

Figure 22: Second Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h) (Run Numbers Indicated)

Discussion of Results from FCR Series #2

A material balance conducted on phosphorus over the second series must reflect, in addition to the items explained in the discussion of the first series results, the effects of adding the Mg solution. To take these into account, the TP concentration in the Mg solution, multiplied by its inflow rate (1.9 L/h) and the run duration, must be added as an input. Also, the flow rate of treated liquor must be increased by 1.9 L/h as a result of the additional inflow. The balance shows inputs of 192 g in raw liquid, 12.7 g in the Mg solution, and 2.3 g in seeds. Outputs were 69.5 g in product and 107 g in treated liquid, while net accumulation was +30.0 g. Inputs are 99.9% accounted for, a very close match given the random experimental error in sampling and analysis, further lending credence to the calculated phosphorus reductions. No period of near-steady state operation was achieved during the second series, so there was no material balance conducted for a shorter series of runs within the second series.

There are at least three explanations for the bed build-up and resulting failure to achieve steady state during this series. First, the slippage of the glass input tube into the manifold, partly obstructing product discharge into the collector, appears to have contributed to the bed build-up. The fact that product discharge increased dramatically, with the accompanying drop in bed weight, immediately after the inlet tube was moved back to the correct position argues powerfully that the problem contributed to bed growth. However, the slippage cannot explain all the bed growth, because the growth resumed and product discharge trailed off again, within five runs after the problem was corrected. The manifold was checked frequently after correcting the slippage to ensure that the problem had not recurred.

Second, the higher rate of seeding could contribute to bed growth. The series was begun with a seeding rate about 2.1 times greater than that used in the first series, to accommodate the higher rate of precipitation expected in the second series due to the addition of Mg. The seeds themselves would add weight to the bed, and the greater number of seeds could also reduce the average particle size in the bed because the precipitating solid would be distributed across a greater number of particles. However, the weight of the seeds added during the series was small in comparison with the 160 g of bed weight increase during the series. Moreover, the bed weight increase continued through the first half of the series and reappeared during the last four runs, but the seeding was terminated at the end of the third run. Therefore, it appears unlikely that the seeding contributed significantly to the bed growth.

The third possible explanation is that the net creation of nuclei in the crystallizer was much greater than the rate during the first series. The rate would need to be at least 18 nuclei per second higher than that in the first series, because the rate of adding seeds was 18 seeds per second lower in most of the second series than it was in the first. An increased rate of nuclei creation could result from small particles entering the crystallizer with the Mg solution and/or from a shortened

spontaneous nucleation time as a result of the Mg addition. If the addition increased the supersaturation of the entering liquid sufficiently to make the spontaneous nucleation time shorter than the time elapsed until the liquid comes into contact with the bed particles, where supersaturation can be relieved by crystallization onto already-formed surfaces, then nuclei will form spontaneously.

A balance on the number of bed particles through the series illustrates that the net rate of creation during the second series increased dramatically over the rate during the near-steady state portion of the first series. The balance was conducted in the same way as the earlier balance, except that the accumulation of particles in the bed must be reflected because steady state was never approached during the second series. In the balance, the estimated number of particles produced is 9.2 million, of which 3.2 million are product and 6.0 million are bed accumulation. Of these, 1.0 million can be accounted for as seed added during the first three runs. The remainder, 8.2 million, are attributed to net generation of nuclei in the crystallizer. The average rate of net generation over the 55-hour series, then is 41 per second. This estimated rate, approximately ten times that estimated for the first series, supports the explanation that bed build-up during the second series results at least in part from faster generation of nuclei. The estimate provides no insight into which mechanism of nucleus generation may be responsible.

Regarding the behavior of the bed, its appearance and observed movement during the second series are consistent with the hypothesis that the bed is more mixed than classified, as discussed for the first series. The fact that the rebound in phosphorus concentration between the upper bed and the treated liquid occurred through most of the series, while the channel was also observed in the bed through most of the series, supports the hypothesis that the two phenomena are linked. The rising of the bed top, enlarging of the top zone, and shrinkage of the bottom zone seem clearly correlated with build-up in the bed. In this series, when those trends in the bed appearance were observed, the bed weight was increasing. When the opposite trend was observed, the bed weight was declining.

