K_L = Langmuir isotherm parameter, m^3 solution/mol
L = bed length, m
m = number of components
n = solute concentration in the solid phase, mol/m^3 sorbent
N = number of theoretical plates
N_c = sorbent capacity, mol/m^3 sorbent
Q_f = feed rate, m^3/s
Q_E = eluent rate, m^3/s
R = resolution
Re = $\rho dV/\epsilon\mu$ = eluent Reynolds number
t = time, s
t_f = time feed is applied to column, s
V = superficial eluent velocity, m/s
VDN = $\epsilon D_z/VL$ = vessel dispersion number
VDN_x = $D_z \bar{\theta}/\omega L^2$ = solute vessel dispersion number
W = solute baseline bandwidth, deg
W_o = initial feed bandwidth, deg
z = axial coordinate, m

Greek Letters

ϵ = bed void fraction, m^3 voids/m^3 bed
θ = angular coordinate, deg
$\bar{\theta}$ = solute peak position, deg
θ_f = angle feed is applied to column, deg
μ = eluent viscosity, kg/m·s
ρ = eluent density, kg/m^3
σ^2 = variance
ω = rotation rate, deg/s

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Influence of Hydrodynamics on Crystal Growth and Dissolution in a Fluidized Bed

Mass transfer coefficients for the growth and the dissolution of potassium alum and sodium thiosulfate in a laboratory-scale fluidized-bed apparatus were determined and correlated in a form of the Frössling equation. The surface reaction rate for potassium alum was found to be dependent on the crystal size.

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SCOPE

The mass transfer in liquid-solid systems has been studied extensively for the dissolution process. Only a few reports, however, exist concerning the mass transfer from the liquid phase into the solid phase. This process is only rarely linearly proportional to the driving force and thus cannot be regarded as a simple reciprocity of the dissolution. The method introduced previously (Karpiński, 1980), based on the two-step growth concept, allows us to determine: (1) a mass transfer coefficient for the crystal growth, and (2) a surface reaction rate constant. The method has not yet been fully verified by joint dissolution-crystallization experiments.

The purpose of this work is to compare the mass transfer coefficients for both dissolution and diffusional steps of crystal growth and their dependence on the hydrodynamics, as well as to verify a possible dependence of the surface reaction rate on the crystal size.

A fluidized bed has been selected as the experimental system since it seemed to ensure well-defined hydrodynamic conditions, particularly when monodimensional crystals were used.

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CONCLUSIONS AND SIGNIFICANCE

Both salts investigated, potassium alum and sodium thiosulfate, were found to be governed by different growth mechanisms. The growth of the latter is volume diffusion controlled whereas both surface reaction and volume diffusion are significant in the case of the former salt.

It was shown that the dissolution mass transfer and the crystal growth mass transfer are not different as regards values of the mass transfer coefficients as well as their dependence on hydrodynamic conditions. The Frössling equation was found to be an appropriate form to express the mass transfer correlation regardless of the direction of mass transfer. The results obtained seemed to verify the previously-developed method used to determine the crystal growth mass transfer coefficient and the surface reaction rate constant.

Both the influence of hydrodynamic conditions on the diffusional step of the crystal growth and the influence of the crystal size on the surface reaction rate were shown to be factors which are usually jointly interpreted as the so-called size-dependent crystal growth.

INTRODUCTION

From the chemical engineering point of view, the most suitable approach to crystal growth from solution is the two-step growth concept (Nývlt, 1971; Garside, 1971; Mullin, 1972), according to which the crystal growth consists of two consecutive steps:

(i) diffusion of growth units (solvated ions, particles, etc.) within the laminar diffusion layer described by the equation

$$\dot{m}_G = k_d(w - w_i) \tag{1}$$

(ii) incorporation of the growth units or their pieces into the crystal lattice, frequently referred to as a surface reaction, described by the equation

$$\dot{m}_G = k_r(w_i - w_{eq})^r \tag{2}$$

An elimination of the intermediate concentration w_i, which is physically difficult to measure, from the above equations, gives

$$\dot{m}_G = k_r\left(\Delta w - \frac{\dot{m}_G}{k_d}\right)^r \tag{3}$$

This equation is very often approximated in terms of the supersaturation, $\Delta w = w - w_{eq}$, by the simple power-law equation:

$$\dot{m}_G = k_G(\Delta w)^g \tag{4}$$

The diffusional step of the crystal growth has its counterpart in an oppositely-directed process, such as the dissolution, for which the following equation is widely accepted:

$$\dot{m}_D = k_D(-\Delta w) \tag{5}$$

When the BCF theory (Burton et al., 1951) is applied, it can be observed that the linear (thus also mass) growth rate is linearly proportional to the supersaturation for elevated levels of the supersaturation, whereas the parabolic proportionality holds for the low supersaturation. It seems to explain the well-known fact that the order g of Eq. 4 is often reported to be included within the close interval $\langle 1,2 \rangle$. In industrial practice, crystallizers usually work under conditions of low supersaturation with an associated linear growth rate of the range $\approx 10^{-8}$ m/s (Mullin, 1979). Therefore, for many cases of practical importance, it may be assumed that the order of the surface reaction, r, is essentially equal to 2.0.

