ANALYSIS OF THE SYSTEM PRECIPITATION REACTOR–SEPARATOR. EFFECT OF CRYSTAL GROWTH MECHANISM ON THE FILTRATION PROPERTIES OF A SUSPENSION PRODUCED IN A CONTINUOUS REACTOR

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The filtration properties of a suspension of a sparingly soluble substance produced in a MSMPR (mixed suspension mixed product removal) crystallizer with a mean residence time t_z have been studied as a function of the crystal growth mechanism. The slope, n, of the $\log \alpha$ *vs* $\log t_z$ plot, where α is the specific mass filtration resistance, takes values of 0, 1, and 2 for the mononuclear, diffusion, and screw-dislocation mechanisms, respectively. If solid phase coagulation occurs, n takes values below 2. For the size-dependent growth, n may become greater than 2.

The filtration resistance of a suspension of a sparingly soluble substance produced in a continuous precipitation MSMPR (mixed suspension mixed product removal) crystallizer depends on the mode of operation, on the crystal growth mechanism for the given substance, and on some properties of the solid phase produced. The only case so far analyzed is that in which the crystals grow by the diffusion mechanism[1] and the filtration cake may be compressible[2]. In general, however, the growth of crystals of a sparingly soluble substance may occur by some other mechanism and moreover, the so-called size-dependent growth may take place. It is therefore of interest to examine the effect of various crystal growth mechanisms along with possible compressibility of the filtration cake and/or size-dependent growth on the filtration properties of a suspension of a sparingly soluble substance in an ideally mixed continuous precipitation reactor.

THEORETICAL

The filtration resistance of a suspension can be expressed by the Kozeny–Carman equation[3]

$$\alpha = 5(1 - \varepsilon)\, s^2/\varrho_s \varepsilon^3 , \qquad (1)$$

where s is the specific surface area of the solid phase defined as

$$s = k_a \int_0^\infty r^2 m(r)\, \mathrm{d}r / k_v \int_0^\infty r^3 m(r)\, \mathrm{d}r . \qquad (2)$$

If the suspension is produced in an ideally mixed continuous precipitation reactor, the frequency function, $m(r)$, of the particle size distribution is given by[4]

$$m(r) = (J_0 V/\dot{r}) \exp\left\{-\left(\left(\int dr/f(r, S)\right)\Big/ t_z\right\}\right. . \quad (3)$$

The function $\dot{r} = f(S, r)$ expresses the dependence of the rate of crystal growth on the crystal size and the supersaturation of solution in which the crystals grow. This function may formally be split into a supersaturation-dependent and a crystal size-dependent component,

$$\dot{r} = f(r, S) = f(r)\, f(S) . \quad (4)$$

Substituting Eqs (4) and (3) into (2), we obtain

$$s = \frac{k_a \int_0^\infty [r^2/f(S)\, f(r)] \exp\left\{-\left[\int dr/f(S)\, f(r)\right]\Big/ t_z\right\} dr}{k_v \int_0^\infty [r^3/f(S)\, f(r)] \exp\left\{-\left[\int dr/f(S)\, f(r)\right]\Big/ t_z\right\} dr} . \quad (5)$$

If the growth rate is not a function of the crystal size, *i.e.* if $f(r) = 1$, Eq. (5) becomes

$$s = \frac{k_a \int_0^\infty r^2 \exp\left[-r/f(S)\, t_z\right] dr}{k_v \int_0^\infty r^3 \exp\left[-r/f(S)\, t_z\right] dr} = k_a/3k_v\, f(S)\, t_z . \quad (6)$$

To solve the general case, Eq. (5), we must know the particular form taken by the function $f(r)$.

The crystal growth rate for the various growth mechanisms is given by the following relations[5]:
screw-dislocation mechanism

$$\dot{r} = \left[DwkTv^{11/3}(c - c_{eq}) \ln S/10x_0\right] \tanh\left(10v^{2/3}\sigma/kT \ln S\right) , \quad (7)$$

i.e., $f(r) = 1$;
polynuclear mechanism

$$\dot{r} = Dwv^{1/3}(c - c_{eq})^{2/3} \exp\left[-\beta' \sigma^2 v^{4/3}/3(kT)^2 \ln S\right] , \quad (8)$$

i.e., $f(r) = 1$;

diffusion mechanism

$$\dot{r} = Dv(c - c_{eq})/r\,, \qquad (9)$$

i.e., $f(r) = 1/r$;
mononuclear mechanism

$$\dot{r} = (6Dwr^2/v)\exp\left[-\beta'\sigma^2 v^{4/3}/(kT)^2 \ln S\right], \qquad (10)$$

i.e., $f(r) = r^2$.

