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REMOVAL OF NUTRIENTS BY SORPTION ON ACTIVATED ALUMINA

by

CHECKMAN MICHAEL YUE, 1933-

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ABSTRACT

REMOVAL OF NUTRIENTS BY SORPTION ON ACTIVATED ALUMINA

by Checkman M. Yue

Advisor: Dr. Sotirios G. Grigoropoulos

1974

Rolla, Missouri

The nutrient enrichment of surface, primarily impounded, water and the associated problems of accelerated eutrophication and prolific algal growth have become a nationwide concern. Phosphorus and nitrogen are considered to be the key elements in abating eutrophication and are contributed from many sources, natural and manmade; prominent among these is the discharge of domestic and industrial wastes.

The purpose of this study was to evaluate the removal of nutrients, primarily phosphorus and nitrogen, with activated alumina using a continuous-flow pilot plant system. Specific objectives were the: development and construction of appropriate bench and field-scale pilot plant units utilizing the rapid mix-sedimentation and column operational modes; evaluation of the efficiency of nutrient removal from wastewater plant effluent; and investigation of the regeneration characteristics of the spent aluminas.

The work was conducted in 2 phases: laboratory studies, undertaken to develop design and operational criteria for the pilot plant units and to establish the regeneration characteristics of exhausted aluminas; and field investigations, employed to evaluate the efficiency of nutrient removal by fresh and regenerated aluminas under actual plant conditions, and to project approximate chemical costs. Three types of alumina, F-1 (-325),* F-1 (-100), and F-1 (28-48), were evaluated. Secondary effluent from the Rolla Southwest Sewage Treatment Plant was used in the laboratory and field studies. Major parameters employed included phosphorus (Poly+ortho), nitrogen (NH_3, Org, NO_3, and NO_2), COD, TSS, turbidity, and pH. The exhausted aluminas were treated with 1M sodium hydroxide followed by a water wash. Doses ranging from 0.085 (rapid mix-sedimentation system) to 0.096 (column system) g OH^-/g alumina, were required, and the regenerant and wash water constituted 1.4 to 4.6 percent of the volume of the secondary effluent treated.

The F-1 (-325) and F-1 (-100) aluminas in the rapid mix-sedimentation mode, and the F-1 (28-48) alumina in the column mode substantially reduced the phosphorus content, but did not significantly affect the total nitrogen concentration of the highly nitrified secondary effluent. The removal of phosphorus averaged 76 percent in the rapid mix-sedimentation system, and in excess of 88 percent in the column system, from an average influent concentration of 7.2 mg P/l; the column system could also effect essentially complete removals of phosphorus, but at significantly reduced volumetric throughputs.

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*The aluminas were products of the Aluminum Company of America, Pittsburgh, PA; the number in parenthesis indicates mesh size.

The removals of NH_3-N and Org-N ranged from 10 to 30 and from 56 to 75 percent, respectively, and the corresponding influent concentrations were 1.24 and 0.40 mg N/l; less than 4 percent reduction was obtained in NO_3-N, which at 12.5 mg N/l represented more than 87 percent of total nitrogen, while NO_2-N increased by 0.02 to 0.07 mg N/l. The effluent from the rapid mix-sedimentation system had approximately 30 percent less COD, however, discharge of alumina particles increased its TSS concentration by an average of 100 [F-1 (-100)] to 822 [F-1 (-325)] percent; the column effluent had 35 percent less COD, and except for initial wash-out of alumina fines, the TSS concentration was not significantly affected.

The average sorptive capacity of fresh F-1 (-325), F-1 (-100), and F-1 (28-48) aluminas, based on phosphorus data, was 4.5, 3.4, and 7.8 (6.1 at column breakthrough) mg P/g, respectively. The reclaimed aluminas lost approximately 34 percent of their sorptive capacity following the 1st regeneration and an additional 22 percent following the 2nd regeneration; this loss could have resulted in part from coating of the alumina particles by calcium carbonate.

