min during which the crystals were dissolved and rounded. At the end of the dissolution, crystal sizes in the observed directions were reduced for at least 20%. While some crystals completely dissolved, others were used as seeds for the third part of the experiments. After that the temperature of the solution was rapidly decreased to a growth temperature T, which was the same as in the first part of the experiments. This procedure provided fast refaceting of the crystals having clear borders between the dissolved and newly growing parts.

Habitus of the observed sodium chlorate crystals is dominantly determined by {100} faces. Faces with higher indices also appear (Figure 1a,b). Observed KDP crystals

Figure 1. Habitus of sodium chlorat crystals, (a) schematic, and (b) observed; and KDP crystals, (c) schematic and (d) observed.

contain two triangular prisms (roofs), at the opposite sides of the crystal, whose central part is a rectangular prism (Figure 1c). Between the central part and the roofs, different faces can appear, for example {301} (Figure 1d). Growth in the $\langle 100 \rangle$ direction of sodium chlorate and KDP crystals is determined by the growth rates of two {100} faces at opposite sides of the crystal.

The triangular prism on top of the KDP crystal is determined by four {101} faces, whereas the roof growth rate (R_{roof}) is

determined by growth rates of two {101} faces. The growth rate in the [001] direction of KDP is the sum of two opposite roof growth rates.

Growth rates prior to the dissolution were calculated using two experimental data after 3 h of growth. In the paper[6] these growth rates are denoted as stabilized, whereas in the paper[7] they are denoted as intermediate because it is shown that some of them slightly decreased. Crystal length versus time dependence was subjected to the least-squares method in order to determine the corresponding average linear growth rates after refaceting.

For the face and roof growth rates measurements, a reference point is necessary.[6] The dissolution and refaceting of the crystals provided the defects formed on the border between seed and the newly grown part. Defects are not further changed, so they were good reference points for face and roof displacement measurements. Face and roof growth rates were determined by measuring their displacement from the reference point during the time of observation. The accuracy of crystal length, roof, and face displacement measurements was about ± 2 μm.

■ **RESULTS**

The growths of 64 sodium chlorate crystals (in the $\langle 100 \rangle$ direction), and 64 KDP crystals (in both the $\langle 100 \rangle$ and [001] directions) were observed. Significant growth rate dispersion occurred for both investigated substances, even though all the crystals grew under the same macroscopic external conditions. As is shown earlier[7] the growth rates for most of the observed crystals decreased during the first two to 3 h of growth. Also, leveling of the crystal growth rates prior to the dissolution is evident.

Histograms representing growth rate dispersions are presented in Figure 2 for sodium chlorate in $\langle 100 \rangle$ direction, and {100} faces, Figure 3 for KDP in $\langle 100 \rangle$ direction, and {100} faces, and Figure 4 for KDP in [001] direction, and roofs. In all figures panel a denotes the directional growth prior to dissolution, panel b is the directional growth after refaceting, and panel c is the faces or roofs growth after refaceting.

To describe the growth rate distributions, the fitting of the finite mixture of normal distributions to the frequency distributions was performed. Details of the fitting procedure were described previously.[14] The growth rates at the beginning and end of the distributions were excluded from the fitting procedure since they did not pertain to any of the maxima. The distributions obtained are also included in the Figures

