MODELING THE BEHAVIOR OF A CONE-SHAPED, FLUIDIZED-BED STRUVITE CRYSTALLIZER

Purpose of Modeling

To design a vessel for carrying out a chemical reaction, it is necessary to relate mathematically the dimensions of a reactor to the flow rate through it, the concentration of reactants in the entering and exiting flows, and the reaction rate. The relation, often called a design equation, enables the designer to specify reactor dimensions given the other information and can be viewed as a model of reactor behavior. Different types of relations are required for different types of reactors, because the character of motion within the reactors varies. Often the character of motion is complex and/or not completely known, resulting in complex or unknown relations. Simplifying assumptions about the character of motion can facilitate the derivation of useful, though only approximate, relations.

Simplifying Assumptions for the Crystallizer

The goal is to model the behavior of a cone-shaped, fluidized-bed struvite crystallizer. Three alternative internally consistent sets of simplifying assumptions have been identified about the character of motion. The first, here called the "mixed liquid, mixed bed," or "MLMB" set of assumptions, is that the liquid in the reaction zone (the part of the cone occupied by the fluidized bed) is perfectly mixed, and that the bed is also perfectly mixed. In other words, concentrations in the bulk liquid will be constant throughout the reaction zone, as well as particle size distribution of the solid. The second set, here called the "plug-flow liquid, mixed bed," or "PLMB" set of assumptions, is that the liquid moves in plug flow; that is, only upward from the entry point at the cone bottom, through the bed and exiting the bed at its top, while the bed is perfectly mixed. The third, here called the "plug-flow liquid, classified bed," or "PLCB" set of assumptions, is that the liquid moves in plug-flow and the bed is perfectly classified. In other words, at any given height, the bed contains particles of only one size, and the particle size decreases continuously from bottom to top. All three sets also

include the assumptions that the reaction is crystallization of struvite at the surface of the particles, that boundary layer resistance to diffusion of ions to the reaction site is negligible, and that struvite product is removed from the reactor bottom at the rate required for steady state. Finally, all three assume that the reaction rate can be characterized by the equation:

$$-\frac{dP}{dt} = mk'(P - P_e) \tag{4}$$

This equation expresses mathematically the relationship that Ohlinger et al. (2000) report as describing struvite precipitation rate. Here, however, the reaction rate constant, which that report designates simply as *k*, has been broken into two factors because the current work needs to consider them separately: *m*, the surface area of bed particles per volume of reaction zone, in units of area per volume; and k', the surface-area-specific reaction rate constant, which is the rate of drop in *P* per unit of *m* and is expressed in units of length per time. *P* is the conditional solubility product expressed in molarity cubed, and P_e is that value for a solution at equilibrium with struvite. The symbol *t* stands for time.

Mathematical relations, or models, for each of the assumption sets are derived below, followed by a comparison of the models. Each symbol is defined the first time it is used and also in the "List of Abbreviations and Symbols" at the front of the present work. The comparison of the models focuses on Figure 11, which displays predicted concentration profiles of the three models on the same plot to show their differences.

MLMB Model

Under this set of assumptions, the portion of the crystallizer occupied by the bed is an example of a continuous stirred tank reactor, because no gradients exist in either the liquid concentrations or the distribution of the bed particles. For such a reactor, Fogler (1999) provides a design equation:

$$V = \frac{F_{j0} - F_j}{-r_j} \tag{5}$$

where V signifies the volume of the reaction zone, which in the crystallizer is the portion occupied by the bed. F_{j0} is the moles per time of the reactant species j entering the crystallizer. For struvite as j, this quantity is calculated in the present analysis as the dissolved moles per time of Mg, TAN, and OP, the sum divided by three. F_j is the moles per time of reactant species j exiting the reaction zone of the crystallizer, calculated for struvite in this analysis in the same manner as F_{j0}. The symbol $-r_j$ means reaction rate, expressed as moles of species j consumed per time per volume of reaction zone. For struvite crystallization, it is one third of the sum of the moles of Mg, TAN, and OP that precipitate per time per volume of solution.