Comparing Figure 18 against the timing of the observation of the double bed top reveals a possible link between the two. The phenomenon occurred at a time when the distribution had two distinct, rather widely separated peaks. Note that the total weight of three intermediate-sized fractions (#30-#35, #35-#40, and #40-#50) shrank to a minimum of around 20 g during this period (about 40 to 45 h of operation time), while the two finer fractions and four coarser fractions were larger. At no other time during the first or second series was there a double peak, so distinct and widely separated, in the particle size distribution.

The comparison of treated liquid concentrations with those expected at equilibrium, which was performed for the near-steady state portion of the first series, was not performed for the second series, because steady state was never approached.

Detailed Results from FCR Series #3

Qualitative Observations

During the first run in the third series, product was drained from the bed by reducing the liquid inflow rate to one-half its normal flow during operation. The inflow rate was held at the low level until the product collector filled, normally requiring 1 to 2 min, then raised to its normal rate to completely re-fluidize the bed before shutting down to empty the product collector. This procedure was repeated until enough bed was removed that the channeling behavior in the bed completely disappeared. Eight performances of the draining and product removal procedure were required to eliminate the channeling behavior. The bed height fell from 30 cm to 27 cm during this time.

For the remainder of the first run and for all the remaining runs in the series, the product was drained from the bed whenever the bed height reached 27.5 cm. The same procedure as that used during the first run was used, except that temporary shutdown after each re-fluidization was unnecessary because the product collector did not fill until the end of the run. Each product draining lasted long enough to lower the bed level about 1 cm; i.e., to about 26.5 cm. The bed top fell several

cm and lost fluidization during the drainings. Each draining was allowed to last long enough to fill about one-third of the collector, equating to about eight to ten g of product. A bed height of 27 cm, plus or minus one-half cm, was thus maintained through the thirteenth run.

During the first run, the bottom zone reappeared, then expanded to a height of about two cm during the subsequent three runs. The middle zone expanded during the first four runs to about ten cm, and the top zone shrank to about fifteen cm. The zones stabilized at those levels and remained quite constant during the fifth through thirteenth runs.

During the fourteenth run, the lagoon water intake was accidentally lifted from the storage tank for a moment, resulting in a loss of pumping force and backflow of liquid and bed material from the crystallizer through the pump discharge line, the pump (which continued to operate), and the pump suction line. The pump discharge line and several cm of the suction line were filled with bed material after the accident, and this material was recovered and loaded into the bed. However, evaluation of the bed at the end of this and the following run showed changes suggesting the accident had changed the bed significantly, thus ending the period of several runs of smooth operation with stable bed characteristics. Given that the bed fluidization and particle size distribution had remained constant enough during the ninth through thirteenth runs to regard it as having demonstrated steady state or near-steady state, it was decided to terminate the series after the fifteenth run.

The fifth run in the series also presented some difficulty. From the start of the run, small bubbles began to appear in the liquid near the top of the bed. The bubbles appeared to form at the top of the bed, forming a ring of bubbles clinging to the inside wall of the cone at the upper surface. Bubbles also frequently rose to the top surface of the liquid in the cone. Small solid particles of bed material could be seen clinging to the bubbles, carrying over with the bubbles with the overflow of treated liquid. A fine sieve screen placed at the end of the overflow tube accrued several g of fine solid bed material within a few minutes. The run was terminated and the bed material on the sieve

was returned to the bed. Because the lagoon liquid in the tank was several days older than any that had been used before, it was hypothesized that digestion had produced dissolved gas sufficient to effervesce. The liquid was discarded and a fresh tank of liquid obtained. The fifth run was restarted, this time with no such problems.

