COMPARISON OF LABORATORY RESULTS WITH MODEL-PREDICTED RESULTS

The PLMB (plug-flow liquid, mixed bed) model predicts results observed in the laboratory better than does either the MLMB (mixed liquid, mixed bed) model or PLCB (plug-flow liquid, classified bed) model. Discussions of each model in light of the actual results follow. The discussions refer primarily to laboratory results from the first stage, i.e. fixed-condition runs (FCRs) because the phosphorus concentration profile with respect to height, a key difference among the models, was evaluated only in that stage. Furthermore, within the first stage, only the two periods of near-steady state operation (one during the first series of FCRs, and the other during the third series of FCRs) are considered, because all three models presume steady-state operation.

MLMB Model

Consistent with a principal assumption of the MLMB model, the bed appeared to be well mixed. In all runs, the bed was observed to be churning. In addition, the particle size distribution appeared homogeneous; that is, instead of seeing all fines at the top of the bed graduating to all coarse material at the bottom, there appeared to be a similar mixture of material of all sizes at all heights in the bed.

However, the observed concentration profile differs sharply from predicted behavior. Because the liquid is assumed to be perfectly mixed, there can be no differences in concentration at varying heights after entering the crystallizer under this model. Figures 40 and 41 present plots of the MLMB-predicted and actual observed OP concentration versus height in the crystallizer for the near-steady state periods in the first and third FCR series.

To produce the MLMB-predicted profiles for each of the near-steady-state periods, the flow rate (49.2 L/h) and average dissolved Mg, TAN, and OP concentrations in the in-flowing liquid, after ammonia and Mg (if any) additions, during each near-steady state period were used as starting points for the model. These concentrations are those shown for the raw liquid centrifugate in Table 9 and the input liquid centrifugate in Table 10 (54.8 ppm OP, 602 ppm TAN, and 24.6 ppm Mg for the first
Figure 40: Observed and MLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #1

Figure 41: Observed and MLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #3
series; 33.2 ppm OP, 435 ppm TAN, and 46.9 ppm Mg for the third series). The model then predicted the profile of dissolved OP, to which was added a constant concentration of OP to account for the suspended solid. This concentration is treated as a constant because the model assumes the suspended solid does not participate in reactions. The constant value used for OP concentration in the suspended solid for the first series is that indicated for the sediment of the raw liquid in Table 9 (15.2 ppm), and for the third series is that indicated for the sediment of the input liquid in Table 10 (11.2 ppm).

A k’ value is required as input. The model was run five times for the first-series period and five times for the third-series period, using k’ values of 0.4, 2, 5, 10, and 15 dm/h for each period. The k’ cited here is the same reaction rate constant as that mentioned in earlier sections; i.e., it is the constant of proportionality between the reaction rate, expressed in molar product per time, and the product of the surface area per reaction volume and the excess molar product.

The MLMB model also requires as input an estimate for total bed surface area. The estimates, 103 and 163 dm² for the first and third series, respectively, were obtained from the bed weight and particle size distribution data averaged over the near-steady state periods. The data for the first series is shown in runs 13 through 16 on Figure 13, and the data for the third series is shown in runs 9 through 13 on Figure 23. The bed particles were assumed to be spherical for the calculation. The reactor dimensions, also needed as input, are those described in the “Equipment, Materials, and Procedures Used” subsection of the “Experiments with Laboratory-Scale Continuous Crystallizer” section. Finally, the pH of the reaction, which is also required input because it determines the equilibrium conditional solubility product, was set equal to the average of the observed values for the runs in the near-steady state periods. These values, 8.32 for the first series and 8.61 for the third series, are converted to equilibrium conditional solubility products of $6.3 \times 10^{-9}$ and $3.55 \times 10^{-9}$ mol³/L³, respectively, by reading from Figure 1.
In the figures, the MLMB-predicted concentrations drop immediately upon entry into the vessel (height of zero cm) to their final values. As expected, the higher the assumed rate constant, the larger is the drop. Also, the MLMB model predicts a greater drop for the third series than the first. In fact, the third-series predictions for all five rate constants lie nearly on top of one another, near struvite equilibrium. The difference in predictions between the series can be attributed to the greater driving force (greater supersaturation, as a result of Mg addition) and surface area of the third series.

In contrast to the MLMB-predicted profiles, the observed values drop at a finite rate that decreases with height. Furthermore, the final observed concentrations are lower than the predicted values. These comparisons suggest that, contrary to the assumption underlying the MLMB model, the liquid is not well-mixed.

PLCB Model

The observed churning motion and homogeneity in the bed contrast with the classified-bed assumption underlying this model. In addition, the PLCB-predicted concentration profile differs from the observed profiles. Figure 42 shows the profile of OP concentrations predicted by PLCB model for a crystallizer operating at the conditions in place during the near-steady state portion of the first series of FCRs, along with the observed profile.