Equation (5) enables us to determine the required reaction volume for entering wastewater of known concentration and desired reduction, provided we have an equation for $-r_j$, the reaction rate. In our case, j is dissolved struvite and $-r_j$ can be represented by (dx/dt), where x is the moles of struvite that have precipitated, per volume of solution:

$$-r_j = \frac{dx}{dt} \quad where \quad x = \frac{\{([M]_0 - [M]) + ([A]_0 - [A]) + ([P]_0 - [P])\}}{3} \tag{6}$$

In equation (6), $[M]$ represents the molar concentration of dissolved Mg in liquid in the reaction zone, while $[M]_0$ is that value in the liquid entering the reaction zone. $[A]$, $[A]_0$, $[P]$, and $[P]_0$ are the analogous values for TAN and OP.

However, our only rate expression, equation (4), expresses the rate not in moles per time but in conditional solubility product per time. In other words, the rate in equations (5) and (6) is the rate at which struvite molar concentration would drop in the solution during an infinitesimally short period in which the struvite concentration in the entering liquid were reduced to zero, while the rate in (4) is the drop in conditional solubility product during that period. Therefore, to use equation (5), we

must convert equation (4) into an expression for $-r_j$. To undertake the conversion, we first recognize that P can be viewed as a function of x:

$$P = P(x) = ([M]_0 - x)([A]_0 - x)([P]_0 - x) \tag{7}$$

By the chain rule for differentiation, we know that:

$$\frac{dP(x)}{dt} = \frac{dP(x)}{dx}\frac{dx}{dt} \tag{8}$$

and, by rearranging (8):

$$\frac{dx}{dt} = \frac{dP(x)}{dt}\left[\frac{dP(x)}{dx}\right]^{-1} \tag{9}$$

Substituting equation (4) into equation (9) and also differentiating equation (7) with respect to x and substituting the derivative into equation (9) at the appropriate point results in:

$$\frac{dx}{dt} = \frac{mk'(P - P_e)}{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)}, \tag{10}$$

which is our required expression for $-r_j$. Substituting this expression into equation (5) results in:

$$V = \frac{(F_{j0} - F_j)\{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)\}}{mk'(P - P_e)} \tag{11}$$

Now, recognizing that m is the reaction surface area per volume of reaction zone and S is the surface area content of the bed material (area per mass), m equates to (S/V) in this case since the bed distribution is homogeneous. In equation (11), S/V can then be substituted for m, and P can be written out as the expression given in equation (7). Also, because of the perfect mixing assumption, x is constant throughout the reaction zone, including the exit point, and therefore ($F_{jo} - F_j$) can be replaced by the product of x and the volumetric flow rate (v_0):

$$S = \frac{(x v_0)\{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)}{k'[([M]_0 - x)([A]_0 - x)([P]_0 - x) - P_e]} \tag{12}$$

Equation (12) is the mathematical relation we sought for modeling the behavior of the reactor under this assumption set. The disappearance of V as a design factor means that, with this assumption set, the volume of the reaction zone is irrelevant to the degree of reduction achieved. Rather, the total surface area in the bed is the determining factor, with a given molar flow rate into the reactor.

With equation (12), the surface area required in the reactor can be calculated, given the entering concentrations, flow rate, and specified reduction in dissolved struvite. Or, with given entering concentrations, flow rate, and S, the resulting reduction can be calculated by finding the x that satisfies the equation.

The relation yields a constant concentration within the reaction zone, as would be expected due to the initial assumption that there are no gradients within the zone. As can be seen in Figure 11 in the subsection "Comparison of the Models" below, the concentration profile is a step function, starting at the initial concentration in the entering liquid and immediately falling to the final concentration at the entry point and continuing at that level through the reaction zone. The profile was obtained from equation (12) by solving for x after inserting the values for all other variables as given in the condition set description associated with the figure. The value for x obtained in this way was converted to the OP concentration shown in the figure by subtracting the x from $[P]_0$ to get the OP molarity in the reaction zone, then using the atomic weight of phosphorus to convert the resulting OP molarity to ppm OP as phosphorus.