Therefore, assuming $r = 2$, Eq. 3 may be linearized (Karpiński, 1980, 1981) by solving for Δw and multiplying the resulting equation by the factor $1/\sqrt{\dot{m}_G}$, to yield

$$\frac{\Delta w}{\sqrt{\dot{m}_G}} = \frac{1}{k_d}\sqrt{\dot{m}_G} + \frac{1}{\sqrt{k_r}} \tag{6}$$

When $\Delta w/\sqrt{\dot{m}_G}$ is taken as the ordinate and $\sqrt{\dot{m}_G}$ as the abscisa, Eq. 6 presents a straight line, the reciprocal slope of which is the convective mass transfer coefficient for growth units diffusing through the supersaturated solution into the outer boundary of the Volmer layer. The value of the surface reaction step rate constant may, therefore, be deducted from the point of the intersection of this straight line with the ordinate.

Dissolution data are very often correlated in a form of the Frössling equation (Frössling 1938):

$$Sh = 2 + 0.6\,Re^{1/2}Sc^{1/3} \tag{7}$$

or in an alternative form of this equation (Akselrud and Molchanov, 1977)

$$Sh = C\,Re^{1/2}Sc^{1/3} \tag{8}$$

Equations 7 and 8 have also been applied to the crystal growth data correlation using the mass transfer coefficient calculated by means of a numerical method based on Eqs. 1, 2 and 4 (Karpiński and Koch, 1979) or determined directly from Eq. 6 (Karpiński, 1980; Karpiński, 1981).

EXPERIMENTAL

Apparatus

The experimental apparatus was a standard fluidized-bed glass crystallizer with a diameter of 0.048 m and a working volume of 0.0022 m^3. The crystallizer, Figure 1, was provided with two sections of velocity profile equalizers (1) to avoid a dispersion of the solution velocity within a growing zone. The crystallizer was closed with a glass stopper with two stub-pipes: the seeding stub (2)and the thermometer stub (3). Grown crystals were removed from the crystallizer using a basket-like device (4) made of the fine stainless steel grid. The crystallizer was a part of the experimental installation which altogether contained about 0.045 m^3 of the solution. Details of the apparatus and equipment were described elsewhere (Budz et al., 1983).

Procedure

Two hydrate-water systems have been studied: potassium aluminum sulfate dodecahydrate and sodium thiosulfate pentahydrate. The purity of the salts used to prepare the solution was analytical reagent grade for *K*-alum and reagent grade for thiosulfate. Seeds were obtained by recrystallizing the commercial salts in a stirred tank cooling crystallizer. The product crystals of the desired sieve cut were further used as seeds. In the case of the thiosulfate it appeared in addition to be necessary to select the well-formed crystals using a magnifying glass. The mass of the individual crystal used as a seed has been determined by weighing 5,000 crystals taken as a random sample from such prepared seeding material. Heating and cooling systems as well as a control system which have been applied maintained the desired temperature level within the crystallizer with an accuracy of ±0.02 K. Both the equalizing of the velocity profile and the application of the narrow CSD of the seeds assured very stable fluidization conditions; therefore, the height of the bed could be measured with an accuracy of ±0.5 mm.

A known mass of crystals measured with an accuracy of $\pm 10^{-5}$ g was placed in the crystallizer and crystals were allowed to grow for a definite

TABLE 1. BASIC OPERATIONAL DATA

Salt		Series	$\bar{\theta}_w$ °C	$u \times 10^2$ m/s	$\bar{L} \times 10^3$ m	$\bar{\epsilon}$ –	No. of Runs in Series
$KAl(SO_4)_2 \cdot 12H_2O$	Growth	A	28.5	4.22	1.73	0.795	18
		B		3.50	1.75	0.778	15
		C		2.90	1.12	0.831	16
		D		2.26	0.780	0.864	23
		E		1.64	0.665	0.838	29
		F		1.98	0.907	0.814	9
	Dis-solution	A_d	28.5	4.22	1.71	0.783	12
		B_d		3.50	1.58	0.753	12
		C_d		2.90	0.997	0.810	17
		D_d		2.26	0.632	0.880	19
$Na_2S_2O_3 \cdot 5H_2O$	Growth	I	27.5	3.12	5.27	0.759	17
		J		2.15	2.85	0.805	10
		K		1.49	2.51	0.757	20
		L		1.00	1.83	0.766	15
		M		2.15	5.09	0.693	17
		N		2.15	2.55	0.830	13
	Dis-solution	E_d	28.2	3.12	5.10	0.748	17
		F_d		2.15	2.89	0.792	11
		G_d		1.49	2.62	0.747	15
		H_d		1.00	1.92	0.738	14

time. Next, the crystals were removed, rinsed with the solution (saturated at an ambient temperature) and acetone, dried and weighed.

Altogether 116 measuring points for the growth and 60 measuring points for the dissolution of K-alum along with respective figures 92 and 57 for sodium thiosulfate were obtained. The most important operational data are shown in Table 1.