The cost of phosphorus removal by sorption on activated alumina was significantly higher than the corresponding cost of treatment by chemical precipitation; however, the sorption process was capable of effecting essentially 100 percent removal of phosphorus and should be considered when the required degree of treatment cannot be obtained by the precipitation method.

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I. INTRODUCTION

The nutrient enrichment of surface, primarily impounded, water and the associated problems of accelerated eutrophication and prolific algal growth have become a nationwide concern. These nutrients are contributed from many sources, natural and manmade; prominent among these is the discharge of domestic and industrial wastes.

The composition of typical green and blue-green algae is shown in Table I. Nutrients needed in macro quantities are carbon, nitrogen, phosphorus, sulfur, calcium, magnesium, potassium, and sodium; of these, only carbon and nitrogen are major components of the algal cell material and all other elements, including phosphorus, generally constitute less than 1 percent of the dry cell weight. Carbon, which comprises 35 to 50 percent of the algal tissue and is derived principally from carbon dioxide, and nitrogen and phosphorus, which are contributed to wastewater in large amounts by human and household wastes, have been considered to be the appropriate points of attack for eutrophication control. The other elements are not thought to be important in algal control because of the chemical composition of natural waters and the relatively small increments added from cultural sources (1).

Kuentzel (2), after reviewing the literature, advocated that carbon would be the growth-limiting factor for algae. His conclusion was primarily based on the findings of a laboratory study by Lange (3); however, this work was conducted under conditions of high nitrogen and phosphorus and low carbon dioxide concentration, which are not comparable to natural conditions. Kuentzel also considered information reported by MacKenthun, *et al.* (4) on an algal bloom in Lake Sebasticook, ME, which indicated that over a period of 1.5 days during the bloom the

TABLE I. COMPOSITION OF GREEN AND BLUE-GREEN ALGAE*

Composition		Green		Blue-green	
Element	Content	Spirogyra	Cladophora	Anabaena	Microcystis
Carbon	%	42.40	35.27	49.70	46.46
Nitrogen		3.01	2.30	9.43	8.08
Phosphorus		0.20	0.56	0.77	0.68
Sulfur		0.27	1.58	0.53	0.27
Calcium		0.57	1.69	0.36	0.53
Magnesium		0.45	0.23	0.42	0.17
Potassium		0.92	6.08	1.20	0.79
Sodium		1.42	0.18	0.18	0.04
Iron	mg/kg	1,368	2,300	80	322
Manganese		1,641	1,040	800	2,751
Zinc		72	10	-	48
Copper		47	190	70	37
Boron		4	85	-	4

*Reported by Sawyer (1).

soluble phosphorus content never exceeded 0.01 mg P/l; on these grounds, Kuentzel theorized that since there was not a sufficient supply of phosphorus present to provide for the amount of algal growth observed, this element could not have been the growth-limiting factor and concluded that carbon must limiting. It is known and generally accepted, however, that algae take up phosphorus in excess of their immediate requirement (luxury uptake) and release it at a later time, and that soluble phosphorus is not the only form available to algae. The photosynthetic activity of blue-green algae can be continuous in the presence of a carbon dioxide concentration as low as 2.5 μmoles/l (5). Carbon dioxide in water is contributed from variety of sources, such as the atmosphere, bicarbonate-carbonate alkalinity, microbial decomposition of organic matter, and decarboxylation of humates (2,5,6), and limiting its concentration would be difficult. The advocacy of limiting carbon dioxide to control eutrophication has been disputed by Sawyer (1), Massey and Robinson (7), King (8), and Goldman, et al. (9) for several reasons, including the following considerations: eutrophication has occurred in numerous instances even when a high degree of secondary treatment had been applied to wastewater before discharge (1); carbon dioxide is always present in the atmosphere and enters the water at increasing rate at pH levels above 8.0 (pH values in excess of 10.0 have been measured in natural waters with active algal growth) (1,7); bacterial degradation of algal tissue releases carbon dioxide to the ecosystem (1,7); natural waters are buffered by a carbon dioxide-bicarbonate and carbonate alkalinity complex, and except for acid or low alkalinity waters, this complex would constitute an adequate storehouse of carbon dioxide (1,7,8,9); eutrophication control by limiting carbon availability would result in predominance of nuisance blue-green algae (8); and maximum growth of 2 species of freshwater green algae has been found to occur at carbon levels far below those present in most natural waters (9).