When the crystal growth occurs by the screw-dislocation or polynuclear mechanism, the specific surface area of the solid phase produced in a continuous reactor is given by Eq. (*6*), where the function $f(S)$ represents the left-hand side of equation (*7*) or (*8*), respectively.

In the case of the diffusion growth, the specific surface area is expressed as

$$s = \frac{k_a \int_0^\infty r^3 \exp(-ar^2)\,dr}{k_v \int_0^\infty r^4 \exp(-ar^2)\,dr} = 4k_a \sqrt{(a)}/3k_v\sqrt{\pi}\,, \qquad (11)$$

where

$$a = \left[2t_z Dv(c - c_{eq})\right]^{-1}. \qquad (12)$$

For the mononuclear growth, the specific surface area is obtained by combining Eqs (*2*), (*3*), and (*10*):

$$s = \frac{k_a \int_0^\infty \exp(b/r)\,dr}{k_v \int_0^\infty r \exp(b/r)\,dr}\,, \qquad (13)$$

where

$$b = \left\{\frac{6Dwt_z}{v}\exp\left[-\frac{\beta'\sigma^2 v^{4/3}}{(kT)^2 \ln S}\right]\right\}^{-1}. \qquad (14)$$

Since the integrals in Eq. (*13*) are divergent, we shall replace the limits 0 and ∞ by r_{min} and r_{max}, respectively. By doing so, we shall not introduce any error, as the size of crystals in suspension does not range all the way from 0 to ∞, but only from a certain minimum size (fixed, for example, by the critical nucleus size) to a certain maximum size. Solving Eq. (*13*) modified in this manner gives

$$s = \frac{Y \exp(b/Y) - X \exp(b/X) + b \int_{1/Y}^{1/X} (1/x) \exp(bx) \, dx}{\frac{1}{2}(Y^2 + bY) \exp(b/Y) - \frac{1}{2}(X^2 + bX) \exp(b/X) + \frac{1}{2}b^2 \int_{1/Y}^{1/X} (1/x) \exp(bx) \, dx} \frac{k_a}{k_v}, \qquad (15)$$

where $X = r_{\min}$ and $Y = r_{\max}$, *i.e.* $X < Y$.
For $b \ll X$, Eq. (*15*) simplifies to

$$s \doteq \frac{2k_a}{k_v(r_{\min} + r_{\max})} \sim \frac{2k_a}{k_v r_{\max}} . \qquad (16)$$

Now, the filtration resistance of a suspension produced in a continuous reactor depends on the mean residence time in the following way:

a) for screw-dislocation and polynuclear mechanisms, where $f(r) = 1$; combining Eqs (*1*) and (*7*) or (*8*) and rearranging gives

$$\log \alpha = A - 2 \log t_z , \qquad (17)$$

where

$$A = \log \{5(1 - \varepsilon) k_a^2 / 9\varepsilon^3 \varrho_s k_v^2 f^2(S)\} , \qquad (18)$$

where $f(S)$ is given by Eq. (*7*) or (*8*), according to which growth mechanism is operative;

b) for diffusion mechanism of crystal growth, where $f(r) = 1/r$:

$$\log \alpha = B - \log t_z , \qquad (19)$$

where

$$B = \log \{40k_a^2(1 - \varepsilon)/9\pi k_v^2 \varrho_s \varepsilon^3 Dv(c - c_{eg})\} ; \qquad (20)$$

c) for mononuclear mechanism of crystal growth, where $f(r) = r^2$ and $b \ll r_{\min}$:

$$\log \alpha = E , \qquad (21)$$

where

$$E = \log \{20(1 - \varepsilon) k_a^2 / \varrho_s \varepsilon^3 k_v^2 r_{\max}^2\} . \qquad (22)$$

DISCUSSION

The filtration resistance of a suspension of a sparingly soluble substance produced in an ideally mixed continuous reactor which satisfies the requirements of an MSMPR crystallizer is a function of the mechanism by which the crystal growth occurs and of the mean residence time of the suspension in the reactor according to Eqs (*17*), (*19*), or (*21*). The crystal growth mechanism determines the value of the constant A, B, or E and the slope of the plot of $\log \alpha$ *vs* $\log t_z$ which takes the values $n = 0, 1,$ or 2. Thus, with the exception of the mononuclear growth, the filtration resistance is a decreasing function of t_z.