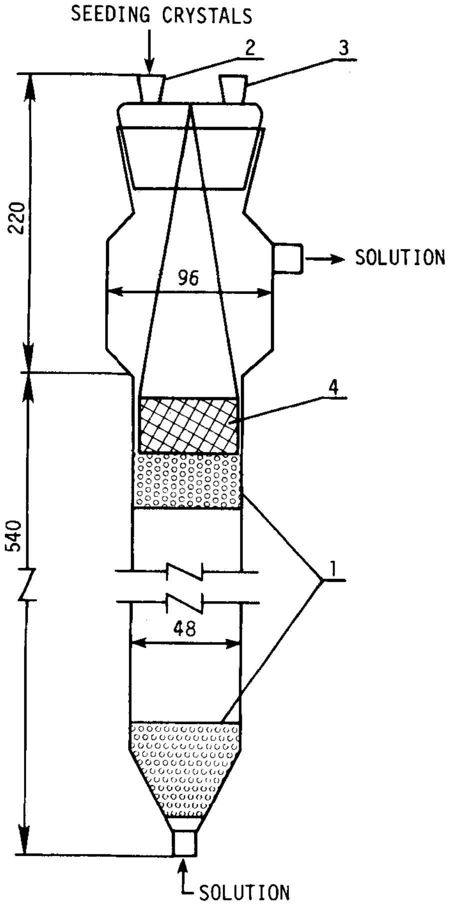


Figure 1. Fluidized bed apparatus (dimensions in mm): 1. packing of glass beads; 2, 3. stub pipes; 4. basket-like device for removal of crystals.

Physicochemical Properties

The saturation temperature of the solution circulating in the apparatus was determined using the dissolution of the last smallest crystal method (Nývlt, 1971). To this end the 200 cm^3 volume of the solution was sampled every third run.

The solubility was calculated based on literature data (Broul et al., 1979) for thiosulfate and on our own data for K-alum. In the latter case the form of the solubility-temperature equations was the same a recommended by Broul et al. The solubility equations are the following:

- Sodium thiosulfate (273–321 K)

$$\log x = -100.04 + (3756.6/T) + 34.892 \log T \tag{9}$$

$$w = [0.07253((1/x) - 1) - 0.3626]^{-1} \tag{10}$$

- Aluminum potassium sulfate (273–358 K)

$$\log x = -77.764 + (2232.3/T) + 27.463\ T \tag{11}$$

$$w = [0.03794((1/x) - 1) - 0.4557]^{-1} \tag{12}$$

The mass fluxes of growth and dissolution were calculated from the equation

$$\dot{m}_{G(D)} = (-1)^j \frac{3(\alpha \rho_c)^{2/3}}{\beta t_{G(D)}} m_1^{1/3} \left[\left(\frac{m_e}{m_i}\right)^{1/3} - 1\right] \tag{13}$$

where:

TABLE 2. BASIC PHYSICOCHEMICAL PROPERTIES OF SALTS INVESTIGATED

Property	$KAl(SO_4)_2 \cdot 12H_2O$ (28.5°C)	$Na_2S_2O_3 \cdot 5H_2O$ (27.5°C)	Source of Data Alum	Thios.
Crystallographic System	cubic	monoclinic	2	2
Volume Shape Factor α	0.47	0.45	3	1
Surface Shape Factor β	3.46	3.80	3	1
Density of Crystals, ρ_c, kg/m^3	1760	1756	2	2
Density of Saturated Solution, ρ_l, kg/m^3	1068	1425	4	5
Viscosity of Saturated Solution, η, Pa·s	1.165×10^{-3}	6.44×10^{-3}	4	5
Diffusivity, D, m^2/s	4.3×10^{-10}	1.7×10^{-9}	4	6

1. Kočová and Nývlt (1972); 2. Broul et al. (1979); 3. Nývlt and Matuchová (1976); 4. Mullin et al. (1965); 5. Naruć (1982); 6. calculated.

TABLE 3. CONSTANTS OF KINETIC EQS. 1 to 6 AND ASSOCIATED CORRELATION ERRORS

		K-Alum						$Na_2S_2O_3{\cdot}5H_2O$					
		Velocity of solutions, u × 10^2, m/s											
Quantity	Units	4.22	3.50	2.90	2.26	1.98	1.64	3.12	2.15	2.15^1	2.15^2	1.49	1.00
$k_G \times 10^2$	kg/m^{2}s	8.29	7.00	7.95	5.71	6.45	4.46	0.600	0.728	0.573	0.660	0.549	0.622
g	—	1.47	1.48	1.51	1.49	1.48	1.47	1.0	1.0	1.0	1.0	1.0	1.0
s_G	%	6.3	4.5	3.9	11.8	3.0	15.8	5.2	7.4	10.9	6.3	8.0	8.9
R_G	—	0.997	0.999	0.999	0.995	0.998	0.976	0.996	0.996	0.994	0.996	0.996	0.987
$k_D \times 10^2$	kg/m^{2}s	2.42	2.53	2.78	2.87	—	—	0.441	0.494	—	—	0.465	0.384
s_D	%	3.7	6.8	4.2	11.4	—	—	9.9	3.7	—	—	3.6	9.8
R_D	—	0.998	0.995	0.995	0.976	—	—	0.994	0.999	—	—	0.998	0.997
$k_d \times 10^2$	kg/m^{2}s	2.54	2.30	2.44	2.07	2.36	2.09	Equation 6 is not applicable since $g = 1.0$.					
k_r	kg/m^{2}s	2.65	1.88	1.76	1.30	1.46	0.927						
s_{d-r}	%	3.2	2.4	2.7	7.3	2.0	10.4						
R_{d-r}	—	0.974	0.984	0.989	0.928	0.973	0.911						
$1 - \bar{L} = 5.09$ mm, $2 - \bar{L} = 2.55$ mm													

