

Incorporation of Ionic Impurities in Crystals Growing from Solution.

The Case of Lead Ions in Potassium Chloride Crystals

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Single seed crystals of potassium chloride were grown from aqueous solutions under conditions of constant temperature, supersaturation, and impurity concentration. With emission spectrography as the method of analysis, the distribution of various metal ion impurities between the grown potassium chloride crystal and the solution was studied. The distribution coefficients of Pb^{++} , defined as the ratio of the impurity concentration in the crystal to the concentration in solution, were found to be greater than unity at very low concentrations. The lead distribution coefficients varied between 2,700 (for solutions containing 10^{-8} moles of lead/mole of potassium chloride to 28 (for solutions of 10^{-5} moles of lead/mole of potassium chloride).

The results suggest a mechanism of nonequilibrium capture of the impurity. The magnitude of the distribution coefficient is shown to depend on the equilibrium distribution coefficient between the solution and surface of the crystal, the rate of growth of the crystal, and the rate of diffusion of the impurity through the crystal lattice. These results are believed to be of significance in the purification of materials by fractional crystallization. For instance, they indicate that in order to produce crystals of lead-free potassium chloride, the conventional techniques or recrystallization should be modified to include rejection of the first crystals grown.

Purification by recrystallization from an impure solution is predicated on the assumption that the ratio of impurity to crystallizing species in the solution is greater than in the crystal. In crystallization practice, this assumption is almost always made. Radiochemists, however, working with radioisotopes, have found that the effective distribution coefficient defined as $k_{eff} = C_c/C_L$, where C_c is the impurity to crystallizing species molar ratio in the crystal, and C_L , the same ratio in the solution, was, for certain impurities, greater than unity at low impurity concentrations. Cases reported are lead in alkali halides (9, 11) (k_{eff} varied for each halide from 10 to 60, for potassium chloride $k_{eff} = 57$), lead and radium in alkali sulfates (9), and cadmium in sodium chloride (3). It was also found that lead in sodium chloride was incorporated in the (100) but not in the (111) faces (4). A few cases of ions (zinc, manganese, mercury, bismuth, chromium, nickel) which were not incorporated in alkali halide or sulfate crystals (that is, $k_{eff} < 1$) were also reported (3, 4, 13). It should be emphasized that in these studies very low impurity concentrations in the solutions were used (molar ratio of impurity $< 10^{-6}$). At higher impurity concentrations, however, the distribution coefficient may be higher than unity. This can explain why the phenomenon of strong impurity incorporation (that is, $k_{eff} > 1$) has not been recognized in industrial crystallization practice.

Recently, however, the interest of chemical engineers in the phenomenon of the incorporation was enhanced for two reasons: First, there is a need for extremely pure

crystals, and second, the recent advancements in crystal growth theory would permit a better understanding of the mechanism of impurity incorporation in crystals grown from solution, provided that meaningful experimental data were available. It was the purpose of this investigation to provide such data and to interpret them by relating the incorporation of the impurity to elementary crystal growth processes.

In previous studies crystals were grown by cooling or evaporating a saturated solution with little or no stirring. Under these conditions, the supersaturation and the temperature and the concentration of the impurity in the solution were not maintained constant. In addition, the liquid phase diffusion of the impurity may have controlled the amount incorporated in the crystal. In the present studies the crystals were grown under carefully controlled and constant conditions of mass transfer rates, temperature, supersaturation, and impurity concentration in the solution.

EXPERIMENTAL PROCEDURE

Single seed crystals of potassium chloride were cleaved from larger melt crystals. As used, the seeds were rectangular parallelepipeds with only (100) faces. Their dimensions were from 1 to 2 mm.

Growth studies were carried out in a crystallizer flask containing a supersaturated solution of potassium chloride. Seeds were held in place by tweezers. Growth could then occur naturally on only four of the six possible faces. The solution was stirred vigorously. Growth rates were not mass transfer controlled as the stirring rate was always maintained sufficiently high so that variation in the rate produced no noticeable effect on the growth rates.