It can be seen from Figures 2−4 that the number of analyzed growth rates provides a good definition of different numbers of maxima in the crystal growth rate distributions. Prior to the dissolution there are three maxima for both substances investigated in all directions (Figures 2a, 3a, 4a). After refaceting (direction) there are two dominant maxima in the distributions for sodium chlorate in $\langle 100 \rangle$ and KDP crystals in the $\langle 100 \rangle$ direction (Figure 2b, 3b), and the three maxima in the distribution for KDP in the [001] direction (Figure 4b),
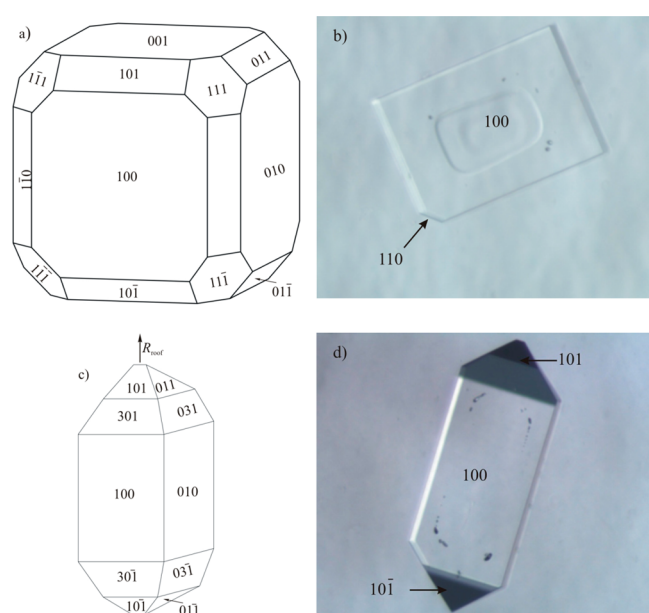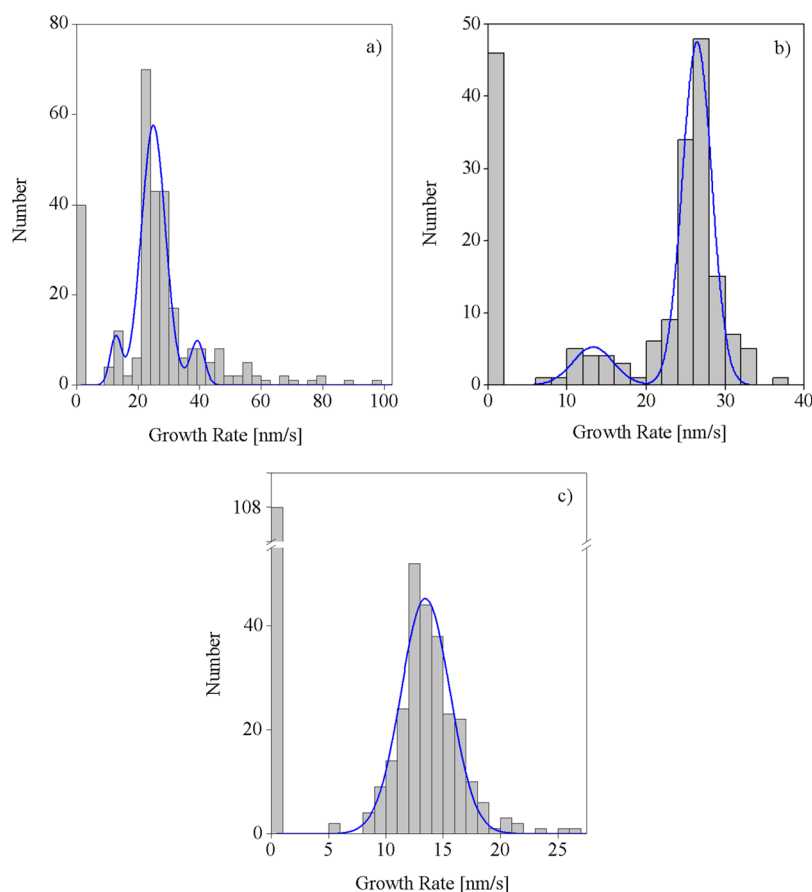
Figure 2. Histograms representing distributions of sodium chlorate crystal growth rates: (a) in $\langle 100 \rangle$ direction prior to dissolution, (b) in $\langle 100 \rangle$ direction after refaceting, (c) of $\{100\}$ faces after refaceting.

After refaceting (face and roof) there is one maximum for sodium chlorate $\{100\}$ face growth rates, and one the for $\{100\}$ KDP face growth rates (Figure 2c, 3c), and two maxima for the KDP roof growth rates (Figure 4c).

A great number of nongrowing $\{100\}$ faces of sodium chlorate (Figure 2c), and nongrowing roofs of KDP crystals (Figure 4c) exist after refaceting. Table 2 presents the growth rates R_1, R_2, and R_3, which correspond to the first, second, and third distribution maxima, respectively.

■ DISCUSSION

It can be seen from Figures 2a–4a that a wide range of growth rates, of all the investigated substances before the crystals dissolution and after the refaceting, exists (growth rate dispersion). The crystal growth rates differ as much as 10 times for crystals in the same growth run, despite the fact that the growth conditions in the cell kept constant. The dissolution and refaceting decreases the dispersion of growth rates.