A great deal of thought and study has been applied to the removal of nitrogen and phosphorus from sewage effluent. Early studies had shown that both elements could be removed almost completely by activated sludge treatment, if the sewage were fortified with adequate amounts of carbohydrate matter (10); however, use of carbohydrates would increase sludge handling requirements and would not be economically feasible for most situations. The removal of all forms of nitrogen (ammonia, organic, nitrate, and nitrite) by means of a single treatment would be extremely difficult (11), and furthermore, some species of blue-green algae, with great nuisance potential, are capable of fixing nitrogen from the atmosphere (8,12). Consequently, attention has been focused on limiting the supply of phosphorus as the only practical alternative for algal control. This is exemplified best by the fact that as of June 1971, 16 states had adopted wastewater effluent standards for phosphorus which specify either an effluent concentration limit ranging from 0.1 to 2.0 mg P/l or a reduction ranging from 80 to 95 percent (13). It should be pointed out, however, that Sawyer (14) has questioned whether phosphorus removal alone will be enough to control eutrophication satisfactorily. In addition, ammonia above a certain critical limit [1.5 mg N/l at pH levels of 8.0 or higher (15)] becomes toxic to fish and aquatic life. Also, ammonia present in a wastewater effluent can exert a singnificant demand for dissolved oxygen in the receiving water, which in view of the more stringent effluent requirements, must be considered in wastewater treatment design; this is illustrated by the following tabulation which reflects the relationship between carbonaceous and ammonia oxygen demand before and after treatment to remove 90 percent of the organic matter (16).

Parameter	Raw Wastewater	Treated Effluent
Organic matter, mg/l	250	25
Ammonia, mg/l	25	20
Oxygen demand, mg/l		
Due to organic matter	375	37
Due to ammonia	112	90
Total	487	127
Oxygen demand due to ammonia, % of total	22	71

It can be seen that even after the efficient removal of carbonaceous material from municipal wastewater by either conventional biological or physical-chemical processes, the effluent would still discharge nearly 100 mg/l of nitrogenous oxygen demand.

Much of the work which has been undertaken to date in the area of nutrient control has emphasized the removal of phosphorus. Biological uptake in a typical wastewater treatment plant would only account for 20 to 30 percent removal of the influent phosphorus (17). Although there are some exceptions, notably the Rilling Plant in San Antonio and the Back River Plant in Baltimore, where removals up to 80 or 90 percent have been reported (18-20), normally domestic wastewater does not contain sufficient organic carbon to enable production of enough microbial cells to incorparate all available phosphorus and nitrogen (10,17). Chemical precipitation using lime, alum, or ferric salts has been found effective in removing phosphorus and has been employed during primary, secondary, or tertiary treatment (21-26). Chemical precipitation, however, would also render certain undesirable effects to the treated water, including an increase in sulfate ion concentration when alum or ferric salts are used, an addition of calcium ions accompanied with pH values as high as 11 when lime is employed, and a disappearance of higher forms of microorganisms in the mixed liquor during alum dosing in the aeration tank (23,27,28). Furthermore, chemical precipitation does not remove any forms of nitrogen from wastewater. Sorption on high surface area activated alumina has also been found to be effective in removing phosphorus. Yee (29,30) pioneered this work testing the removal of phosphorus from a low-level radioactive waste and a synthetic waste by means of a small activated alumina column. He reported that the column could reduce the orthophosphate concentration by more then 99 percent without altering the chemical composition of the treated water, and that the exhausted alumina could be regenerated for reuse with sodium hydroxide and nitric acid. Subsequent studies by Neufeld and Thodos (31) using a synthetic waste, and by Ames and Dean (32,33) and Yue and Purushothaman (34,35) using both synthetic wastes and treatment plant effluents have generally confirmed Yee's findings; however, the latter investigators found that the exhausted alumina could be satisfactorily regenerated with a sodium hydroxide solution alone (32,35), and that the chemical composition of the treated water was changed (34,35). These studies were conducted using small bench-scale column beds whose volume ranged from 2 (Yee) to 1,000 ml (Ames and Dean). There is a need, therefore, to extend this work by obtaining experimental data from the operation of larger pilot plant beds which can be expected to more closely reflect actual operational conditions. This has been recognized by Ames (32) who has recommended that "... this promising phosphorus removal process be scaled up to a portable pilot plant size."

