

EXPERIMENTS WITH LABORATORY-SCALE CONTINUOUS CRYSTALLIZER

Overall Design of Experiments and Reasoning behind the Design

The experiments sought to reveal how the behavior of the crystallizer varies with respect to variations in operating conditions. The organization of the experiments reflects a balance between the need for efficiency in time and materials use and the need for data yielding useful, sufficiently confident conclusions about the effect of the variations upon performance. To strike this balance, it was necessary to recognize the time required for crystallizer performance to achieve steady state after a set of conditions is put in place and the practical demands resulting from this time requirement.

Steady state is achieved for a given set of conditions (liquid entering at a given constant flow rate and composition, and seeds, if any, being added at a given constant size and number per hour) when the liquid flowing out of the crystallizer is constant in composition, and the bed is constant in total weight and particle size distribution. By deduction, the net rate (number per time) of generation of bed particles by seeding and other mechanisms must equal the net rate of removal by product outflow and other mechanisms.

Evolution in behavior of the crystallizer toward steady state can be viewed as occurring in two parts. The first part is the relatively fast change (within 10 min) in behavior that results when the overall liquid flow rate, ammonia addition rate, or Mg addition rate is changed. These changes occur primarily because of the changing driving force in the liquid phase for the reaction, and are completed as soon as the new concentrations work their way through the liquid in the bed. The second part is the relatively slow change (requiring thirty to fifty hours, for example) that results from the change in bed characteristics that can result when the liquid flow rate, ammonia addition rate, Mg addition rate, seeding rate, seeding size, or product removal manner is changed. This type of change is slow because the amount of phosphorus available for crystallization, and thus also the crystal growth necessary to change bed characteristics, in the liquid passing through the crystallizer each hour is

equivalent to only a few percent of the weight of the bed. Therefore the bed changes toward steady state only over a period of hours.

In an ideal experimental design, with “ideal” here meaning “without regard to practical laboratory constraints,” the crystallizer would be allowed to come to steady state at each condition set by passing through both the fast and slow changes after that condition set is put in place. A series of runs is required for the crystallizer operation to pass through the fast and slow changes to reach steady state for one condition set. A single, long run is impossible because the crystallizer cannot be operated continuously for more than about four hours at a time because it must be shut down to remove product when the product collector fills. Also, to monitor adequately the progress of the bed toward steady state, a sieve analysis needs to be performed on the bed every few hours. For time efficiency, this analysis is best performed after each product removal shutdown. The sieve analysis requires removal, drying, sieving, and weighing of the bed, all of which requires at least one extra day. Therefore, runs cannot be spaced closer than alternate days. If about 40 hours of operation are required for passing through both the fast and slow changes, ten four-hour runs are needed, spanning twenty laboratory days or about four work weeks.

Also, the ideal experimental design would prescribe that a variety of condition sets be selected and repeated in a manner yielding data sufficient to support confident conclusions about the effects of the conditions upon the performance. A randomized complete block design, with blocks corresponding with samples of lagoon liquid to adjust for its sample-to-sample variation, would efficiently produce data suitable for a factorial-style statistical analysis that would reveal the nature of the effects of the conditions upon performance. A set of experiments in this design, using three blocks and testing five factors (e.g., ammonia addition, Mg addition, liquid flow rate, seeding rate, and product removal means) at only two levels each would require $3 \times 2 \times 2 \times 2 \times 2 \times 2$, or 96, series of runs. With four work weeks required for each series, at least 384 weeks would be needed. Nearly

eight years would therefore be required to complete all the series, and major components of the system would likely wear out and need to be replaced during this time, introducing changes that would muddle the statistical analysis. Operating multiple crystallizers simultaneously would reduce elapsed time for a given number of series, but would introduce a new variation source that would result in the need for more series of runs and also require more laboratory space and personnel.

The ideal design would also require large volumes of lagoon liquid samples. A single mixed sample of lagoon liquid for each series is needed for properly blocking out the sample-to-sample variation. With an average flow rate of 13 gallons per hour (gal/h), or 49.3 L/h, of lagoon liquid, each of the 96 series would require that a tank containing 520 gal (1,970 L) be brought from a lagoon to the laboratory. This quantity of liquid would weigh about 2.5 tons, or about 2,300 kilograms (kg). Quantities above one-half ton (454 kg), however, become challenging to manage in the laboratory because they are difficult to move on hand trucks.

To reduce the time and lagoon liquid requirements to levels achievable in the laboratory, the experiments were organized into two stages, summarized in Table 5. The first stage, here called the fixed-condition runs (FCRs) aimed to reveal the behavior of the crystallizer for two condition sets after achieving steady state, i.e., after passing through both the fast and slow changes, for each set. (In practice, the second set did not lead to steady state and was therefore modified, resulting in a third series of FCRs.) The behavior observed included the performance, as indicated by reductions in TP and OP between raw and treated liquid; the TP and OP reduction at four different positions within the crystallizer; weight and particle size distribution of the bed; production rate; and particle size distribution of the product.