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Evaporation of the solution during the studies was prevented by seals in the crystallizer flask. The temperature in the crystallizer was about $35 \pm 0.01^\circ\text{C}$. The depletion of the solution by the growing crystal, with respect to both solute and additives, was negligible.

The saturated solutions were prepared by mixing an excess of reagent grade potassium chloride (Baker analyzed) with triple-distilled water and stirring the mixture for at least 18 hr. During this time the flask was held in a constant-temperature bath to within $\pm 0.01^\circ\text{C}$. The saturated solution was transferred to the crystallizer flask through a heated glass tubing. In this transfer a sintered glass filter in the tube prevented carry-over of undissolved crystals. The supersaturation was determined from the difference of the temperatures in the saturation and the crystallization flasks.

The dimensions of the crystals were measured under a microscope ($50 \times$ magnification) before and after growth. From the difference of the two measurements over the duration of growth (1 to 8 hr.), the growth rates normal to each face was calculated.

Impurity concentrations in the dry crystals were determined spectrographically. The impurities determined were Pb^{++} , Fe^{++} , Ti^{++} , Bi^{++} , and Hg^{++} . The incorporation of Pb^{++} , however, was the most thoroughly investigated. The impurity levels which could be detected by the analytical method were: 0.1 p.p.m. for lead and iron, 0.5 p.p.m. for bismuth, 1 p.p.m. for titanium, and 10 p.p.m. for mercury.

EXPERIMENTAL RESULTS AND THEIR VALIDITY

The potassium chloride crystals, which were analyzed for lead content, consisted of two parts: that belonging to the original seed crystal, and the grown part. The lead concentration in the grown part of the crystal was calculated from the weight of each part and the concentration of lead in the seed. The calculated values are summarized in Table 1, together with the experimental conditions under which each crystal was grown.

An uncertainty was introduced in the above calculation by the impurity content of the seed crystal. As noted earlier, these seed crystals were cleaved from a larger melt crystal. Unexpected variations in the impurity level of the melt crystal were noted, that is, such crystals were found to be inhomogeneous. It can be shown that these impurity variations would, however, not affect significantly the magnitude of the final value of the impurity concentration in the grown crystal. They can account, however, for the observed scattering of the data.

Another factor contributing to the overall error is the

difficulty in measuring the small weight of the grown part, as it is obtained as the difference between two large numbers: the weight of the crystal before and after growth. This contribution to the error is presented in Table 1 as the "estimated percentage error."

The precision of the analytical method was checked by making two or three impurity level determinations on samples taken from the same grown crystal. The average percentage deviation among these determinations was about 11%.

DISCUSSION

Crystal Lead Concentration as a Function of the Solution Lead Concentration

As shown in Table 1, the concentration of lead in the potassium chloride crystals ranged from 21×10^{-6} moles/mole of potassium chloride for the most dilute solutions up to 280×10^{-6} for the solution of 10^{-5} moles of lead chloride/mole of potassium chloride. The corresponding effective distribution coefficient k_{eff} ranged from 2,700 to 28. There is a scattering in the values of the distribution coefficients for each lead concentration in the solution. For instance, for a solution concentration 0.1×10^{-6} moles of lead/mole of potassium chloride, k_{eff} varies from 560 to 1,680, depending on the growth rate of the crystal. Nevertheless, there is a definite qualitative trend, indicating that the distribution coefficient decreases with an increase in lead content of the solution.

The work of Yamamoto (13) indicates that at high lead solution concentrations, k_{eff} has values smaller than unity. From his data it also appears that the azeotropic crystallization concentration for lead (that is, $k_{\text{eff}} = 1$) is about 10^{-3} moles of lead chloride/mole of potassium chloride; this is the concentration of lead in the crystal which cannot be reduced by further recrystallization in the conventional manner.

Kading (11) has reported the distribution coefficient for the system lead chloride-potassium chloride to be 57 and independent of the experimental conditions and for all impurity concentrations in the solution up to 10^{-4} moles of lead chloride/mole of potassium chloride. However, his experimental conditions were different from the conditions of this investigation: his crystals were produced in an unstirred solution, and the lead ion concentration was not kept constant during a run.