Bed Weight, Particle Size Distribution, and Height

Figure 23 shows the bed weight and particle size distribution during the third series of runs. The bed weight dropped rapidly during the first run, reaching a little over 150 g. Thereafter, the weight increased slightly on some of the runs, reaching 165-170 g by the ninth run (about 19 h operating time) and remaining there through the thirteenth run (about 30 h). The weight dropped a total of 15 g the last two runs.

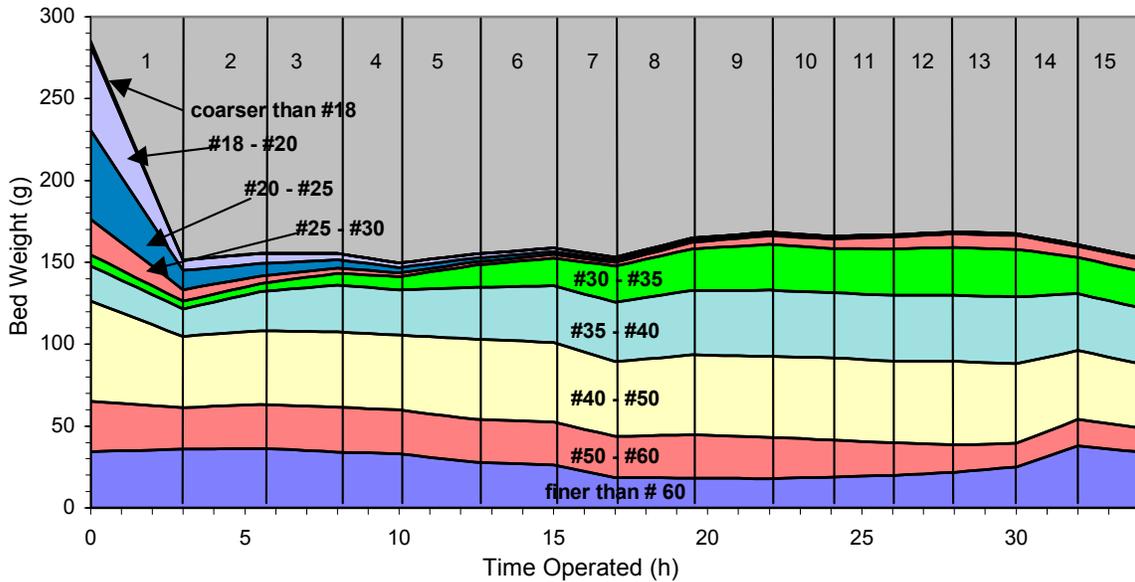


Figure 23: Third Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h) (Numbered Vertical Strips Correspond with Runs)

The particle size distribution became nearly constant by 19 h of operating time. The fractions coarser than #25 dropped to nearly zero by that time, the #25-#30 fraction changed little through the

series, and the #30-#35 fraction first increased to compensate for the loss in the coarsest fractions then stabilized by 19 h. The #35-#40 and #40-#50 fractions also stabilized by 19 h. The finest two fractions, #50-#60 and finer than #60, did not completely stabilize by 19 h, as the former decreased and the latter increased. However, the change was slow and furthermore, the changes in these two fractions compensated for one another, resulting in little net change in the total amount of fines through the near steady-state period.

Figure 24 shows the bed height through the series. The height dropped rapidly during the first run as the system was operated to achieve a bed height of 27.5 centimeters and then was kept near that height for the remainder of the series.