$j = 1$ for dissolution

$j = 2$ for growth

Basic physicochemical properties are listed in Table 2. Since *K*-alum crystals are of the form similar to an octahedron, the shape coefficients α and β were calculated based on the octahedral geometry. Values of α and β for the thiosulfate were taken from the literature (Kočová and Nývlt, 1972).

The mass diffusivity of thiosulfate was calculated according to the procedure recommended by Reid et al. (1977).

RESULTS

Constants of the kinetic Eqs. 1 to 6 and the associated correlation errors are presented in Table 3. The distribution of experimental points along the correlation straight lines for the dissolution, growth and for Eq. 6 are shown by example in Figures 2, 3 and 4, respectively.

Effects of the hydrodynamics as well as of the purity of salts used resulted in quite a wide scattering of experimental results reported by different authors. Figure 5 presents literature data concerning the growth of K-alum in terms of the linear growth rates of the face {111}, reduced to the standard conditions at 40°C by Garside (1977), as well as the results of the series B of this study.

Mass Transfer Correlation

The hydrodynamic conditions in the crystallizer were described by the Reynolds number defined as follows:

$$Re = \frac{u\bar{L}_A \rho_l}{\eta \bar{\epsilon}} \tag{14}$$

where the mean equivalent size has been defined as:

$$\bar{L}_A = \sqrt{\frac{\beta}{\pi}} \left(\frac{\bar{L}_i + \bar{L}_e}{2} \right) \tag{15}$$

The form and the constants of the Frössling Eq. 7 have been established using the mass transfer coefficient and the driving force expressed in m/s and in kg/m^3, respectively. Therefore, constants k_d and k_D were re-calculated by means of a simple formula:

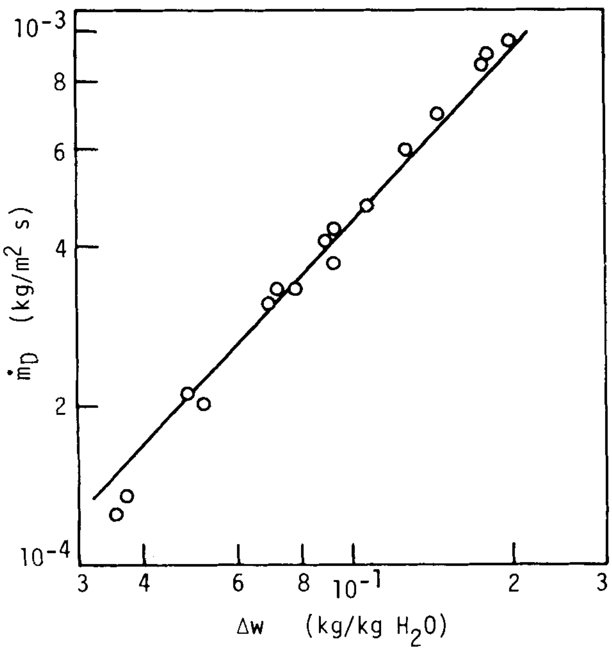


Figure 2. Mass dissolution flux versus supersaturation for $Na_2S_2O_3{\cdot}5H_2O$, series E_d.

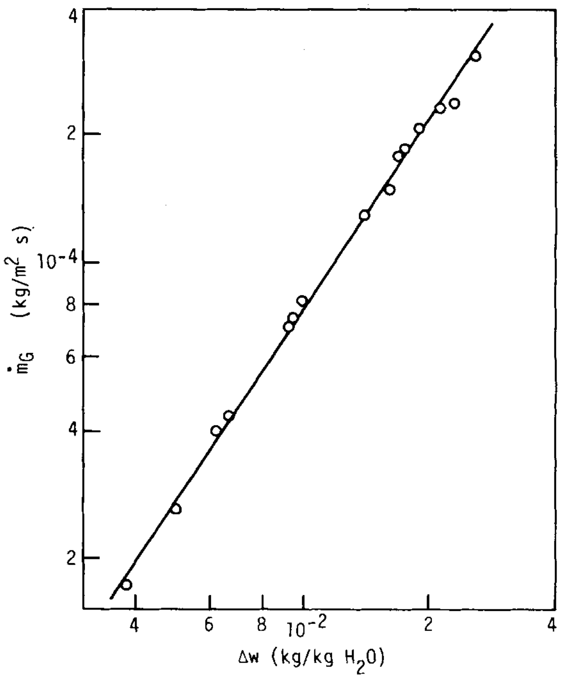


Figure 3. Mass growth flux versus supersaturation for *K*-alum, series B.