As is shown earlier[15] growth rates are grouped around several values. Different number of analyzed growth rates provided a good definition of different numbers of the distribution maxima for investigated dispersions. According to the (Burton–Cabrera–Frank) BCF theory,[16,17] the dislocation structure of the crystals is the cause of the growth rate dispersion that occurred. Growth rate is determined by the activity of the dominant dislocation group (ε) emerging on the crystal surface. The distribution maxima are probably defined by it, whereas dispersions of growth rates around the maxima are a

consequence of different configurations of the dislocation groups.[18]

As is evident from Table 2, the position of the distribution maxima practically stays the same after the dissolution and refaceting. It is in accordance with the earlier occurring constancy of stabilized growth rates.[7,19] Nongrowing crystals existed before dissolution and after refaceting.

Nongrowing faces may be dislocation free or may have the dislocations of opposite signs canceling one another. Assume that ε_1 is minimal, and ε_2 is the smallest after ε_1 activity of the dominant dislocation group. The nongrowing faces activity denotes as 0. After the refaceting, almost all of the $\{100\}$ face growth rates of sodium chlorate crystals correspond to the zero bar and one maximum (Figure 2c). This is probably a consequence of 0 and ε_1 activities. Similarly, one maximum for the $\{100\}$ faces growth rate distribution of KDP crystals corresponds to their minimal activity of ε_1 (Figure 3c).

The zero growth of sodium chlorate and KDP crystals in the $\langle 100 \rangle$ direction is the consequence of zero dislocation activity on opposite sides of the crystals. More than one maximum in growth rate distributions might be a consequence of different combinations of activities of the dominant dislocation groups on the opposite crystal faces. The zero bar and the first several distribution maxima probably correspond to the following combinations of activities 0–0, 0–ε_1, ε_1–ε_1, 0–ε_2, ε_1–ε_2, ε_2–ε_2, 0–ε_3, etc.

As is evident from Table 2, for the growth of sodium chlorate and KDP crystals in the $\langle 100 \rangle$ direction, the growth rates distribution maxima correspond to an integer multiple of the
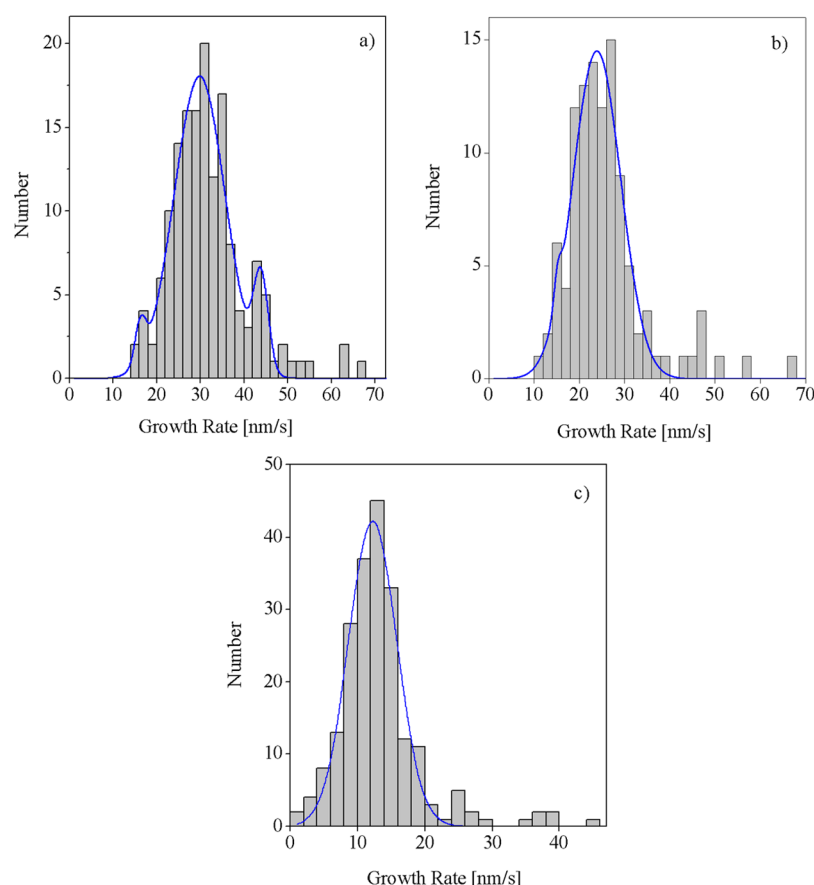
Figure 3. Histograms representing distributions of KDP crystals growth rates: (a) in $\langle 100 \rangle$ direction prior to dissolution, (b) in $\langle 100 \rangle$ direction after refaceting, and (c) of $\{100\}$ faces after refaceting.

