H = non-Newtonian bed factor, (dynes)(sec.^{n})/cm.$^{-1-n}$
k = bed permeability, sq. cm.
K = power law parameter, (dynes) (sec.^{n}) /sq.cm.
K' = from $\frac{D\Delta P}{4L} = K' \left(\frac{8V}{D}\right)^{n'}$; (dynes)(sec.^{n})/sq.cm.
L = length, cm.
n = flow behavior index
n' = from $\frac{D\Delta P}{4L} = K' \left(\frac{8V}{D}\right)^{n'}$
N_{Deb} = Deborah number, $\frac{v\theta}{D_p}$
$N_{Re}{}^{*}$ = Reynolds number, as per Equation (6)
$N_{Re}{}^{**}$ = Reynolds number, $\frac{D_p\, G_0}{(1-\epsilon)\, \eta_{\text{mod}}}$
ΔP = pressure drop, dynes/sq.cm.
v_0 = superficial velocity, cm./sec.
v = average velocity, v_0/ϵ, cm./sec.

Greek Letters

ϵ = bed porosity
ρ = density, g./cu.cm.
η_{app} = apparent viscosity, (dynes) (sec.) /sq.cm.
η_{mod} = $15 \left(\frac{2}{25K'}\right)^{1/n'} \left(\frac{D_p\, P}{L(1-e)}\right)^{1/n'-1}$
θ = relaxation time, sec.
τ = shear stress, dynes/sq.cm.
μ = viscosity, (dynes) (sec.) /sq.cm.

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Crystallization: Kinetics and Design Considerations

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The following nucleation rate and growth rate relationships for the aqueous, continuous, cooling crystallization of potassium dichromate were determined from experimental crystal size distributions: $J = 3.9 \times 10^{10}\ (C - C_{eq})^{0.9}$; $r = 3.0 \times 10^{3}\ (C - C_{eq})^{1.7}$. Since nucleation rate is of lower kinetic order than growth rate, higher levels of supersaturation will yield crystal distributions with a larger mean size. Therefore for this system, batch or plug-flow reactors are preferred to continuous-stirred tanks.

In crystallization, nucleation and growth compete to relieve the level of supersaturation of the metastable state. Their relative kinetics primarily determine resulting size distributions. The objectives of this research were to analyze crystal size distribution data for the aqueous, cooling crystallization of potassium dichromate and to define growth and nucleation kinetics as functions of supersaturation. Using these results and previously published kinetic findings, we discuss the fundamental importance of kinetics on crystallizer design.

CRYSTALLIZATION KINETICS

Volmer's homogeneous nucleation model (*8, 16, 17*) is given by

$$J = K_1 \exp\{-K_2/[T^3 \ln^2 (C/C_{eq})]\} \tag{1}$$

where the equilibrium dissolved solute concentration C_{eq} is defined as the lower limit of Mier's metastable crystallization region. Nielsen (*8*) graphically demonstrates that Volmer's model may be approximated as a power function of C/C_{eq} for several orders of magnitude in concentration.

The application of Volmer's nucleation model to high magma suspension crystallization may be questioned in light of known secondary nucleation phenomena: foreign particles act as catalysts (*9*); crystals act as autocatalysts (*10, 15*). The autocatalytic effect has been called nuclei breeding (*14*) or secondary nucleation (*2*). In high magma suspension nucleation rate can be correlated with crystal growth rate (or supersaturation) and suspended magma concentration (*1, 6, 10, 15*):

$$J = K_N{}'\, r^i\, M^j = K_N\, s^b\, M^j \tag{2}$$

Crystal growth kinetics are generally defined as power functions of supersaturation

$$r = K_g\, s^a \tag{3}$$

where the kinetic dependency a may be close to unity (*5*) or may be significantly different from unity (*3, 13*).