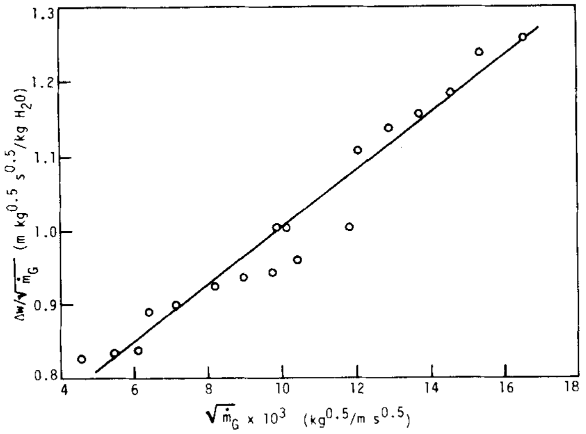


Figure 4. Graph illustrating the use of Eq. 6. Data for *K*-alum, series A.

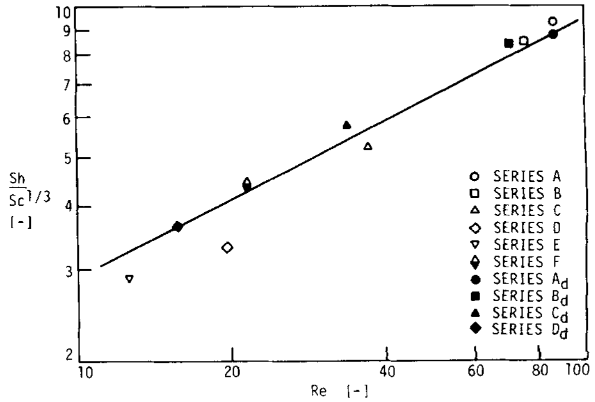


Figure 6. Mass transfer correlation in the form of Eq. 8 for growth and dissolution of *K*-alum in a fluidized bed.

$$K = \frac{k_{d(D)}(1 + w_{eq})^2}{\rho_l} \tag{16}$$

The mass transfer correlation for both dissolutions and growth of K-alum in the form of Eq. 8 is presented in Figure 6. It is worth noting that Figure 6 provides the first experimental proof, valid for this salt, that the direction of the diffusion is the only difference between the diffusional step of the crystal growth and the dissolution process. The straight line correlation shown in Figure 6 has the form:

$$Sh = 0.745\, Re^{0.56} Sc^{1/3} \tag{17}$$

with the mean square relative error of 7% and the coefficient of correlation of 0.984. This equation may be presented in the theoretically more appropriate forms:

$$Sh = 2 + 0.90\, Re^{1/2} Sc^{1/3} \tag{18}$$

or

$$Sh = 0.93\, Re^{1/2} Sc^{1/3} \tag{19}$$

with the same coefficient of correlation as Eq. 17 and the mean errors of 8% and 9%, respectively.

The crystal growth order, g, of Eq. 4 is equal to unity in the case of thiosulfate as shown in Table 3. Therefore, the growth mass transfer coefficient, k_d, is equal to the overall growth rate constant, k_G (Karpiński and Koch, 1979). The mass transfer correlation for the thiosulfate is presented in Figure 7. A discrepancy in the results for the growth and the dissolution, amounting to 40%, is observed. It is due to the fact that during the growth of thiosulfate crystals a number of macro- and "microroughnesses" form on the crystal's surface. Therefore the true mass transfer area is much larger (the smaller is the mass growth flux) than that calculated, based on the mean crystal size and the surface shape factor (the latter assumed to be constant). Accordingly, the true value of the surface shape factor, β, is higher than that originally calculated for the smooth crystal surface. As it follows from Eq. 13 the use of underestimated values of β causes values of the mass growth flux to be overestimated. On the other hand, the volume shape factor, α, can be assumed to remain unaffected since the volume of "roughnesses" is rather small with respect to the crystal volume. In contrast during the dissolution process these "roughnesses" are dissolved first and the crystals surface appears to be very smooth after a very short initial period of the process and for the steady dissolution β is constant. The typical pictures of the sodium thiosulfate crystals after growth and after dissolution are shown in Figures 8a and 8b, respectively.

It is obvious that the mass transfer correlation can be obtained by taking into consideration the dissolution experiments only. Nevertheless, the fact that both straight lines shown in Figure 7