$\{100\}$ face growth rate distribution maximum. Differences between adjacent growth rate maxima are practically the same (Table 2), suggesting that the face with activity ε_2 has double the growth rate of the face with activity ε_1. Consequently, the first maximum in Figures 2a,b and 3a,b probably correspond to $0-\varepsilon_1$, the second to $\varepsilon_1-\varepsilon_1$ or $0-\varepsilon_2$, and the third to $\varepsilon_1-\varepsilon_2$ or $0-\varepsilon_3$ activity combinations. The most probable reason for a dominant second maximum of distributions is the highest probability of both face growth with minimal activity (ε_1). This maximum also corresponds to $0-\varepsilon_2$ activities combination, which additionally contributed to it.

The roof growth rate of a KDP crystal is determined by growth rates of two $\{101\}$ faces, that is, by the activity of dominant dislocation groups emerging on it, whereas growth in the $[001]$ direction (two roofs) is determined by different combinations of possible activities of four $\{101\}$ faces. From Table 2 and Figure 4c it is evident that the second maximum of roof growth rate corresponds to the double value of the first one. It can be assumed that the growth rate of one roof is determined by $0-0$, $0-\varepsilon_1$, $\varepsilon_1-\varepsilon_1$, $0-\varepsilon_2$ combination of activities of $\{101\}$ adjacent faces. The growth rate in the $[001]$ direction distribution maxima corresponds to an integer multiple of the first one.

Because the growth in the $[001]$ direction of the KDP crystal is the sum of two opposite roof growth rates, three maxima in Figure 4a,b are probably consequences of the following combination of face activities on the direct/opposite crystal sides: the first, $0-0/0-\varepsilon_1$; the second, $0-\varepsilon_1/0-\varepsilon_1$, and $0-0/0-\varepsilon_2$; the third, $0-\varepsilon_1/0-\varepsilon_2$, $0-\varepsilon_1/\varepsilon_1-\varepsilon_1$, and $0-0/0-\varepsilon_3$.

As is evident from Figures 2a,b–4a,b, the dissolution and refaceting reduce the ranges of measured growth rates, that is, growth rate dispersions. A number of growth rates pertained to higher order maxima decreases, whereas a number of those pertained to lower order increases because of these processes.

The coexistence of growing and nongrowing crystal faces in supersaturated solutions is unexpected.[6] This phenomenon is even more unexpected after the dissolution and refaceting. Namely, refaceting process produces many defects on the boundary between the seed and newly grown portion, including visible inclusions (see Figure 1). These boundaries are most probably the sources of the greatest number of dislocations in the growing crystal.[20] The emergence of dominant dislocation groups with high activity would be expected. In particular, the occurrence of the dislocation free faces or canceling of the opposite sign dislocations, could not be expected.

One of the possible causes of the growth rate dispersion phenomenon is uneven mosaicity (lattice strain) among the investigated crystals.[21–23] It is shown that slower growing crystals were more strained than the faster ones, which was shown for sodium chlorate too.[24] Reduction of the growth rates by dissolution and refaceting is in accordance with the lattice strain theory. These processes increased the chemical potential of the crystal, which reduces the crystal growth driving force. If it is equal to the chemical potential of the solution, the crystal does not grow. The lattice strain theory does not anticipate the existence of the maxima in the probability of the appearance of the crystals of certain values of the mosaic spread, that is, the established maxima in growth rate distributions.
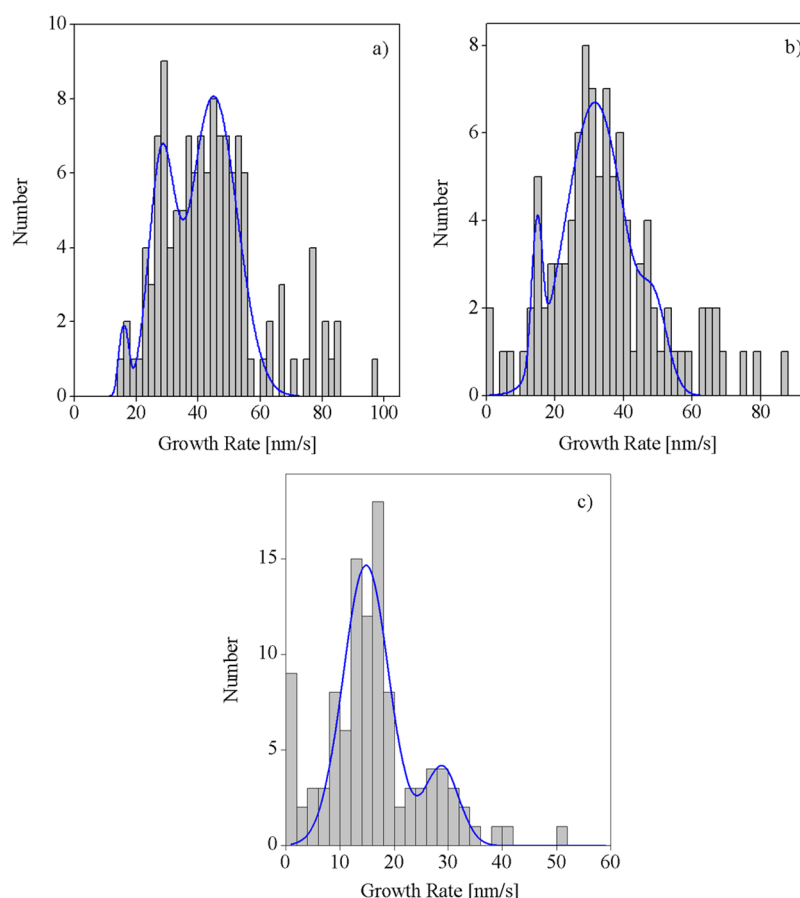
Figure 4. Histograms representing distributions of KDP crystals growth rates: (a) in [001] direction prior to dissolution, (b) in [001] direction after refaceting, and (c) of roofs after refaceting.