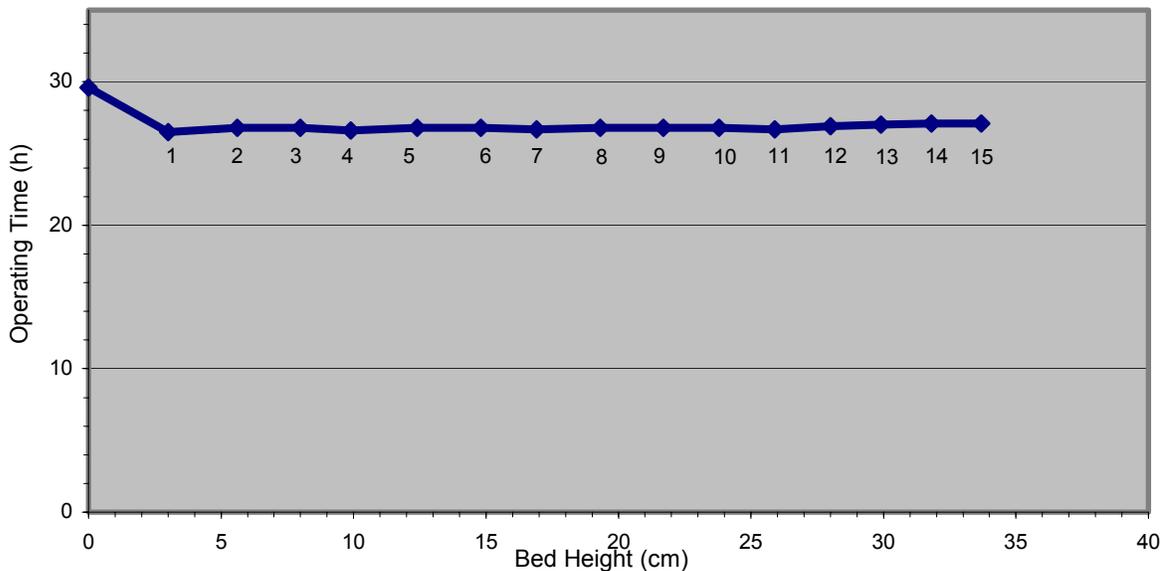
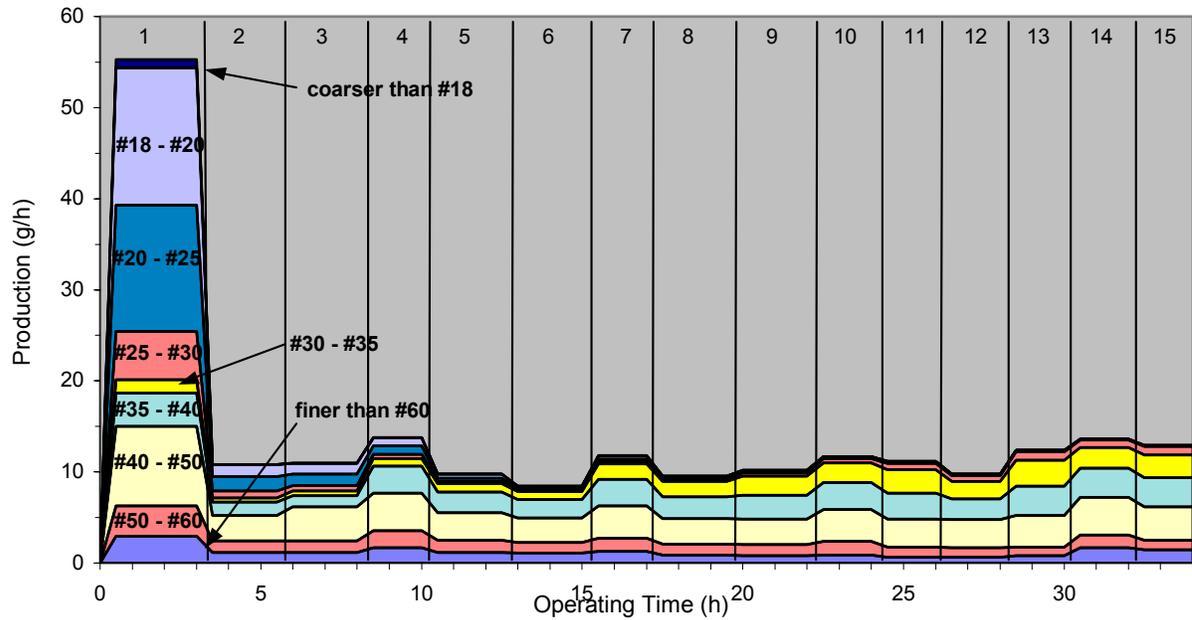


Figure 24: Third Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h) (Run Numbers Indicated)

Product Weight and Particle Size Distribution

Figure 25 shows the weight of product per h, broken down by particle size and averaged over each run. A very high rate, averaging more than 50 g/hr, can be seen for the first run. The rate then



**Figure 25: Third Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve)
(Numbered Vertical Strip Correspond with Runs)**

drops to around 11 g/h and fluctuates around that value, staying in the range of 8 to 13 g/h, for the remainder of the series. The final three runs, especially the last two, show a rate sustained near the top end of that range. The particle size distribution of the product grows richer in the finer fractions during the first five runs then remains relatively constant.