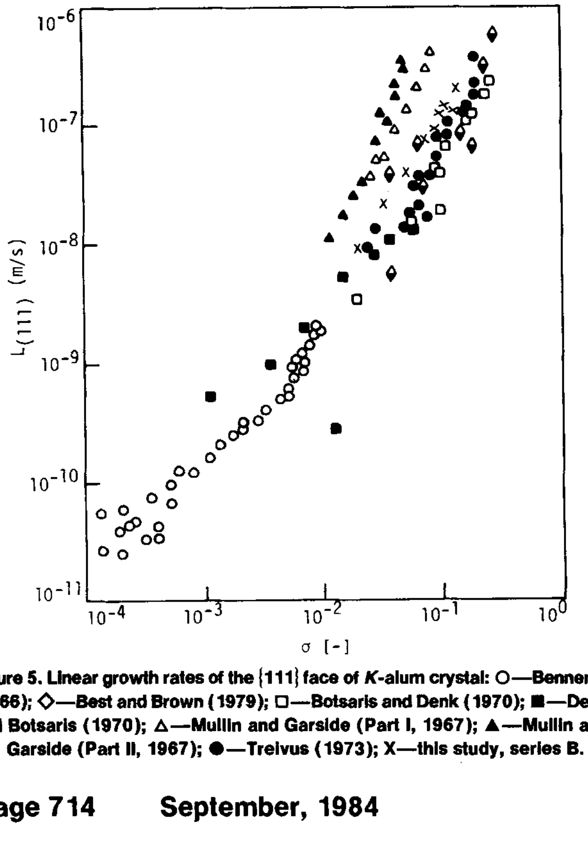


Figure 5. Linear growth rates of the {111} face of *K*-alum crystal: ○—Bennema (1966); ◇—Best and Brown (1979); □—Botsaris and Denk (1970); ■—Denk and Botsaris (1970); △—Mullin and Garside (Part I, 1967); ▲—Mullin and Garside (Part II, 1967); ●—Treivus (1973); X—this study, series B.

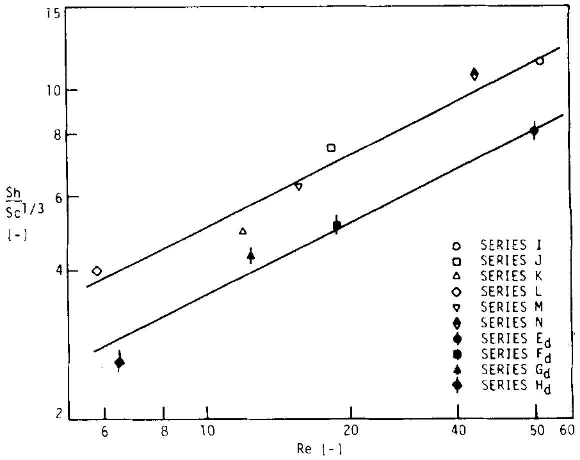
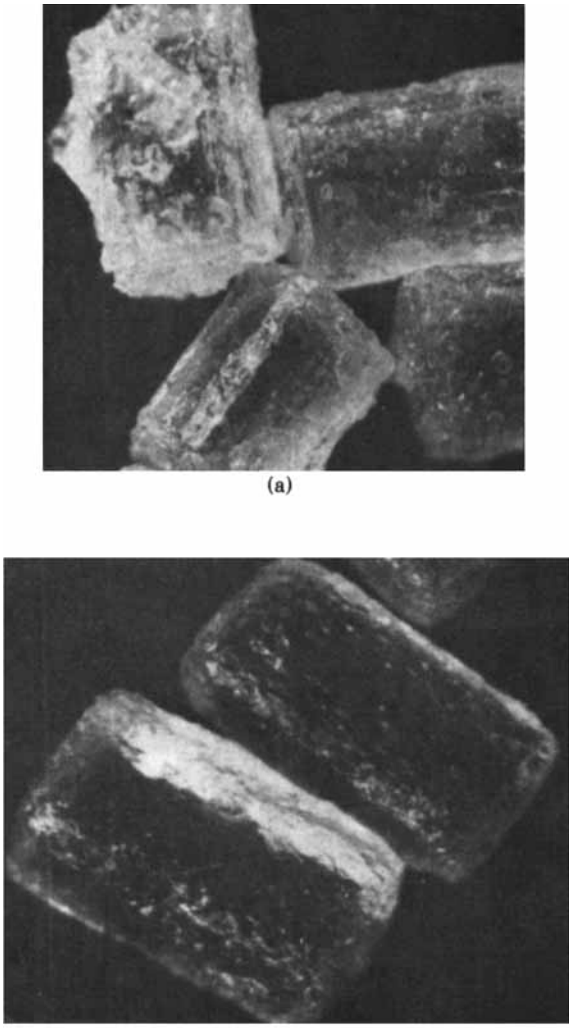


Figure 7. Mass transfer correlation in the form of Eq. 8 for growth and dissolution of $Na_2S_2O_3{\cdot}5H_2O$ in a fluidized bed. Growth rates are on the average 40% higher than true values.



(a)

(b)

Figure 8. Typical crystals of sodium thiosulfate: a. after growth; b. after dissolution.

have the same slope is very valuable and it also confirms the identity of the mechanisms of both oppositely-directed processes from the macroscopic point of view. The mass transfer correlations for thiosulfate take on the forms:

$$Sh = 1.16\, Re^{1/2} Sc^{1/3} \tag{20}$$

with the error of 5.5% and the coefficient of correlation of 0.991 or

$$Sh = 2 + 1.12\, Re^{1/2} Sc^{1/3} \tag{21}$$

with the error of 6.3% and the coefficient of correlation of 0.990. The values of the precoefficients of Eqs. 20 and 21 seem to be too high. It has already been emphasized, however, that the value of the mass diffusivity for thiosulfate is not an empirical one but was calculated as recommended by Reid et al. (1977).