TABLE 1. LEAD CONTENT OF POTASSIUM CHLORIDE CRYSTALS GROWN FROM SOLUTION

Conditions of crystal growth			Concentration of lead, moles/mole of potassium chloride			
Supersaturation, %	Stirring rate, rev./min.	Growth rate of (100) face, μ/hr .	In solution		Estimated percentage error	Effective distribution coefficient
			In solution	In crystal		
0.16	1,000	Dendritic	0.01×10^{-6}	22×10^{-6}	± 5	2,200
0.06	1,000	52 ± 2.5	0.01	21	2.5	2,100
0.09	1,000	57 ± 1.5	0.01	27	3	2,700
0.26	850	6 ± 1.0	0.1	168	20	1,680
0.32	850	15 ± 5.0	0.1	94	17	940
0.35	850	25 ± 7.5	0.1	145	17	1,450
0.38	1,100	25 ± 7.5	0.1	120	20	1,200
0.38	850	27 ± 7.5	0.1	83	17	830
0.38	400	27 ± 7.5	0.1	93	20	930
0.44	1,100	42 ± 7.5	0.1	78	13	780
0.44	850	42 ± 7.5	0.1	165	15	1,650
0.44	650	76.5 ± 12.5	0.1	77	10	770
0.44	400	101 ± 12.5	0.1	56	9	560
0.51	850	Dendritic	0.1	76	9	760
1.60	900	52 ± 2.5	1	200	3.5	200
2.18			10	280	70	28

Variation of the Crystal Lead Concentration with the Crystal Growth Rate

The concentration of lead in the grown potassium chloride crystal as a function of the growth rate [only the rate of the (100) faces was actually measured] is plotted in Figure 1 for a constant lead concentration in the solution of 10^{-7} moles/mole of potassium chloride. In spite of considerable scattering (due probably to the variation in the lead content of the seed crystal), there is a decrease in the lead content as the growth rate increases.

To explain the relationship between the crystal impurity concentration and growth rate, a model is proposed that is actually an extension of the theory introduced by Hall (10) for the incorporation of impurities in crystals grown from melt. According to his theory, at very slow growth rates, the concentration of the impurity in the crystal approaches some equilibrium value, C_o , which is constant for any crystal-impurity system. C_o values for the Pb^{++} -KCl system are, however, not known. The surface (equilibrium) concentration C_s^o is not equal to C_o even in this limiting case, but it is a reasonable assumption that $C_o < C_s^o > C_L$, where C_L is the liquid bulk concentration value.

As the crystal grows, the surface layers (at a concentration C_s^o) are covered, and the net concentration in the crystal exceeds C_o . This sets up a diffusion gradient inside the crystal which tends to decrease the crystal concentration towards C_o . At very slow growth rates—compared to the diffusion rate—the impurity of a top layer would have sufficient time to diffuse to the interface before this layer were covered by a subsequent one. The resulting crystal would then have the equilibrium concentration C_o . If new layers are added too rapidly, however, the impurity atoms would have insufficient time to exchange with the surface and a final crystal containing nonequilibrium concentrations will grow. This increase in impurity concentration has been confirmed experimentally in crystals grown from melt (2, 10). In addition, it has been treated analytically by Chernov (5), who found a relation similar to that shown by curve 1 in Figure 2. He showed that the upper part of the curve, where the impurity concentration remains constant, corresponds to growth rates R , such that $R \gg D_i/h$ where