Attention has been recently focused on the removal of nitrogen from wastewater, and a 3-stage biological nitrification-denitrification system has been found capable of providing dependable and consistent performance but at high capital and operational costs (36-39). In this process, following the oxidation of carbonaceous matter, ammonia nitrogen is converted to nitrate nitrogen and then, in the presence of a supplementary carbon source, nitrates are reduced to nitrogen gas which is released to the atmosphere. Air stripping has also been found effective in removing ammonia from a high pH wastewater stream, which can be obtained by combining this process with lime precipitation for phosphorus control (40-42). However, this scheme has encountered some operational difficulties, such as scaling produced within the air stripping tower from atmospheric carbon dioxide and excessive calcium ions in the water, and freezing which occurs when the wet-bulb temperature within the tower drops to the freezing point. In addition, the efficiency of this process is greatly affected by the pH and temperature of the wastewater; and ammonia is readily soluble in water and when it is liberated to the atmosphere it will be absorbed and returned quickly to the water environment. Ion exchange, using either a clinoptilolite bed or a synthetic anion resin bed, has also been investigated as a means for removing nitrogen compounds from wastewater (15,39,43-46). One disadvantage of this process is the required pretreatment of secondary effluent and the complexity and high cost of operation (15,44). Furthermore, the organic material in the wastewater tends to foul the resins by selective adsorption on the resin particles, while the high volumes of regenerant wastes make the feasibility of the process questionable (39,44). The use of activated alumina to reduce the nitrogen content of treated wastewater has not been reported in the literature; however, on the basis of sorptive characteristics presented by Ames (32), it is believed that activated alumina in the absence of ions such as oxalate, fluoride, and sulfite might be capable of effectively sorbing some forms of nitrogen, primarily nitrate and nitrite. Consequently, this method warrants investigation as a tertiary treatment step.

The requirement by some regulatory agencies of an effluent phosphorus concentration as low as 0.1 mg P/l, coupled with increasing concern over the removal of nitrogen, makes sorption on activated alumina particularly promising as a nutrient control method. Previous studies have been conducted in the laboratory and have employed small, bench-scale alumina columns. Column operation offers the advantage of ease of regeneration and backwashing of the bed; however, difficulties have been encountered (34,35) with smaller grain size aluminas which in a given contact period were found to possess a higher sorptive capacity and faster sorptive rate than the coarser materials. Rapid mix followed by sedimentation might be a means of overcoming these difficulties; this approach should reduce chemical costs because it will enable use of the more effective finer-grained aluminas, but would at the same time complicate the regeneration of the used alumina, thereby increasing operational costs. No work has been conducted with a rapid mix-sedimentation system, other than limited jar-type studies.

The purpose of this research project was therefore to evaluate the removal of plant nutrients, primarily phosphorus and nitrogen, with activated alumina using a continuous-flow pilot plant system.

The specific objectives of the study were: (a) to develop and construct appropriate bench and field-scale pilot plant units utilizing the rapid mix-sedimentation and column operational modes; (b) to evaluate the efficiency of nutrient removal from wastewater treatment plant effluent; and (c) to investigate the regeneration characteristics of the exhausted aluminas.