The second stage, here called the multivariate runs (MVRs), set the bed characteristics at those achieved in the near-steady state period observed during series #3 in the first stage. The second stage explored the effects of eighteen operating conditions resulting from factorial

Table 5: Organization of Experiments with Continuous Laboratory-Scale Crystallizer

STAGE	SERIES#	NUMBER OF RUNS	DESCRIPTION	CONDITIONS
1: FCRs (Fixed- Condition Runs)	#1	16	Reached goal of attaining near-steady state at the first set of conditions	Liquid rate: 13 gal/h (49.3 L/h) Ammonia addition: 100 ppm TAN Mg addition: none Seeding: 18 seeds per s Product removal mode: continuous by gravity during operation
	#2	16	Attempted, but failed, to reach near-steady state at the second set of conditions	Liquid rate: 13 gal/h (49.3 L/h) Ammonia addition: 100 ppm TAN Mg addition: 30 ppm Mg Seeding: 29 seeds per s, dropping to zero through the series Product removal mode: continuous by gravity during operation
	#3	15	Reached goal of achieving near-steady state at the modified second set of conditions	Liquid rate: 13 gal/h (49.3 L/h) Ammonia addition: 100 ppm TAN Mg addition: 30 ppm Mg Seeding: zero Product removal mode: periodic rapid removal to maintain bed height
2: MVRs (Multi- Variate Runs)	#1 (only one series of runs)	3	Each run tested 18 condition sets, for factorial-style statistical analysis. The range in conditions centered on the conditions in series #3 of the FCRs.	All eighteen combinations of: Ammonia addition (0, 100, and 200 ppm TAN), Mg addition (0, 30, and 60 ppm Mg), and Liquid rate (11 and 15 gal/h, or 41.7 and 56.8 L/h) All runs maintained, throughout: No seeding, Product removal by periodic rapid removal to maintain bed height.

arrangement of three operating parameters, after allowing the fast changes in performance to occur.

The three parameters were ammonia addition, at three levels; Mg addition, also at three levels; and total liquid flow rate, at two levels. The range in the level of each parameter centered on the value at

which that parameter was set in the FCRs when the crystallizer reached the steady state condition that yielded the bed characteristics used in the MVRs. Only one series of runs was conducted in this stage, and this series is denoted as #1 in Table 5.

The two-stage approach thus showed the steady state behavior for two condition sets and the effects of variations in three parameters when allowing time for the fast changes to occur. The main advantage with this approach is that it reduces the time required for testing the effects of the three parameters. The main drawback is that the effects observed in the MVRs are not necessarily the same as the effects that would be observed if the crystallizer were allowed to reach steady state for each set of conditions. It is conceivable, for example, that a combination of parameters different than that used to produce the bed characteristics used in the MVRs could, if time were allowed for reaching steady state, produce bed characteristics so different that performance would also be changed materially beyond the fast changes. It was to minimize this risk that the ranges tested in the MVRs centered upon the values used in the FCRs to produce the bed characteristics used in the MVRs.

The two condition sets chosen for the FCRs were two that the PLCB model predicted would result in stable operation. The condition sets were similar; however, only one of them calls for Mg addition. Also, the seeding rate was set higher in the set that included Mg; otherwise, the model predicted that the bed would fall at the bottom due to larger particle size resulting from the greater mass of struvite precipitated. The model does not take ammonia addition directly as an input, but rather pH. The results of the tests measuring pH rise versus ammonia addition, described under “Direct Addition of Ammonia” in “Experiments in Batch Mode and Resulting Design Elements for Struvite Crystallizer,” were used to set the ammonia addition to approximate the pH rise used as input for the model runs. The condition sets for the MVRs centered around the FCR condition set that used Mg addition.

Equipment, Materials, and Procedures Used

Equipment

The system used for continuous crystallization in the laboratory consisted of a main crystallizer chamber; an inlet manifold at the bottom of the chamber, with connections for raw lagoon liquid, Mg solution, and ammonia water inputs; a product collector; an overflow at the top of the main chamber with a connection for exit of treated lagoon liquid; and hoses, tubes, pumps, and storage vessels for the inputs and output. Figure 12 is a sketch of the main chamber, inlet manifold and connections, product collector, and overflow.

The main chamber of the crystallizer was made from a one-liter Imhoff funnel, composed of transparent plastic and normally used for measuring sedimentation rates. The bottom of the funnel was sawn off at the height required to provide an inner diameter of 0.5 in. (1.27 cm) at the bottom of the remaining funnel. The sides of the funnel were straight, forming a cone with diameter increasing at a constant rate with respect to height. The inner diameter at the top of the cone was 4 in. (10.2 cm), and the cone was 15 5/8 in. (39.7 cm) high.

A polyvinyl chloride (PVC) pipe nipple of 0.5 in. (1.27 cm) nominal diameter, with barb connections, initially was attached vertically downward from the funnel bottom by slipping the ends of both tightly inside a section of rigid, clear, vinyl hose until the ends of the nipple and funnel butted together within the hose. The bottom end of the nipple was pressure fit into the top connection of the inlet manifold, which consisted of a PVC cross (four-way tee) of three-quarter-in. (1.91 cm) nominal diameter with socket-type connections. The nipple and hose were removed after the tenth run in the first series of FCRs to ease flow of product from the main chamber into the product collector. For the remainder of the FCRs and for the MVRs, the inlet manifold was bonded directly to the bottom of the funnel with silicone sealant. Figure 12 depicts the apparatus after removal of the nipple and hose and therefore does not show them.