PLMB Model

This assumption set holds that the bed material is well enough mixed that it is distributed evenly throughout the reaction zone, thereby distributing also the reaction surface evenly through the zone, while the liquid moves in plug flow. The crystallizer behavior therefore can be described as a plug flow reactor, for which Fogler (1999) provides a design equation:

$$\frac{dF_j}{dV} = r_j \tag{13}$$

The r_j represents –(dx/dt) rather than the (dP/dt) that our only available rate equation provides, so it must be transformed, using the same method employed under the MLMB model. Doing so, and substituting the transformed expression for r_j into equation (13) yields:

$$\frac{dF_j}{dV} = \frac{mk'(P - P_e)}{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)} \tag{14}$$

Now, the struvite concentration in moles per volume at any point can be expressed as:

$$struvite\ concentration = \frac{[M]_0 + [A]_0 + [P]_0}{3} - x\,, \tag{15}$$

and F_j at any point is equal to the volumetric flow rate, v_0, times the struvite concentration at that point. Because v_0 and all quantities on the right side of equation (15) other than x are constant,

$$\frac{dF_j}{dV} = -v_0 \frac{dx}{dV} \tag{16}$$

Substituting the right side of equation (16) for the left side of equation (14) and rearranging yields:

$$-v_0 \frac{\{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)\}}{mk'(P - P_e)} dx = dV \tag{17}$$

Recognizing that m and k' are constant, writing out P, and integrating equation (17):

$$\frac{-v_0}{mk'} \int_0^x \frac{\{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)\}}{([M]_0 - x)([A]_0 - x)([P]_0 - x) - P_e} dx = \int_0^V dV \tag{18}$$

The integral on the right side of equation (18) equates to simply V, and m is equal to S/V. Equation (18) therefore becomes:

$$S = \frac{-v_0}{k'} \int_0^x \frac{\{3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0)\}}{([M]_0 - x)([A]_0 - x)([P]_0 - x) - P_e} dx \tag{19}$$

Equation (19) is the relation for modeling the behavior of the crystallizer under the PLMB assumption set. As in the MLMB model, volume has been eliminated as a design variable, leaving bed surface area as the characteristic of interest. The integral on the right side of equation (19) cannot easily be integrated analytically and therefore numerical integration will be required.

The relation yields a concentration that varies within the reaction zone. As can be seen in Figure 11, the PLMB concentration profile starts at the initial concentration at the entry point and continuously falls through the reaction zone. For this profile, equation (19) was integrated to x to find S for each in a series of values for x, starting at zero and continuing upward until the S for the entire bed was reached. The variables other than x in equation (19) were the same as those used in equation (12) for the MLMB profile because the same condition set—the one described in association with the figure—was used here. Each S was then converted to a height by calculating the height of the cone that would contain that amount of surface area, using the assumption that the surface area is evenly distributed throughout the reaction zone. This assumption is consistent with the PLMB model.

PLCB Model

The mathematical relation for this model is derived using the same approach adopted by Shiau and Liu (1998) for their perfect classified crystallizer model, except that three extensions are made in the present case: (1) the diameter of the reaction zone is treated as a variable with respect to height rather than as a constant; (2) the solute here is treated as three different dissolved species being taken up from the liquid into the crystal, the concentrations of which all figure in the crystallization rate equation and vary independently of one another in the entering stream; and (3) water of hydration is accounted for in the crystal. The method is demonstrated below, and the points at which the three extensions cause the derivation to diverge from that of Shiau and Liu (1998) are noted.

In the approach, Shiau and Liu (1998) use two material balances. One balance results in an expression for the rate of change in concentration in the liquid phase with height $\left(\frac{dC}{dH}\right)$. Here H is height within the vessel. C is the concentration of struvite in the liquid phase, specifically, the sum of the concentration of all OP species, expressed as mass PO_4^{-3} per mass of water; the concentration of Mg ions, expressed as mass Mg per mass of water; and the concentration of TAN, expressed as mass NH_4^+ per mass of water.

The other balance yields an expression for the rate of change in particle radius, L, of the solid phase with height $\left(\frac{dL}{dH}\right)$. Particles can be any shape, but all particles are assumed to be the same shape. Substitutions are made for several variables in the expressions to ensure that the expressions consist only of constants, one independent variable (height), and two dependent variables (particle radius and concentration). The result is two interlinked differential equations that can be solved numerically when two initial conditions are applied, thus predicting the particle radius and concentration for any height.