The work was conducted in 2 phases: laboratory studies, undertaken primarily to develop design and operational criteria for the pilot plant units and to establish the regeneration characteristics of the exhausted aluminas; and field investigations, employed to evaluate the efficiency of nutrient removal by fresh and regenerated aluminas under actual plant conditions, and to project an approximate chemical costs of the rapid mix-sedimentation and column systems. Three types of alumina, F-1 (-325),[*] F-1 (-100) and F-1 (28-48), were evaluated. Secondary effluent from the Rolla Southwest Sewage Treatment Plant was used in the laboratory and field studies. Major parameters employed included phosphorus (Poly+ortho[*]), nitrogen (NH_3 Org, NO_3, and NO_2), COD, TSS, turbidity, and pH. The exhausted aluminas were treated with a 1M sodium hydroxide solution, followed by a water wash.

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[*] The aluminas were products of the Aluminum Company of America, Pittsburgh, PA; the number in parenthesis indicates mesh size.

[**] For standard abbreviations used in this dissertation see Appendix B.

II. REVIEW OF LITERATURE

The purpose of this literature review is to present information pertinent to the removal from treated wastewater of phosphorus and nitrogen by sorption and ion exchange. Sorption on activated alumina has been found effective in removing phosphates from sewage treatment plant effluent, while ion exchange using clinoptilolite and other strong-base anion resins has been reported capable of removing ammonia and possibly phosphates and nitrates.

A. REMOVAL OF PHOSPHORUS BY SORPTION

Yee (29,30) in 1965 reported the findings of bench scale and pilot plant studies undertaken to investigate the reduction of phosphorus by sorption on activated alumina. In the bench scale tests, he evaluated the sorptive capacity of 3, 80-200 mesh activated aluminas:* ALCOA F-1 and ALCOA F-20 (a chromatographic grade), both with a surface area of 250 sq m/g, and ALCOA H-51, with an area of 400 sq m/g. He employed 2-ml columns, packed with either "as received" or nitric acid-treated aluminas, which were operated in the downflow mode at linear flow rates of 1 and 5 cm/min; the corresponding hydraulic loadings were 0.25 and 1.25 gpm/sq ft (10.2 and 50.9 l/min/sq m) and the liquid detention times were 10 and 2 min. The columns were fed tap water containing either sodium orthophosphate, tetra-sodium pyrophosphate, penta-sodium pyrophosphate, or hexametaphosphate at concentrations of 1.6 and 8.2 mg P/l; the pH of the feed solutions ranged from 7.3 to 7.8. Yee presented breakthrough curves for the F-1 alumina which would indicate that this column had the lowest sorptive capacity for orthophosphate; and reported that the acid-treated F-1 alumina column

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*Products of the Aluminum Company of America, Pittsburgh, PA.

could produce 3,000 and 1,000 cv* of effluent with more than 99 percent reduction in orthophosphate when fed water containing initial concentrations of 1.6 and 8.2 mg P/l. He also stated that the alumina column would become ineffective if the phosphate solutions were prepared with demineralized or distilled water.

In the pilot plant study, Yee employed low level radioactive process wastewater from the Oak Ridge National Laboratory which contained mixed phosphates ranging from 0.3 to 1.0 mg P/l and suspended matter whose concentration was not given. The presence of SS made it necessary to perform the tests in the upflow mode, and 3, 200-ml columns, each containing 1 of the aluminas, were operated at a linear flow rate of 22 cm/min [a loading rate of 5.5 gpm/sq ft (224 l/min/sq m) and a detention time of 2 min]. Breakthrough curves, presented for the F-1 and H-51 aluminas, would indicate that a maximum phosphate removal of only 80 percent was obtained at the beginning of the runs with wastewater containing 0.3 mg P/l. Complete breakthrough occurred at about 33,000 cv for the F-1 alumina, while at the same time only 75 percent breakthrough was observed for the H-51 alumina; phosphate sorption then resumed with increasing efficiency and continued until 40,000 cv, the end of the run, when it had reached a value of 63 percent for the F-1 and 50 percent for the H-51 columns. No data were presented for the F-20 alumina, but Yee reported that it had about the same capacity as the F-1 type. The exhausted aluminas were regenerated with 2 cycles of 1M sodium hydroxide to remove more than 95 percent of the sorbed phosphates, and 1 cycle of 1M nitric acid to convert the