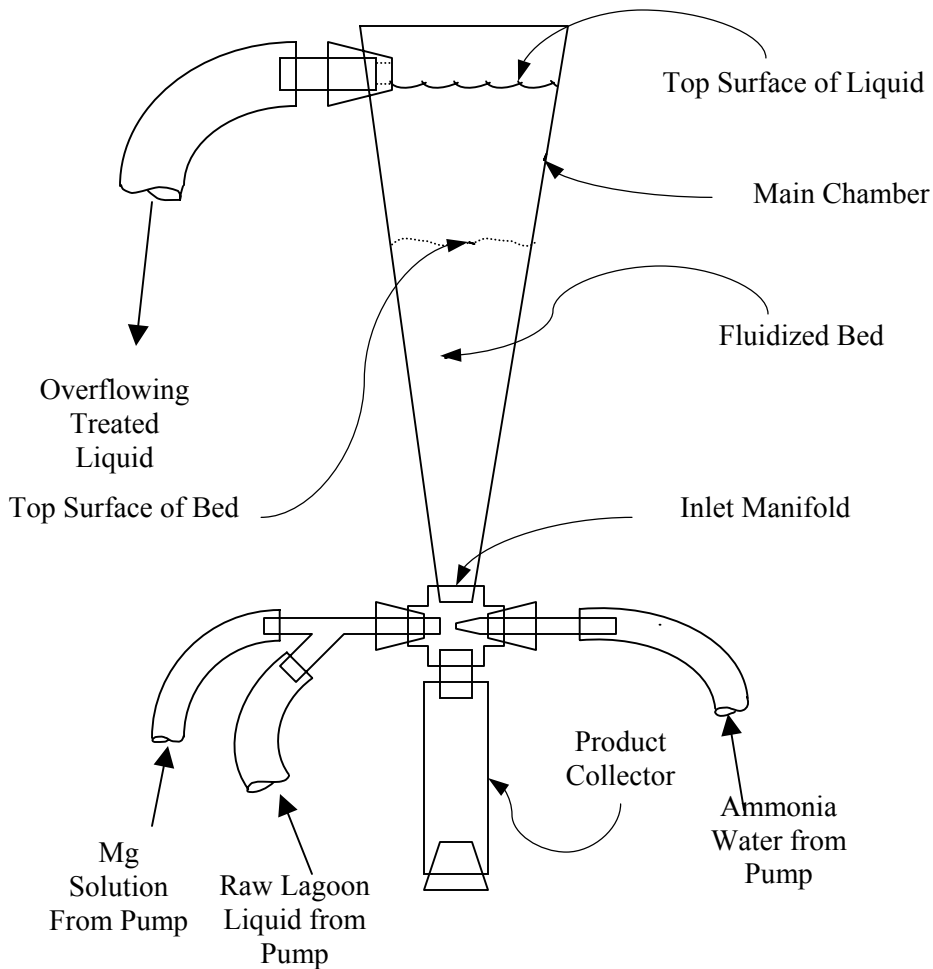


Figure 12: Sketch of Laboratory-Scale Continuous Crystallizer

A nipple identical to that initially used above the manifold was attached to the bottom manifold connection, also by pressure fitting, to accommodate the product collector, which consisted of a six-in. (14.2 cm) length of the same rigid hose used on the funnel bottom. The top of the collector was slipped around the bottom of the nipple, and a rubber stopper was pushed up into the bottom of the collector to close it. A one-hole rubber stopper was inserted into each of the two side connections of the inlet manifold. One of the side connections served as the inlet for lagoon water and Mg solution. Through the hole in the stopper in this connection was pushed, for the second and

third series of runs, the non-bifurcated end of a Y-shaped laboratory glass tubing section with outer diameter of about 3/8 in. (0.95 cm). For the first series of FCRs, in which no Mg was used, a section of glass tubing, approximately 2 in. (5.1 cm) long and 3/8 in. (0.95 cm) outer diameter, was pushed through the stopper in this connection. The other connection served as the inlet for ammonia water. Through the hole in the stopper on this connection was inserted, with the tip inwards, a stub from the bottom of a one milliliter (mL) glass pipet, formed by cutting the pipet about 2 in. (5.1 cm) above the tip.

For introducing the ammonia water, a Fisher Scientific Variable Mini-Flow peristaltic pump drew the liquid from a one-liter Nalgene bottle through Tygon plastic tubing of 0.25 in. (0.64 cm) outer diameter, extending from the bottom of the bottle to the pump suction connection. The tubing was slipped through a hole in a rubber stopper inserted into the mouth of the bottle to minimize ammonia evaporation. Another length of the same type of tubing extended from the pump discharge connection to the outer end of the glass stub in the inlet manifold.

For introducing the lagoon water, an IDEX Corporation Model 020 variable speed gear pump drew the liquid from a 120-gallon (455 L) plastic tank mounted on a wooden pallet. The liquid was drawn from the tank through a length of 0.5 in. (1.27 cm) diameter Tygon tubing, weighted at one end with a steel clamp to maintain its position about 4 in. (10.2 cm) above the floor of the tank, and attached at the other end to the suction of the pump. From the pump, the liquid flowed through a length of 0.5 in. (1.27 cm) rubber tubing connected at one end to the pump discharge and at the other to one of the two ends of the bifurcated side of the Y-shaped glass section in the inlet manifold.

For introducing the Mg solution, a Fisher Scientific Variable Mini-Flow peristaltic pump drew the liquid from a five-gallon (19 L) plastic pail through Tygon plastic tubing of 3/8 in. (0.95 cm) outer diameter, extending from near the bottom of the pail to the pump suction connection. The pail was covered with aluminum foil to minimize evaporation and odors, and the Tygon tubing

passed through a small opening in the foil near the lip of the pail. A length of rubber tubing of 0.5 in. (1.27 cm) outer diameter extended from the pump discharge connection to the other end of the bifurcated side of the Y-shaped glass section in the inlet manifold. Each of the three tubes feeding liquid into the crystallizer was provided with a pinch clamp for closing and opening the tube.