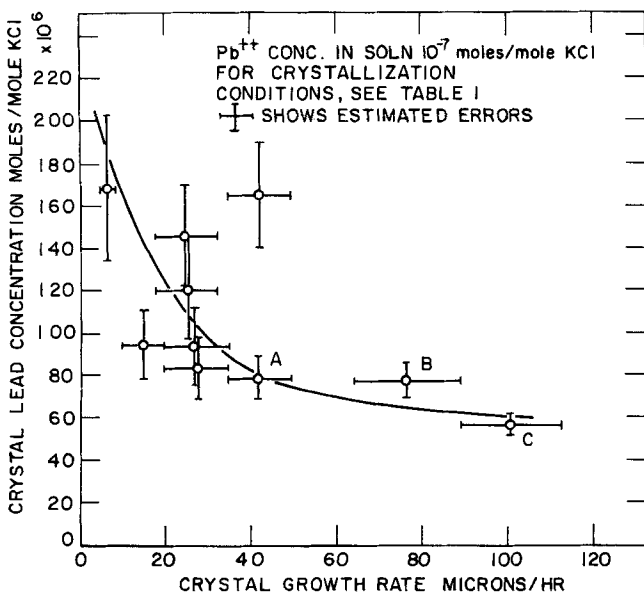


Fig. 1. Concentration of Pb^{++} in crystals vs. growth rate of (100) faces.

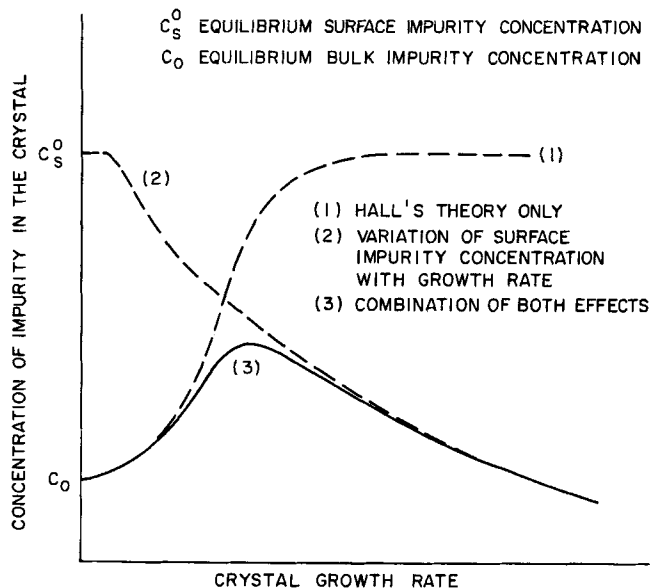


Fig. 2. Variation of impurity concentration in the crystal with growth rate.

D_i is the diffusion coefficient of the impurity ions in the crystal, and h is the thickness of each deposited layer.

The experimental results presented in Figure 1 are contrary, however, to the predictions of the Hall-Chernov model. Thus, to explain the observed reduction in the crystal lead concentration as the growth rate increases, a modification of the Hall-Chernov model is proposed.

The assumption behind Hall-Chernov's treatment is that the impurity concentration at the surface C_s^o is always constant; that is, adsorption of the impurity at the crystal surface attains equilibrium. This assumption, however, is not necessarily true. Actually, Frank, in his theory of the effect of impurities on crystal growth (7), assumed that the concentration of impurities on the crystal surface is time dependent. In other words, in most of the crystal growth cases, the time that elapses between the deposition of successive layers is of the same order of magnitude or smaller than the time required to establish an equilibrium concentration of impurities. Thus, the impurity concentration at the surface does not attain the equilibrium value and actually decreases with the growth rate. This is expressed schematically by the curve 2 in Figure 2.

Frank's concept concerning the time dependency of the impurity concentration at the crystal surface has been used successfully in explaining certain features of crystal growth, for instance, the development of macroscopic growth steps on the crystal surface (7) and the formation of whiskers (1).

Assuming also that in the case of lead chloride in potassium chloride, the adsorption of the lead ion is time dependent, we can combine curves 1 and 2 in Figure 2 to give curve 3, which now expresses the dependence of the impurity concentration in the bulk of the crystal upon the growth rate. For $R \gg D_i/h$ in curve 1, the crystal impurity concentration remains constant, whereas in curve 3, it decreases as the growth rate increases.