In the first material balance, Shiau and Liu (1998) equate to zero the difference between the time rate of increase in the mass of suspended crystals in a horizontal slice of the crystallizer and the time rate of disappearance of crystals' constituent species dissolved in the liquid phase in the horizontal slice. In the present case, the result is:

$$(Q\rho)\frac{1}{(1+C_0)}(C_H - C_{H+\Delta H}) - \frac{(1-\varepsilon)\left[\frac{1}{3}\pi\Delta H(r_H{}^2 + r_H r_{H+\Delta H} + r_{H+\Delta H}{}^2)\right]}{(\alpha L^3)}(\beta L^2)(G\rho_p{}^*) = 0 \qquad (20)$$

In equation (20), the first term is the same as that in Shiau and Liu (1998) and represents the time rate of disappearance of the crystals' constituent species in the liquid phase, and can be broken into three factors:

$(Q\rho)$, equal to the mass of liquid entering the crystallizer per time, where Q is the flow rate of liquid phase entering the vessel (volume per time) and ρ is the density of the liquid phase (mass per volume);

$\frac{1}{(1+C_0)}$, equal to the fraction of the liquid entering the crystallizer that is water, where C_0 is the concentration of struvite in the liquid phase at entry, expressed in the same manner as C; and

$(C_H - C_{H+\Delta H})$, equal to the time rate of decrease in mass of dissolved struvite per mass of water

between the liquid flowing into and out of the horizontal slice, where C_H is equal to C at a given height H and $C_{H+\Delta H}$ is C at a height increment, ΔH, above H.

The second term in equation (20) is the mass per time of Mg, ammonium, and phosphate ions being deposited onto the suspended particles in the horizontal slice. It also can be broken into three factors. The term differs from that in Shiau and Liu (1998) in the first and third factors.

The first factor, $\dfrac{(1-\varepsilon)\left[\frac{1}{3}\pi\Delta H(r_H{}^2 + r_H r_{H+\Delta H} + r_{H+\Delta H}{}^2)\right]}{(\alpha L^3)}$, is equal to the number of particles in the slice. The numerator is the volume of crystals in the slice. The expression in brackets gives the total volume of the slice, using the formula for a horizontal slice of a cone. The symbol α is the dimensionless volume factor for a solid struvite particle. Multiplying it by L^3 gives the volume of the particle. For example, for a sphere, the volume factor is $4\pi/3$. The expression in brackets differs in the present case from that given by Shiau and Liu (1998) because they dealt with a cylindrical vessel instead of a cone. The denominator is the volume per particle. The symbol ε represents void fraction; that is, the fraction of volume occupied by the liquid phase at a given height in the vessel. The symbol r_H is the radius of the cone at height H, and $r_{H+\Delta H}$ is the radius at height $H+\Delta H$ (length).

The second factor, (βL^2), is equal to the surface area per particle. Multiplying it by the first factor gives the total surface area in the slice. β is the dimensionless surface factor for a solid struvite particle. Multiplying it by L^2 gives the surface area of the particle. For example, for a sphere, the surface factor is 4π.

The third factor, $(G\rho_p{}^*)$, is equal to the mass of Mg ions, ammonium ions, and phosphate ions deposited per surface area per time. G is the rate of deposition of struvite onto a solid struvite particle surface, in length per time. It is equal to $\dfrac{dL}{dt}$. The symbol $\rho_p{}^*$ is the density, in mass per

volume, of struvite excluding the weight of the water of crystallization. Shiau and Liu (1998) here used simply ρ_p , the density of the solid phase, because they did not consider that it contained any water of crystallization from the liquid phase.

Now, rearranging equation (20) gives:

$$\left[\frac{C_H - C_{H+\Delta H}}{\Delta H}\right] = \frac{\frac{1}{3}\pi(r_H{}^2 + r_H r_{H+\Delta H} + r_{H+\Delta H}{}^2)\beta\rho_p * (1-\varepsilon)(1+C_0)}{\alpha\rho QL} G \tag{21}$$

where ρ is the density of the liquid phase. Taking the limit as ΔH approaches zero:

$$\frac{dC}{dH} = \frac{A\beta\rho_p * (1-\varepsilon)(1+C_0)}{\alpha\rho QL} G \tag{22}$$

In the limit as ΔH approaches zero, $r_{H+\Delta H}$ becomes equal to r_H, and $\frac{1}{3}\pi(r_H{}^2 + r_H r_{H+\Delta H} + r_{H+\Delta H}{}^2)$ in equation (21) therefore becomes $\frac{1}{3}\pi(3r_H{}^2)$, or simply $\pi r_H{}^2$, which is equal to A, the cross-sectional area of the cone at a given height.