To provide an overflow from the main chamber, a hole large enough to accommodate a 1 in. (2.54 cm) rubber stopper was drilled, centered 0.75 in. (1.9 cm) below the top of the funnel. Into the stopper was drilled a hole large enough to accommodate the end of a 0.5 in. (1.27 cm) nominal diameter PVC pipe nipple with barbed connection, which was pressed into the stopper. The inner edge of the hole in the funnel was covered with a bead of silicone sealing and adhesive compound to provide a leak-free fit with the stopper. After the bead was dry, the stopper and nipple assembly were pushed into the hole and secured with tape and/or wire extending around the funnel. This set-up positioned the lowest point at which liquid could overflow; that is, the lowest point of the inside wall of the nipple, at 7/8 in. (2.22 cm) below the top of the cone. A length of the same Tygon tubing used to connect the funnel bottom to the inlet manifold was pressed onto the outer end of the nipple and extended to a sink with drain leading to a system for treating such wastes.

Teflon tape was used to ensure leak-proof connections at several points in the system. The tape was wrapped around the ends of the two PVC nipples before inserting them into the inlet manifold, around the bottom of the funnel before inserting it into the hose section, and around the suction nozzle of the lagoon water pump before inserting it into the suction hose.

A plugging device was fabricated for supporting the bed in the funnel while the system was shut down. This device would be inserted from the top of the funnel. For the device, a tapered neoprene stopper was selected to fit smoothly and snugly into the bottom of the funnel. A rigid steel spindle approximately 18 in. (46 cm) long and 1/8 in. (0.32 cm) thick was threaded for about 1 in. at

one end. The stopper was pushed onto the threaded end of the spindle and secured with washers and lock nuts. The other end of the spindle was formed into a loop for easier grasping.

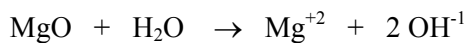
The funnel was supported by a ring clamp and a buret clamp, which were in turn clamped to a sturdy ring stand. The intake manifold and product collector were supported by the funnel. The three metering pumps and the container for the ammonia water were placed on the bench top near the funnel. The lagoon water tank and the container for the Mg solution were placed on the floor.

A pH probe was mounted from the ring stand in such a way that its tip extended below the surface of the liquid in the funnel at a point near the overflow. Connecting wires led from the probe to a digital readout indicating the pH in hundredths of a point.

Materials

Ammonia water for the apparatus was produced by diluting laboratory reagent-grade ammonia water, containing 30% ammonium hydroxide (NH₄OH) by weight, as necessary with distilled water to achieve 7,500 ppm TAN.

Mg solution for the apparatus was produced by dissolving feed-grade magnesium oxide (MgO), which consists of caustic-calcined magnesite (a Mg ore), in water acidified with concentrated hydrochloric acid (HCl), which contained 38.5 % by weight hydrogen chloride. HCl was used in place of compressed carbon dioxide (CO₂) in the laboratory to avoid the complication and expense of handling small amounts of compressed gases. The acid-to-MgO ratio, which was 40 milliliters of concentrated HCl to twelve grams of MgO, was set to provide hydrogen ions sufficient to neutralize all the hydroxide ions generated by dissolution of MgO:



The resulting concentrated Mg solution, containing about 16,000 ppm Mg, was stirred into sufficient lagoon water to dilute it to 800 ppm Mg. Preliminary work suggested this concentration could be achieved by passing lagoon water acidified with compressed CO₂ through a bed of MgO (see

“Magnesium Supplementation Tests” in “Experiments in Batch Mode and Resulting Design Elements for Struvite Crystallizer”). On the second series of FCRs and on the MVRs, a sample of the concentrated Mg solution was taken and diluted 1,000 to 1, and the result used to confirm the Mg content before stirring it into the lagoon water. (The first FCR series did not use any Mg, and the Mg content became so consistent by the end of the second series that analyzing the strong Mg solution before each run was judged unnecessary. The MVRs, composing the basis for statistical analysis, required that the Mg content be known, and therefore sampling and analysis of the concentrated Mg solution resumed for these runs .)

The lagoon water was taken from the primary lagoon for swine waste treatment at the Upper Coastal Plain Research Station between Rocky Mount and Tarboro, North Carolina. The water was drawn by portable pump and hose from the southwest corner of the lagoon, about six feet from shore and one to two feet under the surface.

The particulate solid for the fluidized bed in the crystallizer was produced for the first run by grinding dried crystalline solid with a mortar and pestle. For each subsequent run, the bed used was that recovered from the run preceding it. The crystalline solid was obtained from the farm where the lagoon water was obtained. The solid was taken from a lagoon water recirculation pipe and was dried overnight at 100 to 120 degrees Fahrenheit (°F), or 38°C to 49°C, before grinding. The dried solid was dissolved in weak sulfuric acid (aqueous H₂SO₄) and analyzed for Mg, TAN, and OP, with results as shown in Table 6.

Table 6: Results of Analysis of Acid-Dissolved Crystals from Farm

Species	Expected Concentration if 100% Struvite	Concentration from Analysis	Percent of Expected
Mg	68.4 ppm	65.5 ppm	96%
TAN	40.9 ppm	36 ppm	88%
OP	90.1 ppm	88.6 ppm	98%

The results in Table 6 are consistent with 88% of the material being struvite. Or, if it is recognized that ammonia losses may have occurred during oven drying, the results are consistent with a content of 96% struvite (based on Mg results in Table 6).

The dried, ground solid used in the first run was partitioned into various particle size fractions needed for the bed by using a W. S. Tyler Model RX-24 portable sieve shaker and sieve apparatus. The weight of each fraction used to make up the initial bed for the first run was 75% of the weight predicted for that fraction by the PLCB model for the first set of FCR conditions.

Seeds, to serve as nuclei for formation of new crystals to replace those removed from the bed as product, were taken from the #60 sieve to #70 sieve particle size fraction. Opening sizes, and hence expected particle diameters, corresponding with various sieve numbers are presented in Appendix B.

Operating Procedures

To meter the flows of each of the three liquids, the corresponding metering pump was calibrated by using a stopwatch and graduated cylinder to determine the volume pumped at several settings of the motor speed control dial. The calibration data were then used in setting the dials to achieve prescribed flow rates during operation of the crystallizer. The flow rates were checked periodically during operation and adjusted if necessary to keep the flow rates at the desired values. The flow rates of the ammonia water and Mg solution were checked by tracking the fall of the liquid levels in their containers against the passage of time. The flow rate of lagoon water was checked by measuring the outflow rate from the crystallizer overflow with graduated cylinder and stopwatch, after ensuring that the other two flow rates were correct.

The lagoon water in the tank was kept stirred by circulating it with a submersible centrifugal pump. The pump, which produced a flow of about 500 gal (2,000 L) per h, drew the liquid through the suction on its housing and discharged it through a four-foot (1.2 m) length of tubing

approximately 0.5 in. (1.27 cm) in inner diameter. The pump was positioned on the floor of the tank off-center toward one end of the tank, and the discharge tube was positioned toward the other end of the tank and nearer the surface. This conformation aimed to provide maximum rotation and homogeneity of composition within the tank. The end of the suction hose through which the lagoon water metering pump withdrew liquid to feed the crystallizer was positioned near the recirculating pump. This positioning minimized differences between the composition of lagoon water samples, which were taken from the discharge hose of the submersible pump, and that of the liquid actually flowing through the metering pump to the crystallizer. Samples of untreated lagoon water were taken from the submersible pump discharge rather than from the metering pump discharge because withdrawing a sample from the latter would decrease the flow rate to the crystallizer and, as a result, allow the fluidized bed to drop.

Each run lasted 1.5 to 5 h. The duration of each FCR was generally limited by the length of a work day, with set-up and shut-down tasks, including preparation and submittal of samples, occupying about 4 to 6 h in addition to the run time itself. The runs therefore averaged about 3 to 4 h. Some runs were shorter as a result of running out of lagoon liquid, filling up the product collector, or experiencing some difficulty requiring shut-down to resolve. Each MVR lasted 3 h, the time required to complete the 18 segments corresponding with the 18 condition sets. Two or three runs were generally carried out before having to re-fill the lagoon water tank, except in the MVRs, when only one run was conducted with each tank. Before being re-filled, the tank was completely emptied, rinsed with tap water, and allowed to air dry.

The submersible pump was turned on an hour before each run began, and remained on through each run, to homogenize the lagoon liquid in the tank. A sample of the ammonia water was taken and submitted during this period. Also, just before runs using Mg solution, the pH of the solution was checked with the probe normally mounted at the funnel overflow.

To start the run, the clamp was opened on the lagoon water metering pump discharge hose and the pump turned on and adjusted to the desired rate. Before introducing the fluidized bed, the pH of the lagoon liquid passing through the funnel without any treatment was recorded. The solid granules to form the fluidized bed were placed in a beaker, covered with distilled water, and poured from the beaker into the top of the funnel with the aid of a stream of distilled water from a wash bottle. Once the granules sank into the funnel and fluidized, the ammonia water and Mg solution metering pumps were turned on and set to the desired flow rates. A stopwatch for timing the run was started at this point.

During each of the FCRs, the pH of the treated liquid at the funnel overflow and the height of the bed top above the funnel bottom were recorded at 30-min intervals. On runs with seeding, seeds were added at 30-min intervals, by covering the desired weight of seeds in a beaker with distilled water, then pouring them into the top of the funnel, where they settled into the bed. The desired weight of seeds was calculated by multiplying the average seeding rate desired (particles/time) by 30 min to obtain the number of particles required for each addition. Then, the number required was multiplied by the estimated weight per particle. The estimated weight per particle was calculated by multiplying the estimated volume per particle by the density of struvite (1.7 g/cc). The volume per particle was estimated as that occupied by a sphere with diameter equal to the average between the opening sizes of the two screens used to separate the seeds from the ground material.

During all the FCRs, a sample of untreated lagoon liquid was taken in the manner described above. Also, just before the end of each of these runs, five liquid samples were taken. One was taken from the discharge of the overflow hose. The other four were taken from four heights above the funnel bottom: 5 cm (near the bottom of the bed), 12 cm (near the middle of the bed), 19 cm (in the upper portion of the bed, except when the bed top lay below that height, in which case this position was just above the bed), and in the upper portion of the funnel near the outlet into the overflow. The

four samples taken from within the funnel were obtained by dipping a 25-ml pipet into the funnel to the desired depth. The tip was covered with a 70-mesh wire screen cut from a shaker sieve to prevent particles from the bed from entering the pipet.

In each of the MVRs, the flow rates of lagoon liquid, Mg solution, and ammonia water were adjusted eighteen times during the run, spaced at 10-min intervals, to produce eighteen different combinations of operating conditions (two lagoon liquid flow rates, three Mg solution flow rates, and three ammonia water flow rates). After making each adjustment, pH and bed top height were recorded. Beginning 5 min (approximately four residence times) after each adjustment, four 50-ml sub-samples were taken at 1-min intervals from the discharge of the overflow hose. Each set of four sub-samples was combined into one blended sample corresponding with one set of operating conditions. Also, four sub-samples of untreated liquid were taken at evenly spaced points in time during the run, in the manner described above. These four sub-samples were combined to form a single blended sample of raw lagoon water corresponding with that run.

To end each run, after all sampling was complete, the pumps for the Mg solution and ammonia water were first turned off. Then, the plugging device was inserted through the bed and pushed into its seated position against the cone bottom as the lagoon water pump was turned off. All the tubes leading into the inlet manifold were closed, using the pinch clamp on each tube.

The product from each run, if any, was removed from the product collector by placing a sieve and glass pan under it, then removing the stopper in the bottom of the collector and washing the product out with distilled water from a wash bottle. The product was retained on the sieve, which was a number 70 sieve (0.21 mm openings) in the first two series FCRs, and a number 230 sieve (0.063 mm openings) for the other FCR series and for the MVRs. The liquid in the product collector drained through the sieve into the glass pan. The product on the sieve was transferred onto a non-

stick baking sheet using a spatula and a stream of distilled water from a wash bottle. The product was spread out on the sheet and set out to air-dry at room temperature for at least 24 h.

At the end of each run, the bed was also removed from the crystallizer. To remove the bed, the plugging device was slowly removed and the bed and liquid in the crystallizer allowed to flow slowly down through the product collector and into the sieve and glass pan in the same manner described for the removal of the product. The wash bottle was used to remove any bed material clinging to the plugging device or the sides of the crystallizer, inlet manifold, or product collector. The equipment and method for receiving and drying the bed was the same as that described for the product, except that two baking sheets instead of one were required for spreading out the bed to dry.

Analytical Procedures

Dried Bed and Product Evaluations

The dried bed and product from each run were evaluated by conducting a sieve analysis. For this analysis, the dried bed material or dried product was removed from the non-stick baking sheet by gently tapping the sheet and dislodging the dried material with a soft brush. The material was loaded into the top of a stack of Tyler sieves and shaken with the W.S. Tyler Model RX-24 portable sieve shaker for 10 min. The material on each sieve was removed by inverting the sieve and rubbing and tapping the sieve medium on both sides until smooth to the touch, and then the material was weighed on an analytical balance. The number of sieves used generally exceeded the capacity of the shaker, which only accommodates five sieves. Therefore, each analysis was performed in two phases, with the five coarsest sieves being used in the first phase. The fine material falling to the pan in the first phase was then loaded into the top of the stack of remaining finer sieves and loaded into the shaker for the second phase.

Before adopting the above drying and sieving procedure, it was tested, with the exception that the drying surface was a glass baking pan rather than a non-stick surface, to determine whether it

changes the particle size distribution. For the test, the particle size distribution of a sample of dry struvite was determined using the sieve analysis procedure. The sample was then covered with water, stirred, left to stand overnight, removed from the water, and spread out in the glass pan to dry. The sieve analysis was performed again, and the results compared against those from the first analysis (see Table 7).

Table 7: Results of Sieve Analyses to Test for Particle Size Stability Through Wetting, Drying, and Sieving Again

Sieve Fraction	Weight Before Wetting, Drying, and Sieving Again	Weight After	Loss
Larger than 2.000 mm	12.0 grams	11.5 grams	0.5 grams
1.680 – 2.000 mm	3.6 grams	2.8 grams	0.82 grams
1.000 – 1.680 mm	18.0 grams	18.8 grams	-0.8 grams
0.500– 1.000 mm	20.0 grams	19.9 grams	0.1 grams
0.250 - 0.500 mm	20.0 grams	19.9 grams	0.1 grams
0.125 – 0.250 mm	20.0 grams	18.4 grams	1.6 grams
Smaller than 0.125 mm	0.0 grams	1.6 grams	-1.6 grams
Total	93.6 grams	92.9 grams	0.7 grams

The comparison indicated that the procedure changed the particle size distribution only slightly, with the greatest change occurring on the fine end of the spectrum. Based on observations during the procedure, this loss was judged likely to result from adherence of particles to the glass, with some of the particles remaining on the glass despite scraping and others being flung into the air or otherwise missing the receiving vessel during the scraping activity. New, non-stick drying sheets were therefore obtained. The solid slid easily off the non-stick sheets, nearly eliminating the need for scraping. Because the losses had only been slight even when the glass pan and appreciable scraping were used, the procedure using the non-stick sheets was considered adequate with no further testing.

Analysis of Liquid Samples

Before analyzing chemically, some of the liquid samples were split into two parts, and one of the parts then centrifuged to separate suspended solids from the clear, yellow liquid. The clear liquid was poured off, producing another liquid sample. The pellet remaining in the centrifuge vial was then reconstituted to the volume of liquid from which it came by shaking vigorously and adding sufficient distilled water, thus producing a third liquid sample. All of the samples of raw lagoon liquid, treated liquid, and Mg-supplementing solution were treated in this way. Ammonia water samples were not so treated because they contained no suspended phase.

Table 8 summarizes the types of samples taken and the chemical analyses conducted on them. OP analyses were conducted using EPA Test Method 365.1 (1979), with ascorbic acid method for automated analysis. TP analysis was by the same method, except that samples were subjected to persulfate digestion before automated analysis. TAN analysis was by EPA Test Method 351.2 (1979). For analysis of Mg, calcium (Ca), and the other metals, Standard Method 3111 B (1995) was used. Samples were subjected to nitric acid digestion, and introduced to a spectrometer by direct aspiration. Spectroscopy was of atomic absorption type except for copper, zinc, and iron analyses, which used emission spectroscopy.