In the growth experiments of the present investigation, $D_{Pb^{++}}$ was calculated to be 3.8×10^{-19} sq.cm./sec. The value was found by extrapolating the findings of Glasner et al. (8) to $35^\circ C.$, which was the temperature of the present crystal growth studies. The thickness of a deposited layer was assumed to be 25A. (12). Thus, $D_{Pb^{++}}/h$ is equal to 1.52×10^{-12} cm./sec., while the slowest growth rate was five orders of magnitude larger, $6 \mu/hr.$ or 1.7×10^{-7} cm./sec. Therefore, the

$R \gg D_{Pb^{++}}/h$ and the experiments correspond to the region on the right side of curve 3 in Figure 2, where the impurity concentration decreases as the growth rate increases.

In the growth of crystals from melt the temperatures are high and for this reason the diffusion coefficients are large. The crystals grow under conditions corresponding to the left side of curve 3 (Figure 2), and therefore, it is expected that the impurity concentration would increase as the growth rate increases. Such a dependence has been reported for antimony in germanium crystallized from melt (10).

For the system Pb^{++} in potassium chloride crystals grown from aqueous solution, the dependence indicated by the left side of curve 3 should be observed at temperatures higher than about 150°C.

INCORPORATION OF OTHER IMPURITIES BY POTASSIUM CHLORIDE CRYSTALS

The incorporation by the potassium chloride crystals of other impurities besides lead was also studied: Fe^{+++} , Ti^{+++} , Bi^{+++} , and Hg^{++} . The results are summarized in Table 2.

ENGINEERING CONSEQUENCES

The proposed model for the nonequilibrium capture of impurities and the experimental data of this investigation point to the following practical consequences for the process of purification by recrystallization.

Inhomogeneous Impurity Distribution in Crystals

In the impurity concentration ranges where $k_{eff} > 1$, recrystallization does not remove the impurity but concentrates it strongly in the first crystals precipitated. For instance, calculations with the distribution coefficients obtained in our investigation used show that 99.9% of the lead in the solution will be contained in the first 1.25% of the crystallized potassium chloride (see Figure 3). Thus in a batch crystallization of potassium chloride, if the first crystals grown are not rejected, the distribution of lead among the various crystallites should be extremely inhomogeneous. This was confirmed experimentally to be the case with the Baker analyzed reagent potassium chloride. A certain number of crystallites from each reagent bottle were analyzed spectrographically for lead. While the lead concentration in most of the small crystals was less than 0.1 p.p.m., certain crystallites contained as high as 30 p.p.m. lead.

Production of Very Pure Potassium Chloride and Sodium Chloride

Since the first crystals grown from a solution of potassium chloride (and also sodium chloride) contain most of the lead, those which crystallize later will be of higher

TABLE 2. INCORPORATION OF IMPURITIES BY POTASSIUM CHLORIDE CRYSTALS

Impurity	Concentration of the impurity, moles/mole of potassium chloride		Effective distribution coefficient
	In the solution	In the crystal	
Fe^{+++}	1×10^{-6}	325×10^{-6}	300
Ti^{+++}	1	Not detected	
		$< 8.6 \times 10^{-6}$	8.6
Ti^{+++}	10	200×10^{-6}	20
Hg^{++}	10	Not detected	4
		$< 40 \times 10^{-6}$	
Bi^{+++}	10	Not detected	0.3
		$< 3 \times 10^{-6}$	