To continue with the Shiau and Liu (1998) method, the expression must contain no variables other than C, L, and H, and therefore, expressions containing no variables other than those must be substituted for A (which, unlike the present case, was constant in Shiau and Liu [1998]), ε, and G. However, β, ρ_p*, ρ, α, Q, and C_0 are taken as constants for a reactor operating at steady state and with particles of constant shape.

With the assumption that the diameter of the vessel varies linearly with H, as in a cone, A can removed from equation (22) by expressing it as:

$$A = \left(\frac{\pi}{4}\right)\left[W_0 + \frac{H}{H_t}\left(W_t - W_0\right)\right]^2 \tag{23}$$

where W is the diameter of the vessel at a given height, W_t is the diameter of the vessel at its top, W_0 is the diameter at its bottom, and H_t is the height of the vessel.

To express ε as a function of C, L, and H, Shiau and Liu (1998) started with the equation of Richardson and Zaki (1954):

$$U_S = U_T [10]^{\left(\frac{-L\gamma}{W}\right)} \varepsilon^Z \tag{24}$$

where U_S is the superficial upward velocity of liquid phase, expressed in length per time. At a given point in the vessel, it is equal to the volumetric flow rate of the liquid divided by the cross-sectional area of the vessel at that height; i.e., it is the upward velocity the liquid would have if there were no bed. U_T is the terminal velocity of a bed particle, expressed in length per time, and is the downward velocity a particle would reach if falling by itself through the liquid. The symbol γ is the dimensionless diameter factor for a solid struvite particle. Multiplying it by L gives the diameter of the particle. For example, for a sphere, the diameter factor is 2. Z is the expansion index, which is dimensionless and indicates how much the bed is expanded versus its condition with no flow.

Solving equation (24) for ε:

$$\varepsilon = \exp\left[\frac{\ln U_S - \ln\left(U_T (10)^{-\frac{L\gamma}{W}}\right)}{Z}\right] \tag{25}$$

The variable Z is itself a function of U_T, and thus Shiau and Liu (1998) eliminate it by replacing it with that function. Shiau and Liu (1998) note that the function differs depending on what range the Reynolds number, R_T, is in, with R_T defined by Kunii and Levenspiel, 1969, as:

$$R_T = \frac{U_T \rho L \gamma}{\mu} \tag{26}$$

For calculating R_T in the present case, no data could be found on the value of μ for lagoon water and thus it was taken to be the same as water, resulting in an estimated range for R_T of 1 to 70. Shiau and Liu (1998) note that Z is estimated in this range by Richardson and Zaki (1954) as:

$$Z = (4.4 + 18\frac{L\gamma}{W})R_T^{-0.1} \tag{27}$$

In the present case, unlike the Shiau and Liu (1998) method, the second term within the parentheses may be ignored because $L\gamma / W$ is always very small, leaving:

$$Z = 4.4R_T^{-0.1} \tag{28}$$

As Shiau and Liu (1998) have done, the variable U_T can be eliminated from equation (25) and from equation (28), where it figures as a factor in R_T, by estimating it using the Kunii and Levenspiel (1969) prediction within this R_T range:

$$U_T = \left[\frac{4}{225}\frac{(\rho_P - \rho)^2 g^2}{\rho\mu}\right]^{\frac{1}{3}} L\gamma \tag{29}$$

where g is the acceleration of gravity. The variable U_S is constant in the Shiau and Liu (1998) method, but is variable in the present case. It can be eliminated from equation (25) by recognizing that it is equal to Q/A; thus from equation (23) we see that:

$$U_S = \frac{Q}{\left(\frac{\pi}{4}\right)\left[W_0 + \frac{H}{H_t}(W_t - W_0)\right]^2} \tag{30}$$

We can eliminate the variable W, which does not figure in the Shiau and Liu (1998) method but which has been introduced in the present case in the effort to eliminate other variables, with the relation:

$$W = W_0 + \frac{H}{H_t}(W_t - W_0) \tag{31}$$

Substituting equations (29) into equation (26), and substituting the result into equation (28) yields an expression that can be substituted for Z in equation (25). Substituting equations (29), (30), and (31) into equation (25) for U_T, U_S, and W, respectively, yields the expression we sought for ε in terms only of constants and of the variables C, L, and H: