

flow, bed movements, or product discharge. At the end of each run, the bed drained easily, and could be easily flushed out through the cone bottom and product collector with a jet of distilled water from a wash bottle. The bed spread easily on drying pans. Seed material, if dropped dry upon the liquid surface in the cone, would not wet quickly enough to sink below the surface before some of it was swept out the overflow. For this reason, seed material was first mixed with distilled water and then poured into the cone. In returning the bed, after being dried and evaluated, to the cone at the beginning of each run, it was also washed with distilled water into the upflowing lagoon liquid in the cone in a manner similar to that used for pouring the seeds in.

Bed Weight, Particle Size Distribution, and Height

Figure 13 shows the total weight and particle size distribution of the dry bed at the beginning of the series and after each run in the series. The figure reveals the buildup in bed mass during the runs preceding the alteration made at the cone bottom, rapid decrease following the alteration, and a subsequent leveling off to fluctuate within a narrow range. An increasing preponderance of larger particles (coarser than #18) can be seen as the bed weight increased, and the reverse as the bed weight decreased. Figure 14, the height of the bed during each run in the series, shows a similar trend as the bed weight though not as pronounced.

Product Weight and Particle Size Distribution

Figure 15 shows the total weight, on an hourly basis, and particle size distribution of the product from each run in the series. The weights shown were calculated by weighing the product and particle size fractions from each run, then dividing the weights by the number of hours in the run. Little or no product was released by the crystallizer on any run until the eleventh run, which immediately followed the alterations at the cone bottom. From that point, product release was rapid at first, then slowed to a rate that fluctuated around 7 g/h. As the product release rate decreased and

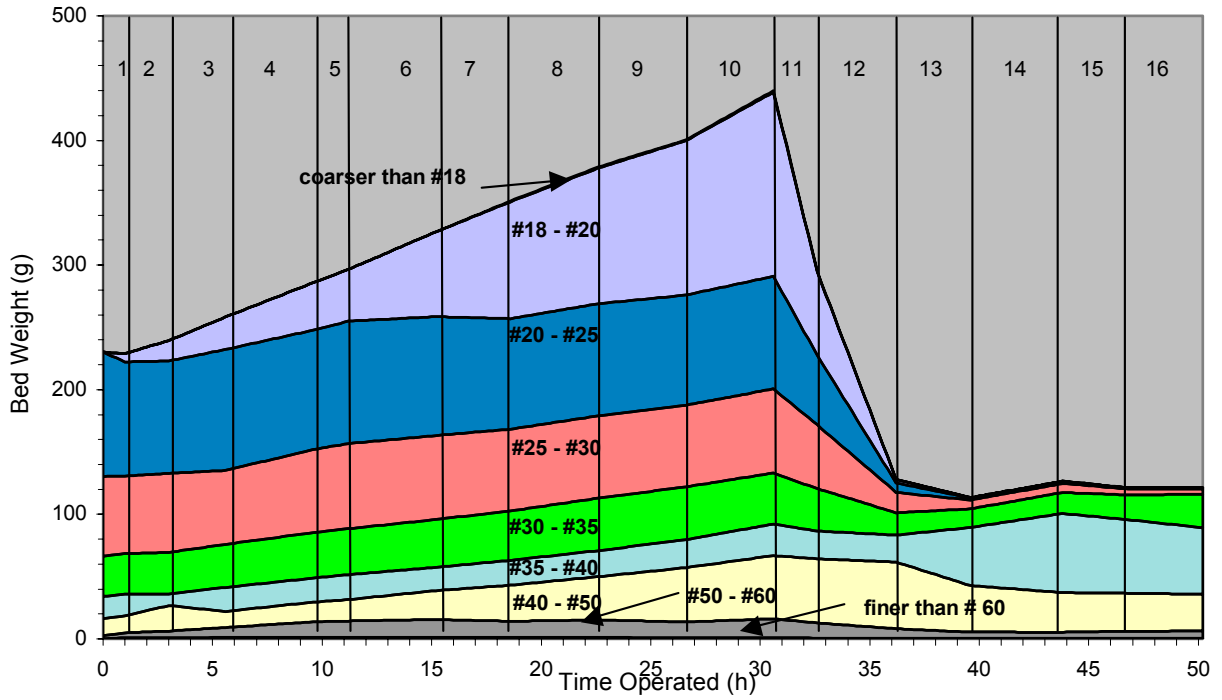


Figure 13: First Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h)
(Numbered Vertical Strips Correspond with Runs)

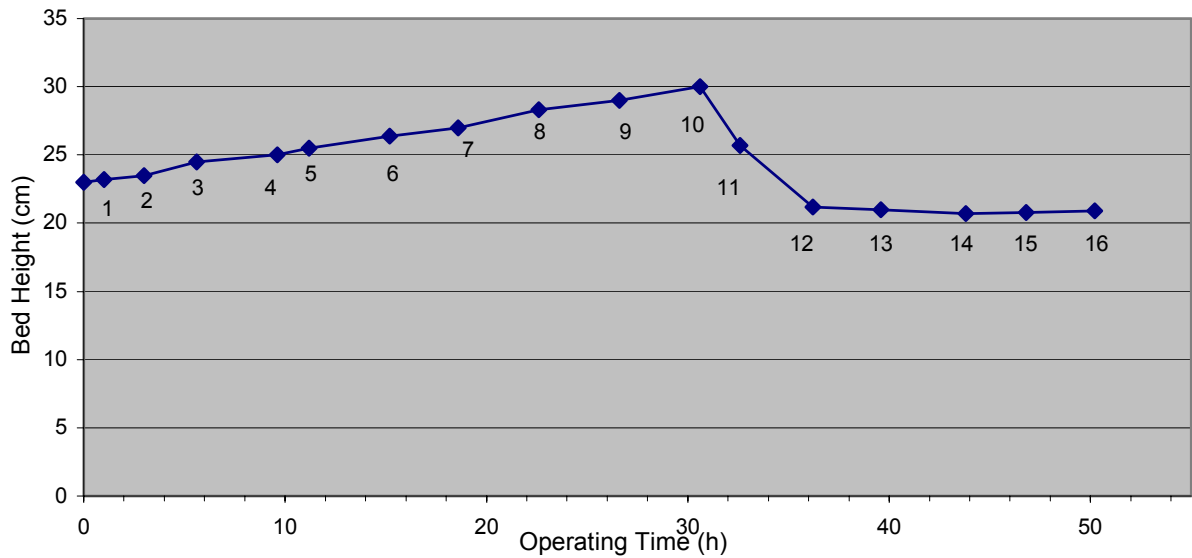


Figure 14: First Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h)
(Run Numbers Indicated)

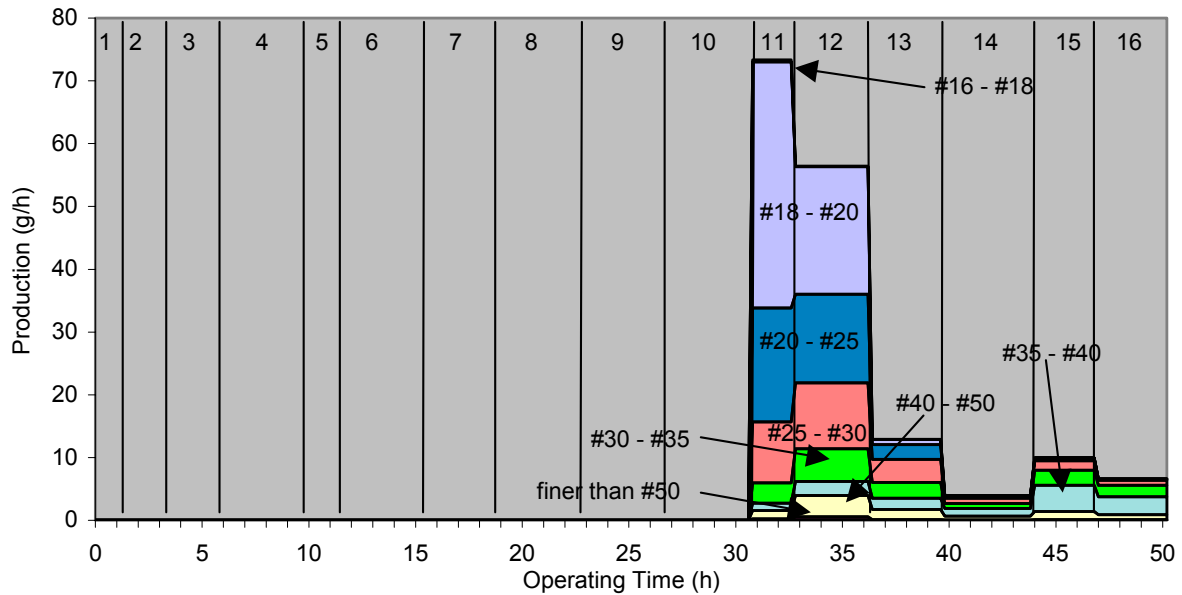


Figure 15: First Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve) (Numbered Vertical Strips Correspond with Runs)

leveled off, the particle size distribution first rapidly decreased in its content of the largest particles (coarser than #25), then leveled off.

Phosphorus Reduction

Because phosphorus exists in lagoon water both dissolved in the liquid phase and as part of the suspended solid phase, and because it exists both in orthophosphate and in non-orthophosphate forms, the phosphorus reduction fraction can be calculated in several different ways. In the present work, it was decided to calculate it in two ways. First, because the overall goal is removal of as much phosphorus as possible, a calculation of TP reduction was made:

$$TP\ reduction = 1 - \left(\frac{TP\ in\ treated\ lagoon\ water}{TP\ in\ raw\ lagoon\ water} \right) \quad (41)$$

Second, because it is only the OP dissolved in the liquid phase that is hypothesized to be removable by struvite crystallization, a calculation of OP removal from the liquid phase was made:

$$\text{Dissolved OP reduction} = 1 - \left(\frac{\text{OP in centrate of treated lagoon water}}{\text{OP in centrate of raw lagoon water}} \right) \quad (42)$$

Figure 16 shows phosphorus reduction, calculated in both ways, versus elapsed running time during the first series. Each of the two calculations was made once for each run, using the TP and OP results from analysis of the samples from the raw liquid tank and the treated discharge from the overflow.

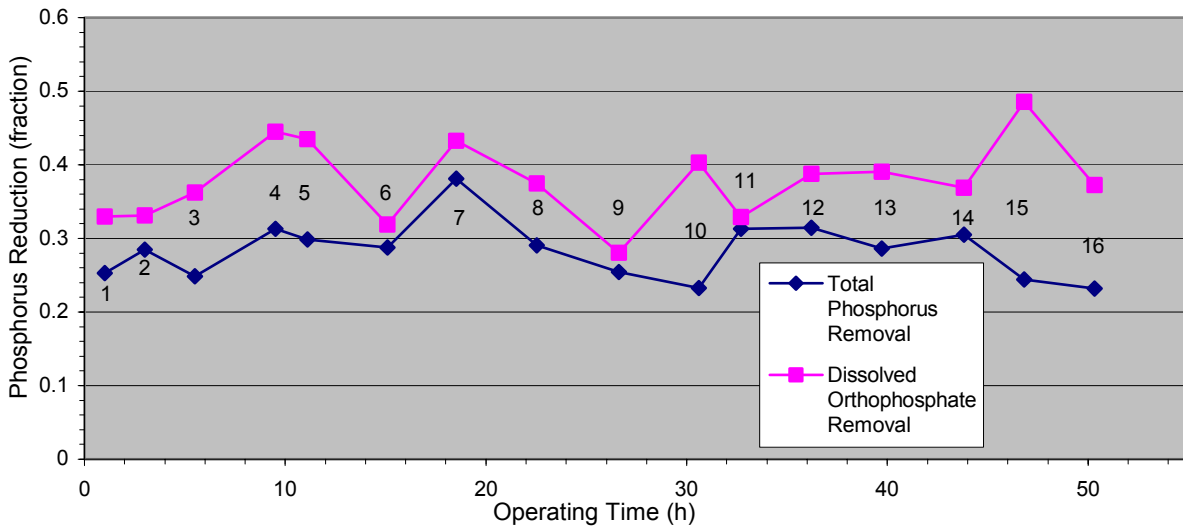


Figure 16: First Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h) (Run Numbers Indicated)

The fraction of TP reduction varied from 0.23 to 0.38, while the fraction of dissolved OP reduction varied from 0.28 to 0.49. No clear trends appear. Visual inspection reveals no obvious correlation of reduction with bed weight or particle size. Furthermore, the two reduction fractions show no obvious correlation with each other.

Variation of Phosphorus Concentration with Height in Cone

Figure 17 shows the OP concentration from the four sampling points in the cone, in the untreated liquid, and in the treated liquid for series one. The untreated liquid sample was taken from

the raw liquid storage tank. The treated liquid sample was taken from the outlet of the overflow hose. The concentrations are plotted against operating time. The apparatus for drawing samples from within the bed failed during the first run, and thus those three data points are missing.

The figure shows a pattern in most of the runs. In the pattern, most of the OP reduction has already occurred by the time the upflowing liquid reaches the sampling point 5 cm up into the cone. The OP concentration is reduced again, but not as much, by the time the liquid reaches the next

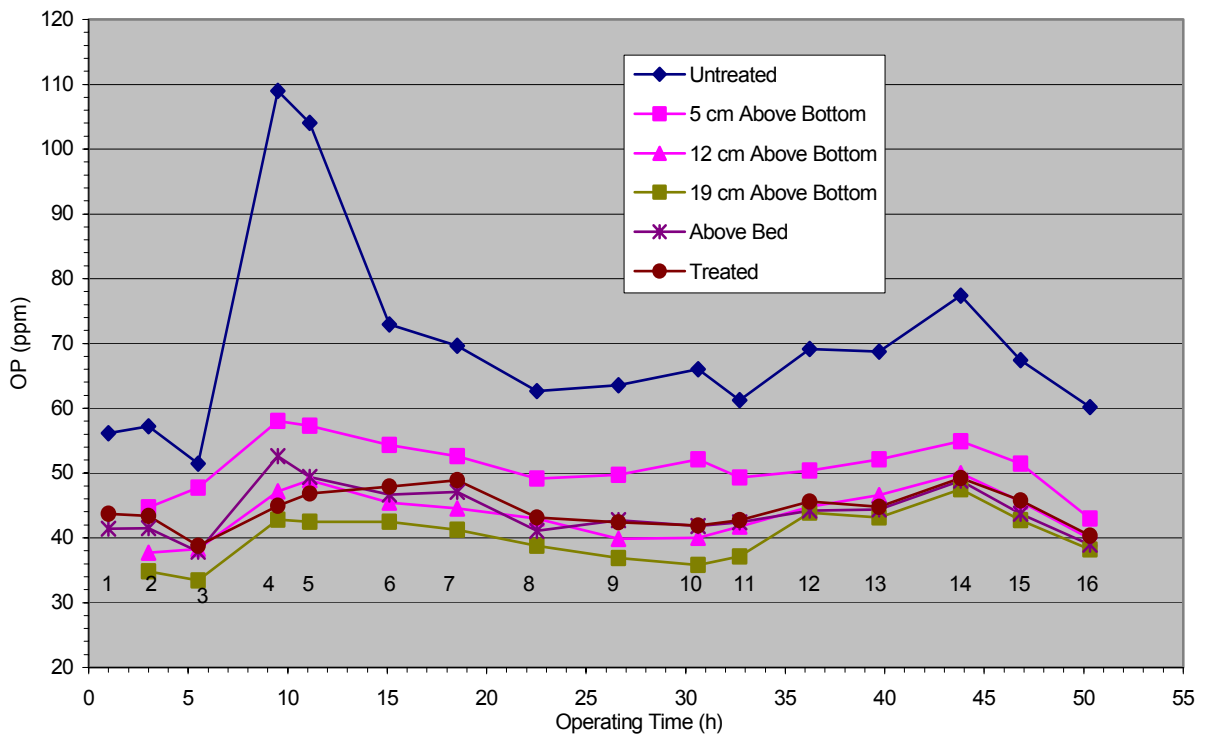


Figure 17: First Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h) (Run Numbers Indicated)

sampling point (12 cm above cone bottom). At the 19-cm point, an additional, but even smaller, reduction has occurred. However, the concentration trend reverses itself, and rebounds a few ppm in the liquid collected above the bed and in the treated liquid flowing from the cone top. The latter two

values are roughly the same. Overlying the pattern is a trend in the latter part of the series. The trend is for the rebound to diminish. The rebound, averaging 5 to 10 ppm in the early runs, has decreased to 1-2 ppm by the end of the series.

Discussion of Results in FCR Series #1

A material balance on phosphorus about the crystallizer serves to check the results and to help interpret them. A balance was conducted for the entire series and for the four consecutive runs at the end of the series. The bed weight and particle size distribution remained nearly constant during these four runs and hence crystallizer operation during the period is considered to be near-steady state.

Phosphorus inputs occurred in the lagoon water inflow and the seeding. Multiplying the duration of a run by the liquid flow rate and multiplying the result by the TP concentration of the raw lagoon liquid for that run yields an estimate for the phosphorus input in the lagoon liquid during that run. Adding the estimates for all sixteen runs gives an estimate, 224 g, for the total phosphorus input in the lagoon liquid for the run. Multiplying the weight of seed material used during the run by its phosphorus content (12.5%) as determined by chemical analysis of the material yields an estimate, 7.8 g, for the phosphorus input in the form of seed material.

Phosphorus outputs occurred in the treated liquid outflow and in the solid product removed. Multiplying the duration of a run by the liquid flow rate and multiplying the result by the TP concentration of the treated liquid for that run yields an estimate for the phosphorus output in the treated liquid during that run. Adding the estimates for all sixteen runs gives an estimate, 145 g, for the total phosphorus output in the treated liquid for the series. The phosphorus output in the form of dry product (86.7 g) is estimated by multiplying the total product during the series (473 g) by its phosphorus content, estimated at 18.3% through analysis of bed material at the end of the series. (The higher content in the product may result from a second removal mechanism, discussed later.)

The net accumulation of phosphorus in the crystallizer, -6.4 g, was estimated by multiplying the beginning bed weight (229 g) by its estimated phosphorus content and subtracting the product from the product of the ending bed weight (121 g) and its estimated phosphorus content. The phosphorus content of the beginning bed was estimated at 12.5% because it was composed of the same material from which the seeds were made. The ending phosphorus content was estimated at 18.3% from the same analysis used for estimating the product phosphorus content.

For the entire first series, then, the total estimated phosphorus input, which is the sum of that occurring in the seeds and in the lagoon liquid input, is 232 g. Of this, 226 g, or 97.3%, can be accounted for in the sum of that occurring as liquid and solid product output and as net accumulation. The unaccounted for phosphorus may have been lost in dust or small spills during bed removal, drying, sieving, and reloading into the crystallizer. Even if there were zero losses, a material balance could easily show this magnitude of unaccounted for differences due to the margin of error in the phosphorus sampling and analyses. Note that, for samples drawn from the same mixed tank of liquid on subsequent days, analyses commonly indicated differences of 5% or more.

A material balance on TP conducted over the runs in which the crystallizer operated at steady state or near steady-state (runs 13, 14, 15, and 16) shows inputs of 54.5 g TP in raw liquid and 2.3 g in seeds. Outputs were 20.9 g TP in product and 39.5 g in treated liquid, while net accumulation was -1.4 g. Inputs are 105.2 % accounted for. That this error is larger than that resulting from the balance on the entire series is not surprising: random error, on a percentage basis, will decrease as the number of runs included in the total increases. That the error is in the opposite direction strengthens a hypothesis that the material balance gaps result from random experimental error rather than material losses. If losses were occurring, then the question would arise as to whether the true phosphorus reductions were not as great as those seen in the results. With random error, the phosphorus

reduction result for an individual run may be several percent off the true reduction, but averaged over several runs the result should approach the true reduction.

An average rate of reduction in TP can be calculated from the material balance estimates on the near-steady state portion. The rate is calculated by subtracting the amount of phosphorus in the treated liquid from the total amount input as liquid and dividing the difference by the latter. This calculation yields a result of 27.5% average reduction in TP, which is in the range expected if the reduction mechanism is precipitation of struvite from dissolved OP. This mechanism cannot remove phosphorus once the supply of Mg ions available for precipitating the OP has been exhausted. Given the relative concentrations of the two species in raw lagoon liquid, the expected TP reduction would be in the range of 20% to 30% if the precipitation proceeds to near equilibrium.

The failure of the crystallizer to discharge product and resulting bed buildup in the beginning of the series, followed by fast product discharge immediately after the change in the bottom configuration clearly evidences the effect that the configuration has. It should be noted that the change in configuration did not change the minimum diameter (and hence maximum upflow velocity) through which the settling product had to pass. Rather, the change reduced the distance through which the product had to settle through that velocity and diameter. This observation suggests that a passage through which falling product must settle in opposition to upflowing current should be larger in diameter than the minimum diameter at the bottom of the cone.

The disappearance of the channel when the bed became lighter and finer suggests the channeling behavior is related to the bed characteristics. The rebound in phosphorus concentration between the upper portion of the bed and the overflowing treated liquid occurred most markedly on the runs in which the channel was observed, suggesting a connection. A possible explanation is that the liquid flowing in the channel flows faster and therefore has less time to react and experiences less reduction in phosphorus. In the surrounding, non-channeling areas, liquid flows more slowly upward

and therefore undergoes greater reduction. The fast- and slow- moving liquid mix together over the bed, and therefore the reduction seen there and in the treated liquid would be intermediate between that exiting the bed in the slow stream and that in the fast stream. The sample points for the liquid from the bed, however, were away from the walls and thus probably away from the channel, also. Therefore the samples from the bed would reflect only the concentrations in the slowly-upflowing areas. Therefore, the appearance of a rebound pattern would coincide with the channeling behavior.

One might guess the channel would reduce the overall reduction achieved because it partially “short-circuits” the reaction zone. However, no tendency for greater reduction during the non-channeling periods can be seen in the results. Perhaps, if the channel does lead to poorer reduction, the difference is small and thus lost in the run-to-run variations. It could also be that the greater reduction in the slower-upflowing portion compensates for the poorer reduction in the channel, resulting in no change in overall reduction between channeling and non-channeling behavior.

The observed movement of the bed suggests that it is highly mixed rather than classified. The observation that fine and coarse particles can both be seen at all points in the bed, as well as in the product, strengthens the suggestion. However, the fact that the product was richer in coarse particles than the bed, and that occasionally the bed looked richer in fines at the top than at the bottom, argues that the mixing was probably not complete.

The overall tendency for the phosphorus concentrations to drop with height in the bed suggests that the character of the liquid flow in the bed more resembles plug flow than highly mixed flow. In addition, plug flow is consistent with the observance of the line between colorless and dark liquid moving up the cone when the feed was switched from water to lagoon liquid at the start of the series. The character of liquid flow, bed movement, and concentration profiles are discussed more fully in the section comparing results with predictions of the three conceptual models.

Comparing the number of seeds added with the number of particles removed as product at near-steady state should indicate the net rate of creation of crystallization nuclei in the crystallizer. Nuclei may be created by sloughing off larger particles, by spontaneously crystallizing from supersaturated solution, or by capture by the crystallizer of particles suspended in the entering lagoon water. Nuclei may be lost by suspension in the treated liquid flowing out through the overflow, by dissolution into the liquid, or by agglomeration with other particles. The difference between the number created and the number lost is the net creation.

The average rate of adding seeds to the crystallizer during the four runs constituting the near steady-state period was estimated at 18 per second by multiplying the weight-rate of seed addition by the estimated number of seeds per g of seeds, following the technique described under "Operating Procedures." The number of seeds per g was estimated by assuming the particles were spheres of density 1.7 g/cm (the density of struvite) with diameters at the average of the opening sizes of the two sieves (#60 and #70) used to separate the seed material from the crushed bulk material. The average rate of particle removal from the crystallizer was estimated at 22.4 per s by dividing the weight of each fraction removed during the four runs by the estimated number of particles per g for that fraction, and dividing the result by the total duration of the four runs. The estimated number of particles per g for each fraction was calculated in the same way as that used for the seeds.

The number balance on particles should be regarded as a rough approximation because of the assumptions required in the calculations. Nevertheless, the balance suggests that the net rate of creation of nuclei is somewhat small compared with the seeding rate. In other words, nuclei for most of the particles, at least, discharged as product can be accounted for by the particles in the seed material that was added. The uncertainty in the calculation prohibits a firm conclusion that there was net creation of nuclei other than the seeding, but if taken at face value the numbers suggest that about

one additional nucleus is being generated in the crystallizer for every four added as seed. It is impossible from this analysis to say which processes might be involved in any net creation.

Comparing the Mg, TAN, OP, and TP concentrations in the treated water with those expected at equilibrium after struvite precipitation helps in understanding how complete the reaction is in the crystallizer. The comparison also provides evidence as to whether the proposed reaction is in fact the means by which phosphorus has been reduced. Table 9 shows the concentrations in the raw and treated liquid for each of the runs in the near-steady state portion of the series.

The concentration of TAN in the centrifugate of the raw liquid includes the amount added for pH enhancement. The numbers shown for each “sediment” fraction result from analyses on a suspension prepared by briskly shaking the sediment into enough distilled water to prepare a total

Table 9: Concentrations for Near-Steady State Portion of First FCR Series: Raw Liquid, Treated Liquid, and Expected in Treated Liquid at Equilibrium

Material Sampled	Sample fraction	Species	Average ppm	Average ppm expected	Divergence from expected (ppm)
Raw liquid	Centrifugate	OP	54.8		
		TP	55.9		
		TAN	602		
		Mg	24.6		
	Sediment, reconstituted to original vol.	OP	15.2		
		TP	27.0		
		TAN	67.3		
		Mg	9.6		
Treated liquid	Centrifugate	OP	34.4	28.5	+5.9
		TP	41.9	29.6	+12.3
		TAN	593	595	+2
		Mg	12.8	3.9	+8.9
	Sediment, reconstituted to original vol.	OP	10.5	15.2	-4.7
		TP	21.2	27.0	-5.8
		TAN	60.6	67.3	-6.7
		Mg	5.1	9.6	-4.5

suspension volume equal to the volume of liquid from which the sediment was centrifuged. Thus, the figures shown for any species can be interpreted as the parts of that species, suspended, per million parts of the original, uncentrifuged liquid. This technique allows adding the centrifugate ppm to the sediment ppm for a given species to estimate the total ppm of that species in the uncentrifuged liquid.

The expected values at equilibrium for the centrifugate were produced by subtracting an equal amount, in moles per liter, from the OP, Mg, and TAN from the concentrations of those species in the centrifugate from the raw liquid. The amount subtracted was that amount needed to reduce the concentrations to the point where their product would just equal the conditional solubility product determined by Ohlinger et al. (1998) at the average pH of the crystallizer for the runs (8.32). It was assumed that non-orthophosphate phosphorus would not participate in the reaction, therefore the expected TP at equilibrium was calculated by adding the difference between the OP and the TP in the raw liquid to the expected OP at equilibrium; i.e, the non-orthophosphate phosphorus was held constant. The concentrations of all species in the sediment were held constant because it was assumed that the suspended solid would not participate in the reaction.

The table shows that all the concentrations moved more than half-way toward levels that would be expected at struvite equilibrium. OP, TP, TAN, and Mg dropped, respectively, 78%, 53%, 78%, and 57% of the way toward their expected values. These concentration drops are consistent with the precipitation of struvite from the liquid phase occurring but not proceeding completely to equilibrium.

The table also shows that the concentrations of the species in the sediment have all decreased by several ppm. This unexpected result suggests that another mechanism is at least partly responsible for the phosphorus reduction achieved by the crystallizer. Perhaps the decrease results from trapping of some of the suspended particles in the bed by gravity or by agglomeration with particles already in

the bed. (Trapping by either mechanism would reduce the amount of phosphorus suspended in the treated liquid and increase the amount of phosphorus in the bed and in the solid product.) Another possible explanation is that those species dissolve into the liquid from the suspended particles, thus liberating Mg and phosphorus to precipitate as struvite. Evidence supporting the latter theory is that the total drop in phosphorus in both phases (19.8 ppm) is equal to 1.21 times the total drop in Mg (16.3 ppm) in both phases, quite close to the 1.28 phosphorus-to-Mg weight ratio in struvite. The total TAN drop in both phases is 0.96 that of Mg, which substantially exceeds the 0.58 nitrogen-to-Mg ratio in struvite. However, one must take care in drawing conclusions from changes in nitrogen because expected drops are small in comparison with the total amount of TAN present, with the result that normal experimental error in sampling and analysis approaches the magnitude of the changes in concentration. In addition, nitrogen can escape to the air, though at pH values below 9.2 the ammonia is primarily in non-volatile form and evaporation is therefore slow.

Detailed Results from FCR Series #2

Qualitative Observations

From the first through the seventh run in the series, the bed grew in height, with little discharge of product. The boundary between the bottom zone and middle zone sank and by the seventh run, the bottom zone disappeared. The middle zone moved lower in the cone as both its upper and lower boundaries sank. The top zone grew larger as its lower border sank and upper border rose, and a channel was observed in it from the third run on. By the fourth run, it was noticed that the bed was becoming increasingly fine and dusty after drying. The material also began to adhere lightly to the drying pans, and it became necessary to push the dried material with the brush to move it off the drying pans and into the sieve analysis apparatus. Reasoning that spontaneous seeding was occurring, the seeding rate was reduced and then terminated. However, the amount of fines and

dustiness continued to increase even after seeding was terminated. Reinforcing the suspicion of spontaneous seeding was the observation of grayish particles in the glass tube admitting the lagoon water and Mg solution. The particles ranged in size from barely visible to that of fine sand particles. Some of the particles were collected and analyzed and found to consist of Mg, TAN, and OP in nearly the same amounts as would pure struvite.

Between the seventh and eighth runs, the glass tube admitting the lagoon water and Mg solution into the inlet manifold was observed to have slipped about 0.5 in. farther into the manifold than originally positioned, possibly interfering with the release of product from the cone through the manifold to the collector. The tube was pulled back to the original position and, on the eighth through twelfth runs the bed shrank and product was released while the zone boundary trends were approximately the reverse of those noted on the earlier runs. However, the channel did not disappear and the rate of product release and bed shrinkage slowed until, by the twelfth run, little product was being released and the bed stopped shrinking. On the tenth and eleventh runs, the top surface of the bed split into two surfaces. The upper surface lay between the particle-free headspace and the bed. Below it lay a zone of very fine and less dense bed. At the bottom of this zone lay the lower of the two surfaces, and below this lower surface lay the rest of the top zone with its usual appearance. The vertical distance between the two surfaces increased to about 1.5 centimeters by the end of the twelfth run. The bed continued to increase in dustiness after drying.

From the thirteenth through sixteenth runs, the bed grew again and discharged little product. The bed top split that developed in the eleventh run disappeared during the thirteenth run. The zone boundary trends reverted to those observed in the first seven runs, and channeling continued. Dried product continued to increase in dustiness. The series was terminated when the bed top rose high enough that it appeared likely bed particles would begin to overflow the crystallizer with the treated liquid stream.

As in the first series, no color or clarity difference between the raw and treated lagoon liquid could be detected. However, the color of the lagoon liquid used for making up the dilute Mg solution shifted toward dark pink after the concentrated Mg solution was stirred into it.

Bed Weight, Particle Size Distribution, and Height

Figure 18 shows the total weight and particle size distribution of the dry bed at the beginning of the series and after each run in the series. The increase in total bed weight to the end of the seventh run, when the correction in the input manifold was made (around 25 h), can clearly be seen, as can the subsequent decrease until the end of the twelfth run (about 40 h) and re-growth thereafter.

The trends in particle size distribution do not directly parallel the bed weight trends. Consistent with the observation that dried bed dustiness increased from the fourth run on, the figure

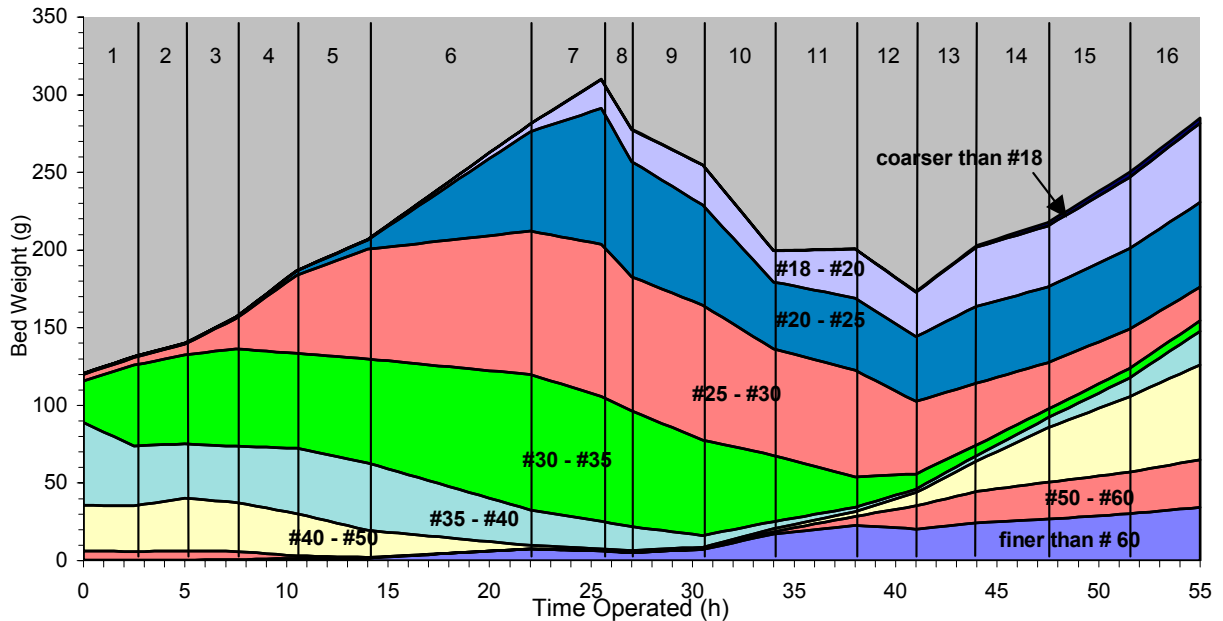


Figure 18: Second Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h)
 (Numbered Vertical Strips Correspond with Runs)

shows the increase in the amount of the finest particle size fraction (smaller than #60 mesh) from the fourth run on. The next finest fractions, from #60 to #35, show a decrease early in the series, followed by an increase in the later runs. The intermediate-sized fractions, from #35 to #25, first increase, then decrease. The rather coarse fractions of #25 to #18 increase then seem to hold rather steady, while the coarsest fraction (larger than #18 sieve) gradually increases but remains low.

Figure 19, the height of the bed during each run in the series, shows a similar trend as the bed weight, peaking at around 25 h of operating time, falling to a minimum around 40 h, then again rising for the remainder of the series.

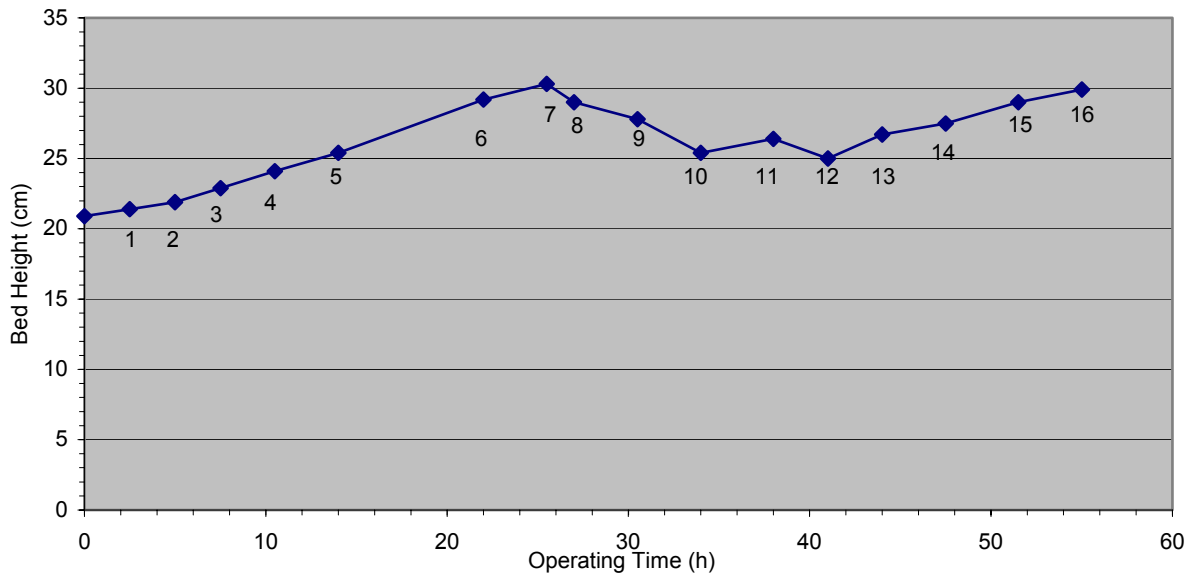


Figure 19: Second Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h) (Run Numbers Indicated)

Product Weight and Particle Size Distribution

Figure 20 shows production, averaged over each run and broken down by particle size, for the second series. Production remained low up through 25 h of operating time, with only one run during this time averaging greater than 5 g/h, and most averaging much less. Production leapt to an

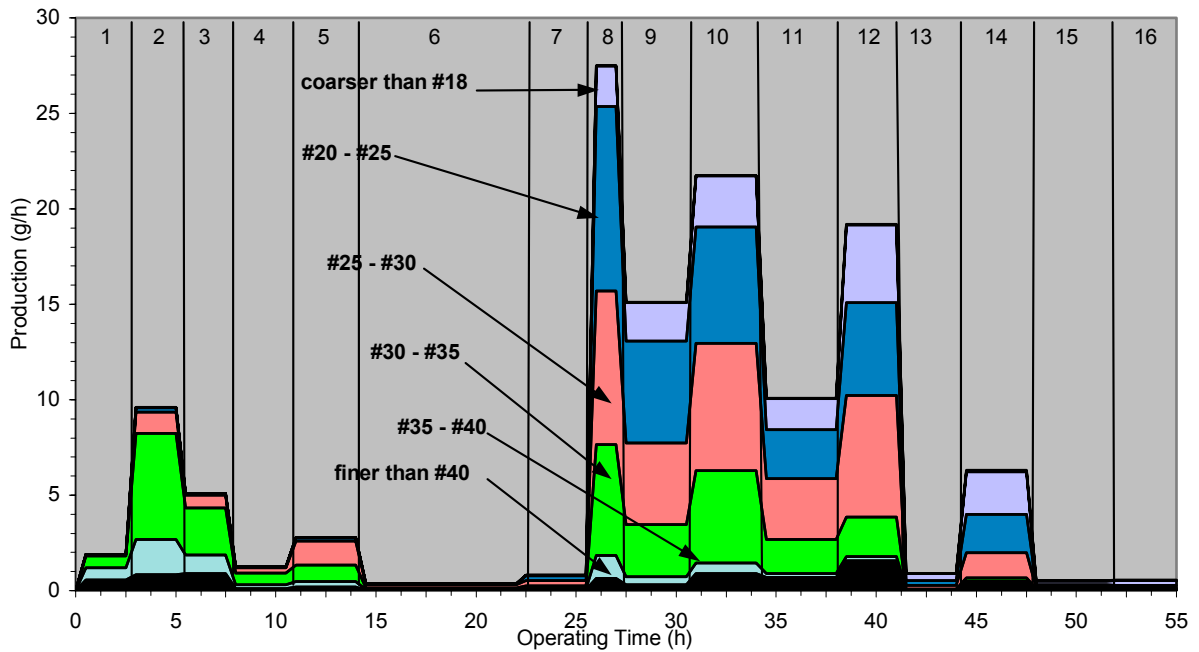


Figure 20: Second Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve) (Numbered Vertical Strips Correspond with Runs)

average of more than 27 g/h for the first run following the correction of the inlet manifold configuration, and thereafter fluctuated from run to run but trended quickly down, reaching near zero by 48 h. A trend toward coarser product can be seen in the figure, also. Little of the product was coarser than #25 sieve before 25 h operating time. The proportion rose to around half for runs between 25 and 40 h, and then to greater than half after 40 h. This trend runs counter to the observation that the bed grew finer in appearance throughout the run, but comports with the trend of increasing weight of particles coarser than #25 sieve in the bed.

Phosphorus Reduction

Figure 21 shows reduction in phosphorus during the second series. Reductions were greater in this series than in the first. TP reduction ranged from 0.30 to 0.65, and dissolved OP reduction ranged from 0.62 to 0.84. No trends or correlations are apparent from visual inspection of the figure.

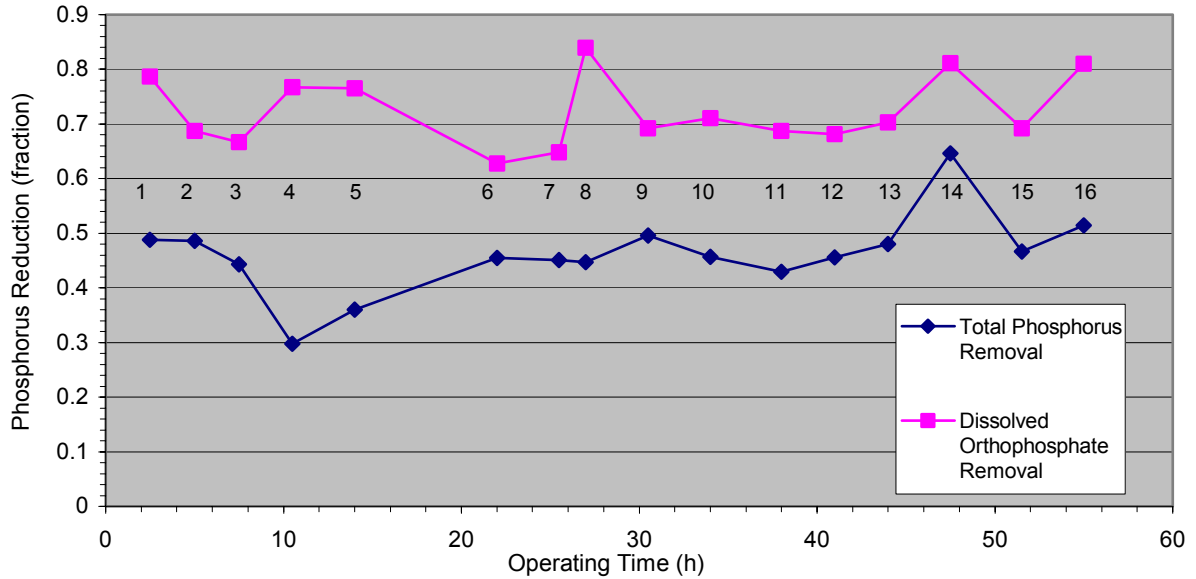


Figure 21: Second Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h) (Run Numbers Indicated)

Variation of Phosphorus Concentration with Height in Bed

Figure 22 reveals that the profile of dissolved OP concentration with respect to position in the cone assumed a similar pattern for most of the runs in the second series as that observed in the first series. The degree of rebound in concentration between the liquid sampled at a height of 19 cm and the treated liquid overflowing the cone top was very little at the beginning of the series. The rebound quickly increased to the 5 to 10 ppm typical of the early part of the first series and stayed in that range for the remainder of the second series except for three scattered points.