Results in the FCRs And Discussion

Overview of FCR Results and Implications for Future Design

This overview summarizes the most important outcomes of the FCRs. Results for each FCR series are presented in more detail and discussed more thoroughly in the sections that follow. Three series of FCRs were conducted, each operating at the condition sets presented in Table 5. The FCRs aimed to find how differently the crystallizer would behave for different condition sets, given sufficient operating time to reflect both the fast and the slow changes.

Table 8: Summary of Samples and Analyses

Liquid Sample Type	TP	OP	TAN	Mg	Ca	Other Metals*
FCR Series #1						
Raw lagoon liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	
Samples from crystallizer	X	X	X	X	X	
Treated liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	
Ammonia water			X			
FCR Series #2						
Raw lagoon liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	
Samples from crystallizer	X	X	X			
Treated liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	
Ammonia water			X			
Mg solution (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	
FCR Series #3						
Raw lagoon liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X			
Samples from crystallizer	X	X	X			
Treated liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X			
Ammonia water			X			
MVR Series #1 (the only MVR series)						
Raw lagoon liquid (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X**	X**	X**
Samples from crystallizer	X	X	X			
Treated liquid, uncentrifuged	X	X	X			
Ammonia water			X			
Mg solution (Uncentrifuged, centrifugate, and reconstituted pellet)	X	X	X	X	X	

* Sodium, potassium, copper, zinc, and iron.

** These analyses conducted only on the uncentrifuged samples of the first run.

The first series, operating at the previously selected condition set, which did not include Mg addition, moved initially toward an unacceptable steady state. Product did not discharge, leading to growth of bed particles so large and heavy that the bed fluidized improperly and grew so high that

overflow of the bed was imminent. A configuration change at the crystallizer bottom then solved this difficulty, and the behavior converged on an acceptable near-steady state in the remainder of the first series. During this period, calculated TP reduction averaged near 27.5%, in the range expected. Careful inspection of the composition changes in the solid and liquid phases suggested that some of the reduction occurred from the solid phase. A balance on the number of particles indicated that spontaneous seeding (4 per s) amounted to no more than one quarter of the total seeding rate (22 per s). The bed developed a channel when it was heaviest and coarsest, but the degree of phosphorus reduction appeared not to be associated with the phenomenon. The bed appeared well mixed regardless of whether there was a channel. A line, demarcating the boundary between lagoon liquid below and water above, was observed moving upward through the bed at the beginning of the first run, when the feed to the main pump was switched over from tap water to lagoon liquid.

The second series of FCRs began with the second selected condition set, which included Mg addition. The series began with the called-for seed addition rate of 29 per s, but the rate was gradually reduced to zero during the first few runs in an attempt to achieve steady state when it became apparent that seeding was also occurring spontaneously. Even when seed addition was discontinued, the spontaneous seeding was high enough that the bed particles were too small to fall by gravity during normal operation, and the bed continued to grow. A balance on the number of particles through the series estimated that 41 seeds per second were being created spontaneously. Channeling developed in the first half of the series and continued to the series end, though the bed appeared well-mixed throughout the series. The bed growth eventually reached the point where it appeared bed particles would soon begin to overflow the crystallizer in the treated liquid stream, and the series was terminated. Total phosphorus reduction ranged from 30% to 65% through the series.

For the third series, the conditions set was the same as that in place at the end of the second series except that the product removal method was changed to periodic rapid removal between

periods of normal operation to maintain a bed height of 27.5 cm. This height was chosen during the first run in the series by draining the bed down until it fluidized smoothly, in an apparently well-mixed state without a channel, and was maintained throughout the remainder of the series. An acceptable near steady-state was achieved by the middle of the series. Smooth operation continued until the final run in the series, when an accident led to loss of part of the bed. A particle number balance indicated spontaneous seeding of 52 per s. Total phosphorus reduction during the near-steady state period averaged 64%, in the range expected. Careful inspection of the composition changes in the solid and liquid phases suggested that some of the reduction occurred from the solid phase.

The ammonia addition rate, which was the same for all three FCR series (100 ppm TAN), was observed to raise the pH by 0.7 to 0.9 pH points. The raw lagoon liquid ranged in pH from 7.4 to 7.8.

From the results there emerged several points to help guide future design and operation. First, the overall design concept appears sound, achieving phosphorus reductions in the range expected. Second, if product removal is to occur continuously by gravity during operation, the zone under the cone bottom must be wider than the cone bottom; otherwise, particles that are large enough to be released according to the cone design will not fall through adequately, leading to bed buildup. Third, the bed appears to be mixed, not classified, and the liquid approximates plug flow through the bed, at least when channeling is not occurring. Fourth, the heavier the bed and the larger its particles, the more likely a channel will develop. Fifth, when adding Mg, spontaneous seeding may occur, obviating the need for deliberate addition of seeds. Finally, there may be phosphorus removal mechanism at work in addition to precipitation of dissolved OP. This other mechanism may remove phosphorus from the suspended phase.

Detailed Results from FCR Series #1

Qualitative Observations

From the start of the series, the bed behavior was observed to vary according to the vertical position within the bed. The behavior can best be described by classifying the volume inside the cone into four vertically stacked zones.

The first zone, called the bottom zone for the present work, occupied the lowest one to two cm in the crystallizer cone. In it, clusters of bed particles swirled occasionally downward from the denser bed above, followed by clearing of the particles from the zone as they were swept upward by the current, and then almost instant re-appearance of clusters of particles swirling in again from above.

The second zone, called the middle zone here, stretched upward then for several cm and was occupied continuously by the bed particles. The particles were closely spaced throughout the zone yet free to swirl in rapid, random eddies.