However, experimental data for α as a function of t_z fit an equation of the type[6]

$$\log \alpha = F - n \log t_z , \qquad (23)$$

where n mostly varies between 0 and 2.

The primary reason for the difference between the theoretical values $n = 0, 1,$ and 2 and actually found figures is that the solid phase particles agglomerate or coagulate in suspension so that the actual specific surface area, s_{eff}, that comes in contact with the liquid phase in filtration, *i.e.* which is effective for filtration, differs from that of free particles[7]. For example,

$$s_{eff} = (s/s_1)^m s_1 , \qquad (24)$$

where $0 < m < 1$, and s_1 is the size of a single particle formed by agglomeration of all particles in the system; if the mass of all the crystals is m_c, s_1 for *e.g.* a spherical particle is $s_1 = (36\pi)^{1/3} m_c^{2/3}$.

Introducing s_{eff}, we can formulate Eqs (*17*) and (*19*) as the semiempirical relations

$$\log \alpha = A' - 2m \log t_z \qquad (25)$$

and

$$\log \alpha = B' - m \log t_z , \qquad (26)$$

respectively. Since $m \in (0, 1)$, the quantity n in Eq. (*23*) may now take values $n \in \in \langle 0, 2 \rangle$ as a consequence of solid phase coagulation in suspension.

Another factor that affects the distribution $m(r)$, which in turn usually determines the specific surface area, is the so-called size-dependent growth, in which crystals of different sizes growing by a size-independent mechanism, *i.e.* by the screw-dislocation or polynuclear mechanism, grow at different rates, the growth rate being the slower the smaller the crystals. The rate of size-dependent growth may be expressed[8] formally as

$$\dot{r} = f(S)\, r^x , \qquad (27)$$

where $0 < x < 1$. After substitution of Eq. (*27*) into (*4*) and (*5*) and some manipulation, we obtain

$$s = \frac{k_a \int_0^\infty r^{y+1} \exp(-cr^y)\, dr}{k_v \int_0^\infty r^{y+2} \exp(-cr^y)\, dr}, \tag{28}$$

where $y = (1 - x)$ and $c = 1/f(S)\, t_z y$. Since $c > 0$ and at the same time $y > 0$, the solution to Eq. (*28*) is

$$s = \frac{2k_a}{3k_v} c^{1/y} \frac{\Gamma(2/y)}{\Gamma(3/y)}. \tag{29}$$

Substituting Eq. (*29*) into (*1*) gives

$$\log \alpha = A'' - [2/(1 - x)] \log t_z. \tag{30}$$

Since $y \in (0, 1)$, the slope of the log α *vs* log t_z plot is greater than 2.

The present analysis of the effect of crystal growth mechanism on the filtration resistance of a suspension produced in a continuous reactor has shown that n in Eq. (*23*) takes one of the values 0, 1, and 2 provided that no other phenomena take place. Non-integral positive values of n smaller than 2 may be accounted for by solid phase coagulation, while $n > 2$ is a consequence of size-dependent growth of crystals of the precipitated substance.

LIST OF SYMBOLS

A, A', A''	constants
a	defined by Eq. (*12*)
B, B'	constants
b	defined by Eq. (*14*)
c	concentration of solid phase in solution
c_{eq}	equilibrium solubility of solid phase
D	diffusion coefficient
E, F	constants
J_0	steady-state nucleation rate
k	Boltzmann constant
k_a, k_v	surface and volume shape factors, respectively
m	exponent in Eq. (*24*)
$m(r)$	frequency function of particle size distribution
n	slope of log α *vs* log t_z
$\dot{r}$	crystal growth rate
r	crystal radius
s	specific surface area of solid phase

s_{eff}	specific surface area of solid phase effective for filtration
S	supersaturation
T	temperature
t_z	mean residence time of suspension in reactor
v	volume of molecule
V	volume of reactor
w	correction factor
x	order of size-dependent growth
α	specific mass filtration resistance
β'	geometrical factor
Γ	Γ-function
ε	porosity
ϱ_s	density of solid phase
σ	crystal-solution interfacial tension

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