Table 2. Parameters Describing Growth Rate Distributions

crystal	rate in		R_1 [nm/s]	R_2 [nm/s]	R_3 [nm/s]
SC	$\langle 100 \rangle$	prior to dissolution	13 ± 1	25 ± 1	39 ± 2
		after refaceting	13 ± 2	26 ± 1	
	$\{100\}$	after refaceting	13 ± 1		
KDP	$\langle 100 \rangle$	prior to dissolution	15 ± 2	30 ± 1	45 ± 1
		after refaceting	14 ± 1	25 ± 1	
	$\{100\}$	after refaceting	14 ± 1		
KDP	[001]	prior to dissolution	16 ± 1	28 ± 1	45 ± 2
		after refaceting	15 ± 1	32 ± 1	49 ± 2
	roofs	after refaceting	15 ± 1	29 ± 2	

In summary, the BCF and lattice strain theories anticipate growth rate dispersion. The existence of the maxima in growth rate distributions can be explained by the BCF theory, but coexistence of growing and nongrowing crystal faces in supersaturated solution contrary to the theory. On the other hand, a decrease of the growth rates induced by dissolution and refaceting is in accordance with the lattice strain theory, but this theory did not predict the existence of the maxima in growth rate distributions.

As is mentioned above, the dissolution and refaceting reduce the growth rate dispersions, and decrease the higher order maxima. A similar effect of leveling of the crystal growth rates during the long growth period was noticed recently.[7] It is shown that in most cases, the growth rate of sodium chlorate, KDP, and Rochelle salt crystals decreases with time (size). After

3 h, a wide range of growth rates (intermediate growth rates) of sodium chlorate crystals in the $\langle 100 \rangle$ direction, initially sized 0.018−0.288 mm, occurred. About 10 h was needed for the leveling of crystal growth rates (stabilized growth rate). Then, rare growth rates were out of the first two distribution maxima, and crystals reached sizes in the range 0.171−0.884 mm.

Our results show that dissolution and refaceting level growth rates of small 0.171−0.884 mm sodium chlorate crystals—all growth rates in $\langle 100 \rangle$ direction pertain to two maxima and the $\{100\}$ face growth rates pertain to one maximum. Even though the mechanisms of influence of these processes on crystal growth kinetics are not clear, obtained results might be important for the industry, because product properties, especially crystal size distribution, strongly depend on the crystal growth kinetics. By the dissolution and refaceting of small crystals, it is possible to obtain crystals with more similar size.

■ CONCLUSION

Under the experimental conditions presented in this paper, prior dissolution of both sodium chlorate and KDP crystals exhibits a wide growth rate dispersion, which can be described by normal distributions with more maxima. After dissolution and refaceting, the growth rate dispersions became significantly narrower. The majority of face growth rates placed under a single maximum; that is, crystals continued to grow at leveled rates. Some of obtained results are in accordance with BCF theory, but some of them are in contrast to it. The increase of

the crystal lattice strain during the refaceting explains only a few results that have been obtained.

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Notes

The authors declare no competing financial interest.

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