Phosphorus Reduction

As seen in Figure 26, the crystallizer achieved greater phosphorus reduction in the third series than in either of the two preceding series. Reduction in TP ranged from 0.50 to 0.72, and reduction of dissolved OP ranged from 0.75 to 0.93.

TP reduction showed no trend that was sustained through the series. However, the figure suggests a possible trend toward increasing reduction in dissolved orthophosphate through the series. TP reduction exhibits two peaks of nearly equal height.

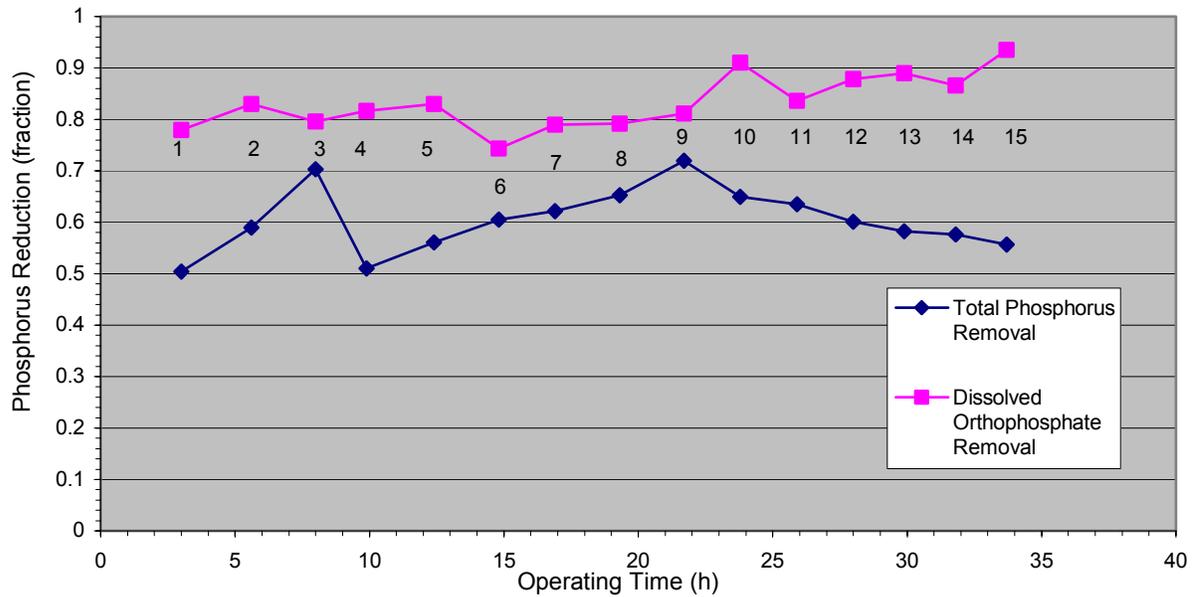


Figure 26: Third Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h) (Run Numbers Indicated)

Variation of Phosphorus Concentration with Height in Bed

Figure 27 shows the profile of OP concentration across the six sampling points. For the first thirteen runs, the figure shows the typical pattern of most of the reduction occurring between the untreated liquid and the 5-cm sample point, with additional reductions of decreasing magnitude at the 12-cm and 19-cm points. The rebound in concentration seen at the end of the second series has disappeared, and the concentrations in the 19-cm sample, above-bed sample, and treated liquid are very close on the second through twelfth runs. The final three runs show a more even reduction in concentration with respect to height, but the total reduction achieved is about the same, and there is no rebound.