The third zone, called the top zone, stretched upward several cm from the middle zone. In this zone, bed particles appeared densely packed against the wall of the cone, and were moving slowly downward (no more than 1 cm/s) at all positions around the circumference of the cone except where a rapidly upflowing channel pierced through part of the time. The channel was 1 to 2 cm wide, and carried less densely packed bed particles upward at a speed on the order of 10 cm/s. The channel shape evolved and over a period of several minutes could often be seen to change from straight to sinuous and vice versa. The position also changed slowly, and could be made to move from one side to another by very slightly altering the tilt of the cone. The upper boundary of the zone was marked by the bed top surface, which swayed and waved in approximately the same way as an interface between two non-miscible liquids of differing density. At the bed top, the channel terminated, and

the bed particles carried up in it were observed to spread out rapidly from the top of the channel across the bed top.

The fourth zone, here called the headspace, lay above the bed. It stretched from the bed top up to the overflow from the crystallizer cone. Most of the time, few or no bed particles could be seen in it. However, occasionally some solid or solid-like aggregations that appeared softer and lighter than the rest of the bed particles could be seen to rise from the bed top through this zone.

During the first ten runs, only a few grains of product could be seen to exit the bed through the cone bottom from time to time. The zones in the cone were observed to change in ways consistent with product removal rate falling short of the rate of increase in bed mass. The bottom zone shrank, with the boundary between it and the middle zone progressing farther toward the cone bottom with each successive run. The top boundary of the middle zone also moved downward; it was not clear whether the height of this zone changed. The top zone clearly expanded, with its bottom boundary sinking and its top boundary rising. The head space continued to shrink, i.e., the top of the bed rose until it appeared likely that continuing the series with no changes in operation would cause the bed top to reach the overflow. A channel developed soon after the series began and remained through the tenth run.

After the tenth run, a short experiment was conducted to determine how large bed particles must grow to be able to fall by gravity out of the bed and thus become product. Struvite samples of varying particle sizes were dropped into the crystallizer cone as lagoon water was pumped through it at the rate being used in the first series of runs. It was found that only particles passing through a #12 sieve, which has opening size of 1.68 mm, could pass through the cone bottom and completely through the nipple and cross at the bottom of the cone to fall into the product collector. Particles as small as those passing through a #20 sieve, which has opening size of 0.841 mm, could sink as far down as the cone bottom and into the top of the nipple. Even though the inner diameter of the nipple

matched that at the cone bottom, these smaller particles did not pass through the nipple but instead were always swept upward from some point within the nipple and thus returned to the cone. To allow particles of this size to drop from the bed into the product collector, the nipple was removed, and the cross, which has a larger inner diameter, was adhered directly to the cone bottom with a silicone compound.

In the two runs following the alteration at the cone bottom, bed particles fell through the cone bottom and into the product collector so rapidly that each run had to be interrupted several times to empty the product from the collector. Though there remained a zone near the cone bottom that was sometimes swept clean of particles, some of the particles among the clusters that did occasionally swirl through this zone to the cone bottom did sink through the bottom and settled into the collector. This discharge of product was observed through the transparent collector walls to occur generally in short bursts a few seconds apart, with several particles in each burst. The bursts during the first and second runs after the alterations were frequent and at first nearly continuous. In the subsequent runs, the bursts occurred less frequently, settling to an average of several seconds apart, and the bursts were smaller.

The bed zones were observed after the alteration to change in directions generally opposite to those observed in the runs before the alteration. The bottom zone increased in height, and the boundary of the middle zone moved higher, also. The bed top (boundary between the third and fourth zones) moved lower. The change continued in this manner until the state of the zones approximated their state at the beginning of the series. Then the boundary between the middle and top zones rose as the middle zone grew and the top zone shrank. During the twelfth run, the channel in the top zone disappeared. By the thirteenth run, the zone heights, positions, and appearances were stable.

Regarding the liquid motion, of particular interest was whether the liquid moved in a plug flow manner through the main chamber or more resembled a well-mixed liquid. During normal operation, it was not possible to see any liquid motion because all the liquid was nearly the same color and opacity. However, before the first run, the crystallizer was run briefly with tap water in place of lagoon water to ensure that the system was set up properly. Once all appeared in order, the main pump intake was switched quickly from the vessel containing tap water to the lagoon liquid tank. At the moment the lagoon liquid reached the main chamber, there appeared a line marking the boundary between the two liquids. The line moved up through the bed as the lagoon liquid replaced the water that had previously fluidized the bed. The line became somewhat less sharp as it moved upward, but clearly maintained its visibility until it reached the bed top. Once at the bed top, the line diffused more rapidly, and the liquid space above the bed appeared to darken almost everywhere at the same rate. It should be noted that there was no channel visible at the time these observations were made.

The above observations of the bed behavior, motion, and product discharge in this series are addressed further, primarily in the discussion section following the presentation of quantitative results from the series. Linkages between the observations and the quantitative results are developed.

There were a few additional qualitative observations of note from the first series of FCRs. These observations are mentioned because they suggest how a larger, on-site system may behave. No differences in clarity, color, or odor could be observed between the raw lagoon liquid and the treated liquid during any of the first series of runs. A small amount of fouling occurred in the intake manifold (the cross at the cone bottom) and on the inside walls of the lowest one third of the cone. The fouling first became visible as a light transparent film after the second run, and by the tenth had built to a white coating. The coating was cleaned off with a dilute HCl solution mainly to preserve good visibility into the cone. The cleaning made no apparent difference in the nature of the liquid