The obtained mass transfer correlations are compared with some literature data in Table 4. The correlations obtained for K-alum are very much consistent with those by Akselrud and Molchanov (1977) and by Garner and Suckling (1958). It seems to confirm the usefulness of Eq. 6 in the determination of the mass transfer coefficient for the crystal growth. The lack of full agreement with Mullin's data (Mullin, 1972) for the same system is due to the different experimental techniques applied in each study. Mullin did not use any velocity profile equalizer which could result in a different true turbulence than that formally defined by Eq. 14. The same remark holds for the case of sodium thiosulfate to explain the discrepancy, Table 4, of exponent values at the Reynolds number obtained in this study and by Kočová and Nývlt.

Dependence of Growth Rate on Crystal Size

There is an opinion that a number of substances crystallizing from solution do not obey McCabe's ΔL-rule. Bransom (1960) introduced the following empirical expression:

$$\dot{m}_G = k'_G L^b (\Delta w)^g \tag{22}$$

to emphasize the dependence of growth rate on crystal size. The Bransom model and a number of others, especially those used in the MSMPR-crystallizer approach to explain deviations from expected behavior of the particular system, are useful in correlating experimental data but are not essential in understanding a possible mechanism of this phenomenon. There are two possible explanations of the so-called size-dependent growth:

(i) k_d depends on the crystal size
(ii) k_r depends on the crystal size

The first case is quite a rule. From the form of the mass transfer correlation it follows that:

$$k_d L = C' Re^{1/2} \tag{23}$$

thus, since the Reynolds number itself contains the crystal size, we obtain

$$k_d = C' L^{-1/2} u^{1/2} \tag{24}$$

Such a dependence has been stated for both salts investigated.

The problem of the possible dependence of k_r on the crystal size may be clarified by a concept first introduced by Garside et al. (1975). Crystal-crystal and crystal-crystallizer collisions result in a number of microdamages to the crystal's surface. Therefore, new defects on the crystal's surface are introduced, and according to the BCF theory, new growth spirals may be formed and the resultant crystal growth rate is faster. The effectiveness of collisions, however, depends on their energy which is proportional to the mass

TABLE 4. SELECTED MASS TRANSFER CORRELATIONS FOR LIQUID-SOLID SYSTEMS

Author(s)	Correlation	Remarks
Akselrud and Molchanov (1977)	$Sh = CRe_s^{1/2}Sc^{1/3}$; $C = 0.8 - 0.95$	Mass transfer into a solid sphere, a theoretical correlation, verified experimentally for $100 < Re_s < 10^4$
Garner and Suckling (1958)	$Sh = 2 + 0.95\, Re_s^{1/2}Sc^{1/3}$	Mass transfer into a solid sphere, an empirical correlation valid for $2 < Re_s < 840$
Hixson and Knox (1951)	$Sh = 0.48\, Re_s^{0.6}Sc^{0.33}$	Growth of single crystal of $MgSO_4 \cdot 7H_2O$ in a stirred tank, $10 < Re_s < 3{,}200$
Karpiński (1981)	$Sh = 0.56\, Re^{1/2}Sc^{1/3}$	Growth of $CuSO_4 \cdot 5H_2O$ in a fluidized bed, $20 < Re < 55$
Mullin (1972)	$Sh = 0.37\, Re^{0.62}Sc^{0.33}$	Dissolution of K-alum in a fluidized bed, $20 < Re < 160$
Karpiński and Nývlt (1982)	$\log (k_d\overline{L}) = C + 0.71 \log (u\overline{L})$	Growth of K-alum in a fluidized bed, correlation based on 3 series of experiments with relative slip velocities 1.26, 1.80 and 2.80 cm/s
Kočová and Nývlt (1972)	$\log (k_G\overline{L}) = C + 0.75 \log (u\overline{L})$	Growth of 20–50 sodium thiosulfate crystals in a vertical glass tube, settling velocities: 1.26–4.94 cm/s
This study, Eqs. 18 and 19	$Sh = 0.93\, Re^{1/2}Sc^{1/3}$ or $Sh = 2 + 0.90\, Re^{1/2}Sc^{1/3}$	Growth and dissolution of K-alum in a fluidized bed, $10 < Re < 90$

and thus to the cubed size of colliding crystals. In the fluidized bed crystallizer, the velocity of upward-flowing solution is proportional to the size of crystals forming the bed. On the other hand, the frequency of collisions is proportional to the porosity of the bed, $\bar{\epsilon}$. Both variables are present in the Reynolds number and formally one may even expect the dependence of k_r on the Reynolds number. Since the application of Eq. 6 also gives values of the surface reaction rate constants, Table 3, the dependence of k_r on the mean growing crystal size can be obtained. The empirical form of this dependence for K-alum is:

$$k_r = 388\bar{L}^{0.81} \tag{25}$$

with the mean relative square error amounting to 13%.

The experimentally-stated size-dependent growth is therefore only a symptom in fact of the more complex correlation between the rate constants of the individual steps and the hydrodynamic (or energetic) factor.

CONCLUSIONS

The following conclusions seem to be valid when the two-step growth concept is assumed.