Discussion of Results in FCR Series #3

A phosphorus balance on the third series estimates that inputs were 108 g in the lagoon liquid and 7.7 g in the Mg solution. There was no phosphorus input in the form of seeds because

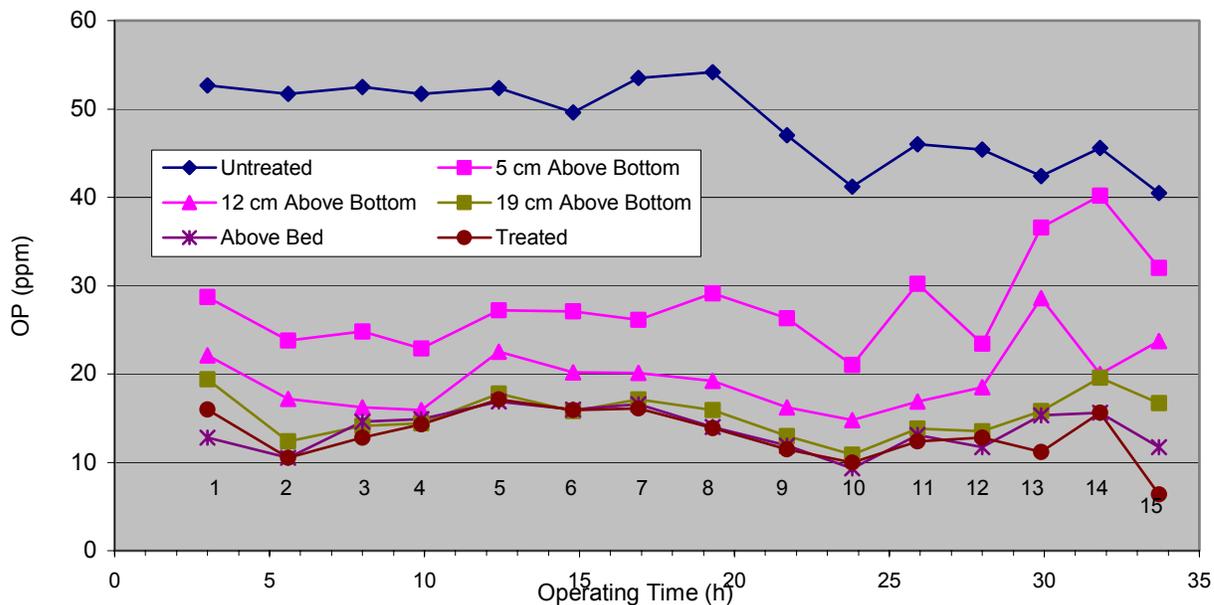


Figure 27: Third Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h) (Run Numbers Indicated)

there was no seeding in this series. Outputs were 44.0 g in the treated liquid and 92.2 g in the product. Net accumulation in the bed was -24.1 g. The total input is 97.5% accounted for in the output and net accumulation; however, it should be noted that the pump failure in the fourteenth run likely caused a loss in product. The amount of the loss can be estimated at 7 g, because that is the reduction in bed weight that occurred during the run. In the five previous runs, the bed weight had remained constant to within plus or minus 1.3 g. If adjusted for a loss of 7 g of bed, the accounted-for percentage rises to 98.6%.

It should also be noted that the phosphorus input in the Mg solution has been estimated by assuming the concentrations in the solution remained at the average for the second series through all of the third series. This approach was required because the phosphorus concentrations in the Mg solution were not analyzed after the second series. The approach may introduce some error, which may be responsible for some of the mis-match in the material balances.

A phosphorus balance limited to the five runs where the bed changed little, runs 9 through 13, estimates phosphorus inputs of 38.1 g in lagoon liquid and 2.7 g in the Mg solution. Outputs were 14.5 g in treated liquid and 25.9 g in product, and net accumulation was 0.4 g. Inputs were 100.8 % accounted for, again showing a good match given the uncertainties in sampling and analysis.