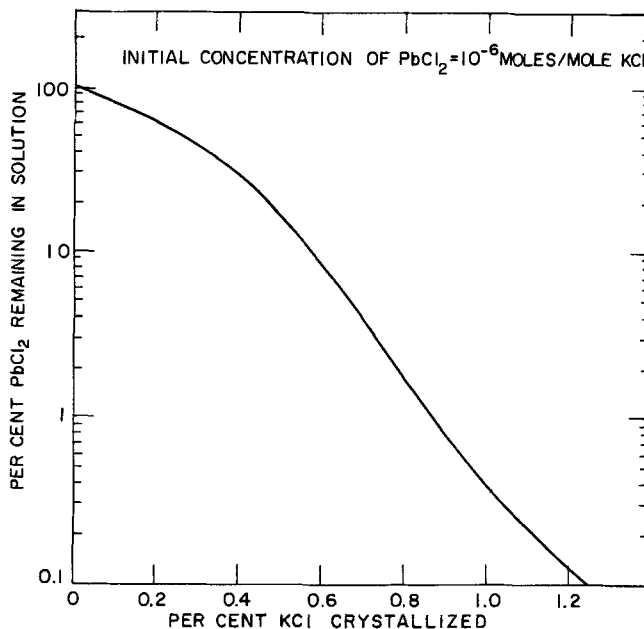


Fig. 3. Amount of lead chloride remaining in solution vs. amount of potassium chloride crystallized.

purity than the original potassium chloride. Thus rejection of the first crystal fraction should lead to very pure potassium chloride and sodium chloride crystals.

There is a considerable need for such high purity reagent for the growth of large sodium chloride and potassium chloride crystals from melt. The latter are used extensively for various physical measurements. Egli and Johnson (6) recently complained that "there is no commercial source for such a common substance as NaCl that will produce satisfactory crystals for physical measurements; . . . certain brands of table salt have proved to be better than the best material from chemical reagent companies."

In the light of the above discussion, Egli and Johnson's statement is not surprising. A conventional recrystallization process is not expected to reduce the lead content of the table salt unless the technique is modified to include rejection of the first crystals grown.

CONCLUSIONS

Potassium chloride crystals grown from solutions containing lead ions in concentrations less than 10^{-5} moles of lead/mole of potassium chloride contain a higher concentration of lead than in the crystallizing solution. Lead distribution coefficients, crystal-to-solution, ranged from 2,700 to 28, depending upon the lead concentration in the solution and the crystal growth rate.

The results suggest a mechanism of nonequilibrium capture of the impurity, according to which the magnitude of the distribution coefficient in such cases depends on the distribution coefficient between the solution and the surface of the crystal, the rate of growth of the crystal, and the rate of diffusion of the impurity through the crystal lattice.

The results indicate that in order to produce crystals of potassium chloride free from Pb^{++} , the conventional techniques of recrystallization should be modified to include rejection of the first crystals grown.

NOTATION

C_c = impurity concentration in the crystal (molar ratio of impurity to crystallizing species)

C_L = impurity concentration (molar ratio) in the mother liquor
 C_o = equilibrium impurity concentration (molar ratio) in the crystal
 C_s = impurity concentration (molar ratio) on the crystal surface
 C_s^o = equilibrium impurity concentration (molar ratio) on the surface
 D_i = diffusion coefficient of component i in the crystal
 h = thickness of a single layer
 k_{eff} = effective distribution coefficient of an impurity (crystal-to-solution)
 R = linear growth rate of a crystal face

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Process Control by Digital Compensation

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Discrete control algorithms, suitable for programming in a direct digital control computer, are presented. For processes whose dynamics can be adequately modeled as first order with delay, digital compensation algorithms are derived to yield theoretically a response with finite settling time, when the system is step forced in either set point or load. The utility of the proposed designs is experimentally verified by application to a higher order physical process whose dynamics are not fully described by the model. The results demonstrate that sampling frequencies may be reduced considerably below presently accepted values while still maintaining transient response characteristics of the system comparable with those obtainable from conventional continuous control.

The small digital computers now available for process control have demonstrated their ability to replace adequately conventional analog control systems. In designing new plants and modernizing existing facilities, the process industry is giving more consideration to the possibility of direct digital control (DDC) as an alternative to conventional pneumatic or electronic techniques. Williams (24, 25) reports that computers have been reduced to one-

quarter of their original cost, while reliability has increased tenfold. In addition, computer capability has greatly expanded.

Several workers in the field have reported the use of discrete versions of conventional control algorithms (4, 6, 17, 23). The performance of these systems under computer control is of course limited to that which is obtainable from their continuous-data analogs. In these studies sampling is performed as often as 1/sec., which is essentially continuous control for most chemical processes.

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