The same input data on composition, pH, equilibrium conditional solubility product, crystallizer dimensions, k’, and flow rate as that used in the MLMB for the first series were used here. In contrast to the MLMB model, the PLCB does not require input as to the characteristics of the bed. Rather, it requires input on the product particle size and the seeding rate, and then predicts the bed characteristics. The seeding rate input was that used during the period, 18 seeds per s, and the product particle size was set equal to the size that produces the observed weight rate of production at 18 particles per s. Note that the observed average size was somewhat smaller, as the actual number of product particles per s was calculated at around 22. However, the additional 4 particles per s were
occurring by a process other than seeding, contrary to the assumptions of the PLCB. The slightly larger particle size input was used to better adhere to the assumptions of the PLCB model.

Additional input required by the PLCB model include the liquid viscosity and the particle shape factors, which relate the diameter, surface area, and volume to the particle radius. For the former, the viscosity of liquid water, 0.001 kg/(m-s), was used. For the latter, the particle shape was assumed to be spherical, as in the MLMB model, resulting in values of 2 for $\gamma$, the diameter-to-radius factor; $4\pi$ (12.57) for $\beta$, the surface area-to-radius-squared factor; and $4\pi/3$ (4.19) for $\alpha$, the volume-to-radius-cubed factor.

Note in Figure 42 that the PLCB-predicted profiles all exhibit OP concentration decreases that start somewhat slow, then steepen to a more rapid drop-off of OP with respect to height. The trend in slope in the lower and middle portion of the bed is therefore opposite to that seen in the observed profile in the same figure. The difference in the slope trend between the observed and
PLCB profiles can be explained by the difference in degree of bed mixing. In the perfectly classified bed assumed under PLCB, the lowest part of the bed contains only the coarsest particles, which offer the least surface area for reaction. The finest particles, which offer the greatest area, are concentrated at the top, so the fastest reaction and rate of OP concentration drop would also be found at the top. However, a well-mixed bed provides equal surface area for reaction throughout. With equal area throughout, the fastest reaction would be located where the supersaturation, which is the driving force for the reaction, is greatest. Supersaturation is greatest where the liquid enters at the bottom and decreases toward the top as the reaction proceeds, and therefore the rate of reaction and drop in concentration would reflect that trend.

The better matching of the observed profile with the latter condition indicates that, contrary to the assumption in the PLCB model, the bed is not classified. This conclusion is consistent with the visual appearance of the bed.

The PLCB model was not applied to the third series, because the actual conditions were inconsistent with the basic assumptions of the model. Specifically, the seeding rate, which was zero, is an impossible condition under the PLCB assumptions because it would result in no product, no bed, and no reaction. The fact that a stable bed, production rate, and reaction were in fact observed while the seeding rate was zero is further evidence against the validity of the PLCB model.

**PLMB Model**

Figures 43 and 44 show the PLMB-predicted OP concentration profiles for the near-steady state periods in the first and third runs, along with the corresponding observed OP profiles. For both periods, the observed profile can be seen to lie near the PLMB lines corresponding with $k'$ values of 10 and 15 dm/hr. Hence, the PLMB model, with $k'$ in that range, best fits the observed crystallizer behavior.
Figure 43: Observed and PLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #1

Figure 44: Observed and PLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #3
The input required by the PLMB models is the same as that described for the MLMB model. Therefore, the data used as input for the PLMB profiles presented in Figures 43 and 44 is the same as that used for the MLMB profiles.

The PLMB profiles at the higher k’ values exhibit the same rate trend—that is, concentration decrease that starts out rapid and slows as height increases—as that actually observed. The profiles at the lower values for k’ show some delay in reaching the fastest rate in concentration decrease. For k’ of 5 dm/h in the first series, the decline in the second segment (from 5 to 12 cm of height) in the reaction zone is as fast as the decline in the first segment (0 to 5 cm), while the fastest declines occur in the second and third (12 to 19 cm) segments, respectively, for k’ of 2 and 0.4 dm/h. For the third series, a similar trend with increasing k’ can be seen in Figure 44. Comparing Figures 42 and 43, however, shows that, with the same conditions, the PLCB predicted greater delay than PLMB in reaching the steepest point, predicting the steepest profile no earlier than the second segment even for the highest k’ values.

Though the PLMB profiles in the k’ range of 10 to 15 dm/hr approximate the observed profiles quite well, there is a difference evident for both periods. The observed rate of decrease slowed slightly in the 5-to-12 cm segment in comparison with the PLMB profiles, resulting in a slightly higher observed than PLMB-predicted concentration for both periods at the 12-cm height. This difference may result from some mixing in the liquid. As the liquid flows up from the bottom toward the top of the cone, the diameter through which it flows increases, resulting in greater opportunity for mixing. Mixing, even if it is only slight and occurring within an overall plug-flow pattern, would at each height where it occurs inject some higher-concentration liquid from below, thus raising the observed concentration.

The positive divergence from PLMB-predicted concentration observed at the 12-cm height disappears at greater heights for both the first-series and third-series comparisons. In the third series, the divergence even reverses itself, the final observed concentration being lower than the PLMB
prediction. This continuing decrease in observed concentration high in the cone may result from easing of mixing of the liquid or from another mechanism for phosphorus removal not reflected in the model. As discussed earlier in the results, material balances on these periods indicated that some of the phosphorus removal occurs from the suspended solid phase, a process not reflected in the model. Perhaps this process occurs in the upper portion of the cone and is thus responsible for the continuing concentration decrease seen in that region.