Calculating an average reduction in TP during the near-steady state period, using the same method used for the analogous period during series one, yields a reduction percentage of 64%. Assuming again that precipitation of orthophosphate ions in the liquid is the mechanism of reduction, this reduction percentage is in the range expected. The addition of the Mg should be sufficient to precipitate all the phosphorus were it all in the form of dissolved OP. However, other forms of phosphorus in the raw lagoon liquid generally constitute 20% to 40% of the TP, so even if the struvite precipitation proceeded completely to equilibrium, TP reduction could not exceed 60% to 80%.

Table 10 presents a comparison of the concentrations in the treated liquid with their expected values if struvite precipitation reached equilibrium. The comparison was conducted for the near-steady state portion of the third series, using a method similar to that used for the comparison covering the analogous portion of the first series. It should be noted that, because there are two liquid input streams (raw liquid and Mg solution), the table presents concentrations for “input liquid” rather than “raw liquid.” The concentrations for input liquid have been calculated by arithmetically aggregating the two streams.

The fact that Mg analyses were suspended before the third series led to two complications with the calculations for the comparison. First, no Mg analyses are available for any of the streams. Therefore, for the purposes of this comparison, the concentrations of Mg in the raw liquid stream and in the Mg solution were each approximated by setting them equal to the average of the analogous concentrations averaged across the second series. Because the sources and methods of preparing the

**Table 10: Concentrations for Near-Steady State Portion of Third FCR Series:
Input Liquid, Treated Liquid, and Expected in Treated Liquid at Equilibrium
(OP and TP Corrected for Adsorption on Sample Bottle Walls)**

Material Sampled	Sample fraction	Species	Average ppm	Average ppm expected	Divergence from expected (ppm)
Input liquid	Centrifugate	OP	33.2		
		TP	37.3		
		TAN	435		
		Mg	46.9		
	Sediment, reconstituted to original vol.	OP	11.2		
		TP	21.8		
		TAN	35.7		
		Mg	10		
Treated liquid	Centrifugate	OP	5.1	3.7	+1.4
		TP	8.7	7.8	+0.9
		TAN	430	421	+9
		Mg	--	23.8	--
	Sediment, reconstituted to original vol.	OP	6.4	11.2	-4.8
		TP	16.4	21.8	-5.4
		TAN	40.4	35.7	+4.7
		Mg	--	10	--

liquids were identical for the two series, this method should produce a fair approximation. However, no approximation is possible to substitute for analyses of the treated liquid.

The second complication stems from the fact that the sample sizes of centrifugate and sediment were reduced when the Mg analyses were suspended. The Mg analysis requires more sample volume than the other analyses combined. On the fourth run into the series, this fact was recognized and the volumes of the centrifugate and sediment samples were reduced to economize on time, as those samples require additional work to prepare. The lower sample volumes filled the bottles for the centrifuged samples less than half full, as opposed to being nearly full before the fourth run.

After the series was completed, the analytical results showed a change beginning on the fourth run. Through the 35 runs completed up to that time (32 in the first and second FCR series),

with few exceptions, the OP and TP concentrations in uncentrifuged samples were equal to, within one or two ppm, the sum of the corresponding phosphorus concentrations in the centrifugate and in the sediment. For almost all the remaining runs, however, the sum of the OP concentrations in centrifugate and sediment fell significantly short (10 to 20 ppm) of the concentration in the uncentrifuged sample. The shortfall in TP was about the same as the OP shortfall, indicating that non-orthophosphate phosphorus was not being affected. An experiment comparing phosphorus analyses of liquid poured from the same large vessel into sample bottles of equal size but filled to different depths then demonstrated that bottles filled less than half full test 20% to 30% lower in OP than bottles completely filled with the same liquid. The data is consistent with a hypothesis that OP is adsorbed onto sample bottle walls in amounts large enough to significantly reduce the analytical result when the bottles are filled less than half full.