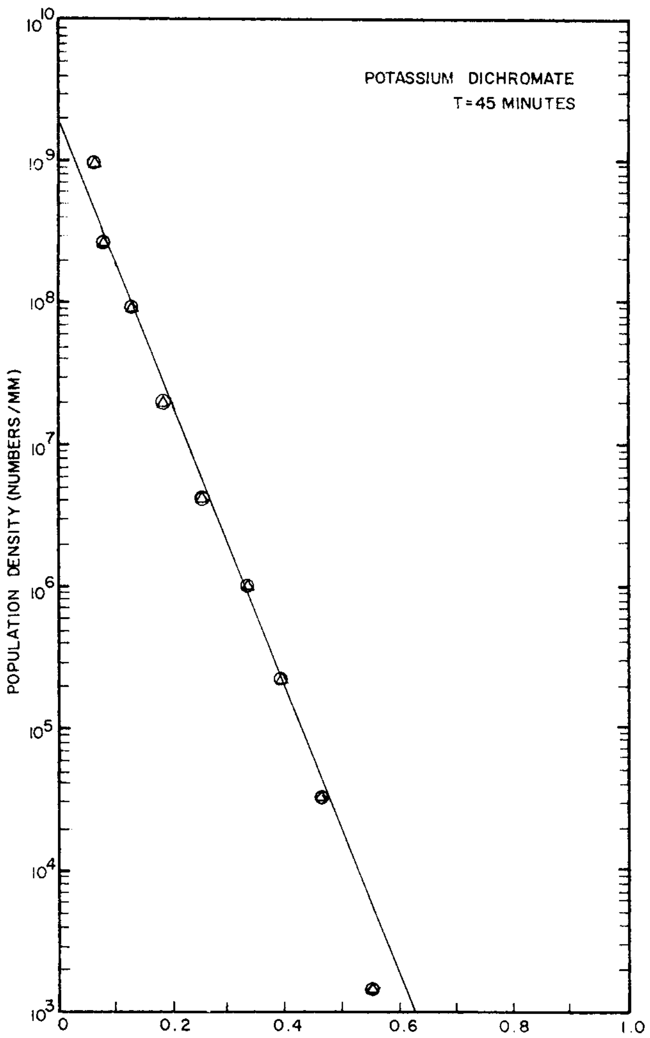

Fig. 1. Crystal population density distribution at 45-min. residence time.

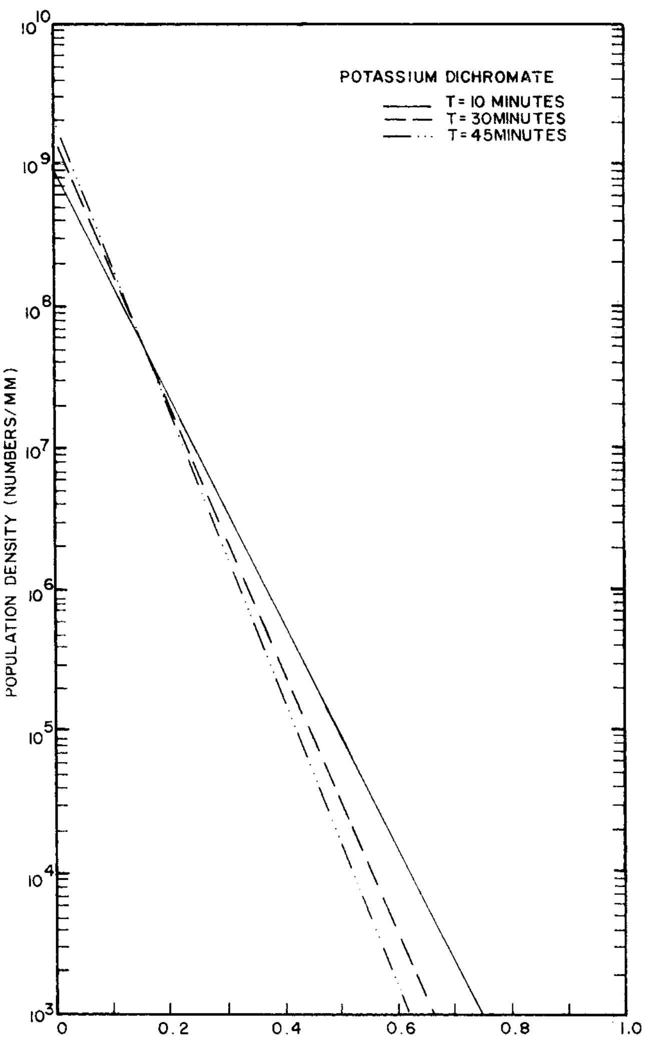

Fig. 2. Effect of residence time on crystal distributions.

The proportionality constants are functions of temperature, environment, and crystal size phenomena.

STEADY STATE CRYSTAL SIZE DISTRIBUTIONS

Larson and co-workers (*11*) and Katz and co-workers (*4*, *12*) have described mathematically crystal size distribution dynamics. For a continuous, unseeded, well-mixed, isothermal crystallizer with nonclassified product removal, crystallization dynamics can be related to crystal population density. At steady state

$$n = n^0 \exp\,(-L/rT) \tag{4}$$

where nucleation rate, growth rate, and nuclei population density are related by

$$J = n^0\, r. \tag{5}$$

In addition to conservation of population, mass must also be conserved. The mass of the crystalline phase is related to population density by

$$M = K_m \int_0^\infty n\, L^3\, dL = 3\,!\, K_m\, n^0\, (rT)^4 \tag{6}$$

At constant suspension density

$$n^0 \propto (rT)^{-4} \tag{7}$$

Utilizing growth and nucleation rate expressions and conservation of mass [Equations (3), (2), and (7), respectively]

$$s \propto T^{4/(b+3a)} \tag{8}$$

Thus, for a given perturbation in residence time, supersaturation, growth rate, and nucleation rate can be correlated. For highly soluble solutes, suspension density has frequently been observed to be independent of residence time.

CRYSTALLIZATION KINETICS AS FUNCTIONS OF SUPERSATURATION

Isothermal crystallizations of potassium dichromate were conducted in a manner to satisfy the constraints of the above model. Population densities were calculated from steady state size distribution data at constant suspension density following the methods of Murray and Larson (*7*) and Timm and Larson (*15*).

Steady state data are shown in Figure 1 and demonstrate the applicability of Equation (4). The intercept is equal to the nuclei population density and the slope is proportional to $1/rT$. Results of similar experimental runs are summarized in Figure 2. From a knowledge of nuclei population density at different levels of growth rate (or supersaturation), nucleation rate may be expressed in terms of growth rate, Equation (2). Figure 3, a log-log plot of nuclei population density versus growth rate, shows

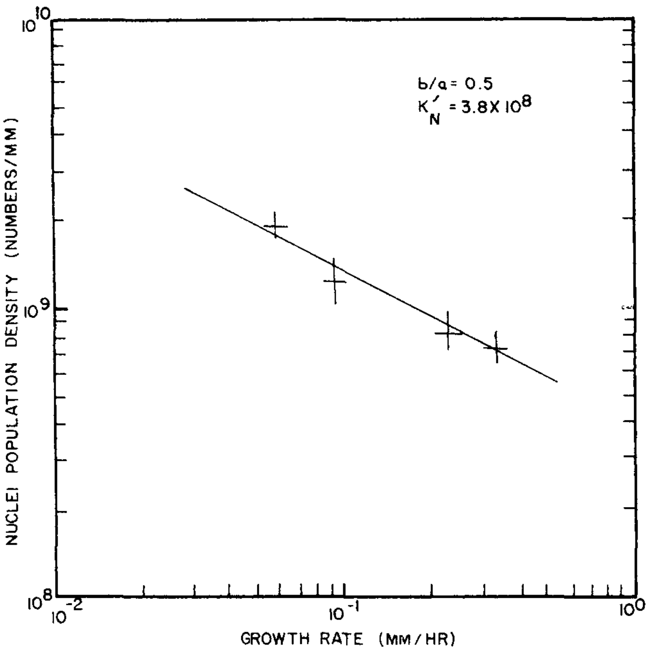

Fig. 3. Determination of nucleation kinetics, function of growth kinetics.

that the relative crystallization kinetic order, $b/a = i$, is equal to 0.5.

A second objective of the investigation was to determine crystallization kinetics as a function of the fundamental mass transfer driving force, supersaturation. A gravimetric technique was utilized. Clear mother liquor samples were withdrawn from the crystallizer, filtered, weighed, and evaporated to dryness. Weights of solid residue and liquor allowed calculation of steady state concentration. To obtain a saturated mother liquor, slurry remaining in the crystallizer after a steady state run was agitated at constant temperature in batch crystallization for several days. Resulting saturated liquors indicated $C_{eq} = 0.1025$ g./ml. at 60°F.

Growth rates, consistent with Equation (3), are shown in Figure 4. The slope of the log-log relationship implies that the kinetic order of growth rate a with respect to supersaturation is 1.7 ± 0.4 and that the proportionality constant K_g of Equation (6) is 3.0×10^3 for growth rate given in millimeters per hour.

Nucleation rates, consistent with Equation (2), are graphically summarized in Figure 5, and indicate that the nucleation kinetic order b with respect to supersaturation is 0.9 ± 0.2. From the intercept of this graph, the proportionality constant K_N is 3.8×10^{10} when the nucleation rate is expressed as numbers per hour per liter. Experimental data were also collected at several cooling rates, the results of which indicated that nucleation rate was not a function of heat exchanger duty. Thus it is assumed that nucleation occurred in the bulk suspension and is not a function of local gradients in the vicinity of the cooling coils.

The parameters n^0 and $1/rT$ were determined from steady state data consistent with the conservation of mass criterion [Equation (6)]. A family of solutions satisfies this criterion. The extremes of the solutions satisfying the mass criterion and acceptably fitting the crystal distribution are graphically shown by the respective bars of the several graphs. The corresponding uncertainties in the kinetic orders have been calculated.

KINETIC DESIGN CONSIDERATIONS

Nucleation and growth are parallel kinetic reactions. The former determines the rate of particle formation (in

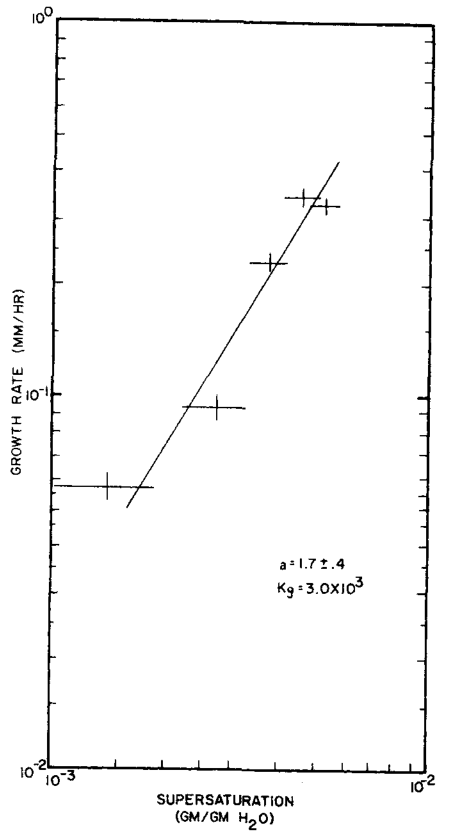

Fig. 4. Growth kinetics, function of supersaturation.

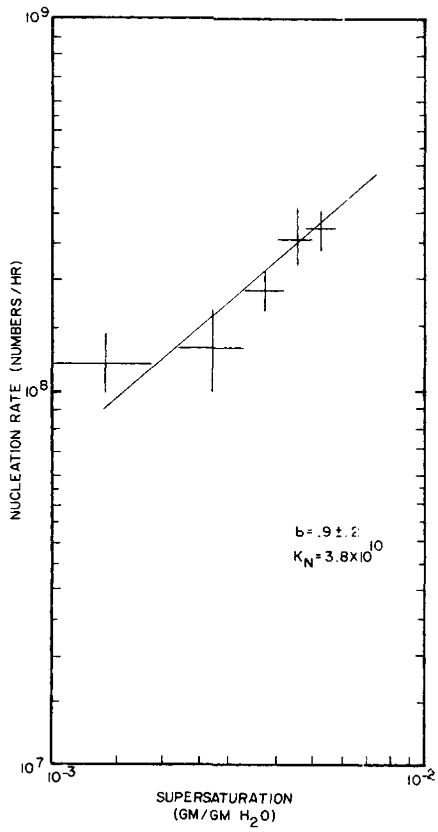

Fig. 5. Nucleation kinetics, function of supersaturation.

the absence of attrition or agglomeration); the latter determines the rate of deposition of solute on existing crystals. To control the size distribution of particles, the relative rate of particle formation compared to the rate of enlargement is of prime significance. To increase the mean particle size, nucleation must be surpressed relative to growth, resulting in fewer but larger crystals. Relative crystallization rate may be defined as

$$R = \frac{J}{r} = \frac{K_N}{K_g} s^{b/a} M^j \tag{9}$$

Depending on the respective kinetic orders, different levels of supersaturation will result in drastic changes in crystal size distributions. If the magnitude of supersaturation is small compared to magnitudes of dissolved and precipitated solute concentrations, orders of magnitude changes in supersaturation will be accompanied by an invariant suspension density. Thus for two levels of supersaturation, s_1 and s_2, at constant suspension density, $M_1 = M_2$

$$\frac{R_1}{R_2} = \left(\frac{s_1}{s_2} \right)^{b/a} \tag{10}$$

For $s_2 > s_1$ and $b > a$, $R_2 > R_1$. At the higher level of supersaturation the rate of formation of particles has increased relative to the rate of crystal enlargement. The consequence is a crystal size distribution composed of a greater percentage of fines. If $b < a$, $R_2 < R_1$; growth rate has increased relative to nucleation rate and the mean crystal size will be larger. If $b = a$, $R_2 = R_1$, and the crystal size distribution will be invariant.

Assuming a market demands large crystals, crystallization design should be based on increasing growth rate relative to nucleation rate. If growth rate is of higher order than nucleation, increasing supersaturation is beneficial. A batch reactor or a tubular reactor is preferred to a continuous well-mixed reactor. Alternately, a continuous stirred-tank crystallizer with short holding times will be favorable compared to longer residence times. However, if growth rate is of lower kinetic order than nucleation rate, decreasing supersaturation will decrease growth rate less than the corresponding reduction in nucleation rate, a reduced relative crystallization rate. The preferred kinetic design will be a continuous stirred-tank crystallizer operating at long residence times.

DISCUSSION

Crystallization kinetics for the laboratory crystallization of potassium dichromate are presented to experimentally substantiate the previously developed theory, and to express crystallization kinetics in terms of supersaturation. The results are of primary interest since they demonstrate that growth rate may be of higher kinetic order than nucleation rate.

The experimentally observed crystal size distributions encompass the size range of crystalline raw material supplied by Diamond Shamrock. Therefore the study was realistic as pertaining to crystal size dependencies. However, the authors realize that several experimental constraints are not always industrially realized, the major being perfect mixing. Frequently commercial equipment is designed to classify hydraulically the crystalline phase according to particle size. Thus crystals of different size are exposed to different environments and will consequently enlarge at different rates. In addition, other major factors, such as impurities and crystal habit, will have major influences on crystallization kinetics. The consequence of these factors should be known before design is based solely on published kinetics.

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NOTATION

A = suspension area concentration, sq.mm./liter
a = kinetic order for crystal growth
b = kinetic order for crystal nucleation
C = solution solute concentrations, g.-solute/g.-solvent
C_{eq} = solubility concentration, g.-solute/g.-solvent
i = relative kinetic order, $i = b/a$
J = nucleation rate, 1/hr.
j = secondary nucleation dependency
K = proportionality constants
K_g = growth rate constant
K_m = proportionality constant relating mass to volume
K_N = nucleation rate constant
L = characteristic crystal dimension, mm.
M = suspension density, g.-crystal/liter
$n(L)$ = steady state crystal population density, number/mm.
r = linear crystal growth rate, $r = dL/dt$, mm./hr.
s = supersaturation, $s = C - C_{eq}$, g.-solute/g.-solvent
T = absolute temperature
T = residence time, $T = V/Q$, hr.
t = time, hr.

Superscripts

(0) = property associated with nuclei

Subscripts

(i) = feed to crystallizer
(0) = effluent from crystallizer
(1) = reference steady states
(2) = reference steady states

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