1. Equation 6 gives reliable values of the mass transfer coefficient characterizing the diffusional step of the crystal growth process.
2. It has been stated for K-alum that both mass transfer coefficients—that of the diffusional step of crystal growth and that of crystal dissolution—take on very much the same values and may be jointly correlated by means of the Frössling equation.
3. The crystal growth of sodium thiosulfate pentahydrate is first order with respect to the level of supersaturation, and the whole process is volume diffusion controlled.
4. The mechanism of the diffusional step of the crystal growth as well as that of the crystal dissolution process are the same.
5. The surface reaction rate constant for K-alum was found to be interrelated with the crystal size according to Eq. 25.
6. The term "size-dependent growth" is very often misused, since this dependence is only a symptom of a normally composite situation which includes both true size-dependent surface reaction and the effect of hydrodynamics on the diffusional step of crystal growth.

NOTATION

b = constant in Eq. 22
C = precoefficient in Eq. 8
C' = precoefficient in Eq. 23
D = mass diffusivity, m^2/s
g = overall growth order
j = exponent in Eq. 13
k_d = mass transfer coefficient for crystallization, kg/m^2s (kg/kg solvent)
k_D = mass transfer coefficient for dissolution, kg/m^2s (kg/kg solvent)
k_G = overall growth rate constant, $kg/m^2s\ (kg/kg\ solvent)^g$
k_r = surface reaction rate constant, $kg/m^2s\ (kg/kg\ solvent)^r$
K = mass transfer coefficient, m/s
$\bar{L}$ = mean growing crystals size, m
$\bar{L}_A$ = equivalent crystal size, Eq. 15, m
$\bar{L}_e$ = mean final crystals size, m
$\bar{L}_i$ = mean initial crystals size, m
$\dot{L}$ = linear growth rate, m/s
m_1 = mass of individual seeding crystal, kg
m_e = final mass of crystals, kg
m_i = initial mass of crystals, kg
$\dot{m}_D$ = mass dissolution flux, kg/m^2s
$\dot{m}_G$ = mass growth flux, kg/m^2s
r = surface reaction order
R_{d-r} = coefficient of correlation of Eq. 6
R_D = coefficient of correlation of Eq. 5
Re = Reynolds number defined by Eq. 14
Re_s = Reynolds number for sphere, $Re_s = uL_A\rho_l/\eta$
R_G = coefficient of correlation of Eq. 4
Sc = Schmidt number, $\eta/\rho D$
s_{d-r} = mean relative square error of Eq. 6, %
s_D = mean relative square error of Eq. 5, %
s_G = mean relative square error of Eq. 4, %
Sh = Sherwood number, $K\bar{L}_A/D$
t_D = duration of crystals dissolution time, s
t_G = duration of crystals growth time, s
T = absolute temperature, K
u = superficial velocity of solution, m/s
w = concentration, in kg of hydrate/kg solvent
w_{eq} = equilibrium concentration (solubility), kg/kg solvent
w_i = concentration at an outer boundary of the Volmer layer, kg/kg solvent
Δw = supersaturation, kg/kg solvent
x = mole fraction

Greek Letter

α = volume shape factors
β = surface shape factor
Δ = increment
$\bar{\epsilon}$ = mean porosity of a fluidized bed
η = viscosity, Pa·s
θ_w = mean working temperature, °C
ρ_c = density of crystal, kg/m^3
ρ_l = density of solution, kg/m^3
σ = relative supersaturation, $\sigma = \Delta w/w_{eq}$

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Incomplete State Feedback for Time Delay Systems: Observer Applications in Multidelay Compensation

This paper demonstrates how a recently developed observer for time delay systems may be used to estimate needed state variables for implementation of multivariable time delay compensation. The general results are illustrated by an example of a multireactor plant in which only one reactor concentration can be measured. The observer worked well in simulation for both multivarible PID control and multidelay compensated PID control and allowed both schemes to function with estimated state variables in the feedback loop.

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SCOPE

The problem of incomplete measurement for feedback control is a serious difficulty in the design of process control systems. This paper discusses how limited primary and secondary measurements may be integrated into an estimator for systems having time delays. The estimator is demonstrated for multiloop PID control and for a control system employing multidelay compensation.

CONCLUSIONS AND SIGNIFICANCE

Techniques for estimation of unmeasured states in systems with time delays are presented and illustrated by example. The simulation results indicate that the estimator should perform well when put in tandem with a multidelay compensator or other multivariable control scheme.

INTRODUCTION

In many industrial processes, transportation lags in pipes, long recycle loops, and sampling and analysis delays are frequently responsible for introducing time delays into the overall control system. These time delays very often inhibit good control system performance.

As a result control algorithms which specifically take the presence of time delays into consideration have been proposed. For systems having multiple time delays, the multidelay compensator has been developed (Ogunnaike and Ray, 1979) and has been shown to work well on an experimental system (Ogunnaike et al., 1981)

For the implementation of this time delay compensator it is tacitly assumed that all the required measurements can be made available to the controller. For systems described by input/output relations (as in the frequency domain with transfer function matrices), this assumption usually holds. In the event some of the outputs are not measured on-line, there must be other auxiliary outputs from which the unmeasured ones can be inferred (e.g., product compositions from tray temperature measurements in distillation). This requires the use of some simple correlating