For the comparison in Table 10, then, a correction was made to the raw data in order to avoid exaggerating the phosphorus removal percentages. The correction was made allocating the missing OP to the centrifugate and sediment samples. The shortfall in OP was calculated as the difference between its concentration in the uncentrifuged sample and the sum of its concentrations in the centrifugate and sediment. The centrifugate and sediment concentrations were then increased by an equal percentage to eliminate the shortfall. TP concentrations in centrifugate and sediment were increased to reflect the corrections to the OP, thus eliminating the shortfall in TP, also.

Comparing this table of concentrations against the corresponding table for the first series reveals similarities and differences. First, the removal of phosphorus from the suspended phase has occurred here as it did in the first series, with the amount removed being nearly the same. Second, the loss of phosphorus from the dissolved phase has progressed most of the way toward the struvite solubility equilibrium point, as it did in the first series. However, in the present case, the loss has reached to within one or two ppm of the equilibrium point. When coupled with the fact that the

equilibrium point is lower in phosphorus due to the Mg supplementation, the closer approach to equilibrium leads to a much lower amount—less than one-quarter—of phosphorus remaining in the liquid. Note that the overall phosphorus removal from both phases combined is greater than that predicted by struvite precipitation, even if the precipitation proceeded all the way to equilibrium. This result stems from the fact that the removal from the suspended phase is greater than the separation between the equilibrium point and the actual remaining concentration in the liquid.

The closer approach to equilibrium may be explained by the fact that the bed was both finer and heavier during this near-steady-state period than during that portion of the first series. Both differences result in greater surface area available for the precipitation reaction, allowing for a more complete reaction.

Due to the lack of Mg data, phosphorus-to-Mg and TAN-to-Mg ratios cannot be calculated as they were for the first series. Therefore, these concentration data offer no additional clues as to the mechanism for reduction of phosphorus from the suspended phase. The rise of TAN in the suspended phase opposes the pattern seen in the first series, and is inconsistent with all the hypotheses offered earlier for how the phosphorus reduction in the suspended phase might occur. No hypothesis accommodating loss in phosphorus and gain in nitrogen analysis results simultaneously in the suspended phase can be offered, other than the possibility of sampling or analysis error.

Comparisons of the appearance of the bed with its particle size distribution and with the profile of OP concentration versus reactor position comport with earlier discussion. The bed lightening and reduction in coarseness associated with the draining down of the bed early in the series coincided with upward movement of the boundaries between the bottom and middle and between the middle and top bed zones. They also coincided with the disappearance of the channel in the top zone of the bed. Furthermore, the disappearance of the channel coincides with dissipation of the rebound

of phosphorus concentration between the top zone and the treated liquid, further strengthening the link between those phenomena hypothesized in the discussion of the first series.

The calculation of net generation of particles during the near-steady state period, using the same method used for that portion of the first series, indicates a net generation of nearly 2.1 million particles during the period. This figure equates to 52 particles per second, and is about 27% higher than the rate calculated for the second series. The difference provides some evidence in favor of the spontaneous nucleation hypothesis. The bottom bed zone grew higher in the third series, resulting in more of the incoming liquid spending more time in the supersaturated state before coming into contact with the bed particles, in turn leading to generation of more nuclei.

The mode of product removal used in this series proved successful in achieving and maintaining a near-steady state condition. Changes in bed characteristics were no greater than the changes in the raw lagoon liquid during the period of near-steady state behavior. The loss of near-steady state behavior at the end of the period seems very likely related to the pump failure. The evaluation of the bed at the end of that run showed a loss in weight, consistent with the observation that bed material had backed through the pump and been lost into the raw liquid feed tank. On the following, final run, the evaluation showed further loss in total weight, but increase in the weight of fines. The fines may have increased due to grinding by the pump of bed material that had backed through the pump but had not moved far enough back to be lost. When the pump was restarted, this material was drawn through the pump and flowed into the bed. The two exposures to the shearing action of the gear pump may have ground this portion of material into fines. The increase in fine material could have caused the bed top to rise higher than it would have otherwise, resulting in greater product removal to maintain the desired bed top height and a decreased bed weight.

The bubbling observed in the crystallizer during the aborted fifth run may have resulted from biological reactions in the raw liquid. The liquid had sat considerably longer than liquid used for any