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*Column or bed volumes.

alumina to the acid form for reuse; 1 additional cycle of the hydroxide solution was required for the F-20 alumina. Losses during regeneration ranged from 5 percent for the F-20 to 8 percent for the F-1 to 35 percent for the H-51 aluminas. Considering the performance, regeneration characteristics, and economics of the 3 aluminas, Yee concluded that the F-1 bed, with an estimated 8 percent loss at each regeneration cycle, represented an optimum material for use. According to Yee the aluminas, at the pH range tested, did not change the chemical composition of the treated water.

Neufeld and Thodos (31) conducted column studies using 28-48 mesh ALCOA F-1 alumina in order to determine the removal of phosphorus from distilled water with added orthophosphate. They employed a short column bed (4.5 cm diam, 1.97 cm high) and a long column bed (4.2 cm diam, 26 cm high) and operated both in the upflow mode. The alumina was sequentially pretreated by washing with distilled water, contacting with 1M nitric acid, and drying overnight in an oven at 125° C; it was then weighed and packed between layers of glass wool in the borosilicate glass columns. Five runs were conducted using the short column bed with the flow rate ranging from 14.2 to 130 ml/min [0.22 to 2.01 gpm/sq ft (9.0 to 81.8 l/min/sq m) loading rate and 2.2 to 0.24 min liquid detention time] and the initial phosphorus concentration varying from 3.3 to 9.8 mg P/l; and 2 runs were made with the long column bed using flow rates of 30.5 and 58.1 ml/min [0.54 and 1.03 gpm/sq ft (22.0 and 41.9 l/min/sq m) rate; 11.8 and 6.1 min detention] and an initial phosphorus content of 39.2 mg P/l. The temperature was maintained at 71° F (21° C) throughout all runs. A breakthrough curve was presented for a short bed run; the column contained 31.3 g of alumina and was operated at 21.5 ml/min [0.33 gpm/sq ft (13.4 l/min/sq m)]. The bed processed 14.8 l of effluent with 100 percent removal of phosphate from an initial concentration of 3.3 mg P/l. Neufeld and Thodos, on the basis of their experimental data, developed a mathematical model to describe the mechanism of sorption and evaluate the sorptive capacity of the alumina.

Winkler and Thodos (47) employed a differential bed to establish the reaction kinetics associated with the removal of phosphates from aqueous solutions at concentrations ranging from 4.9 to 16.3 mg P/l using the ALCOA F-1 alumina. The differential bed consisted of a borosilicate cylindrical glass tube (4.7 cm diam) and was equipped with 2 stainless steel screens separated by a thin Teflon ring (4.1 cm diam). The volume between the 2 screens constituted the differential bed and could be varied by inserting the rings at different heights. Winkler and Thodos established the forward and reverse rates of reaction using a flow rate of 200 ml/min [2.94 gpm/sq ft (119.6 l/min/sq m)] and particle size of 50-60 mesh, which were selected on the basis of evaluation tests in order to eliminate the effects of film and particle diffusion. They found that the reaction kinetics of the removal of orthophosphates from aqueous solutions using activated alumina at equilibrium produced a relationship conforming to an adsorption isotherm of the Freundlich type; this obervation has also been made by other investigators (34,35). Winkler and Thodos concluded that the reaction rate depended on the concentration of the nitric acid solution used to activate the alumina; however, this finding is not in agreement with other information presented in the literature (32-35), and has been revised by Gangoli and Thodos

(48) on the basis of results obtained in an experimental study.

Gangoli and Thodos (48) conducted batch equilibration studies using 2 ALCOA aluminas, F-1 and AHB, and fly ash and phosphate solutions in distilled water. The large size (5-6 mesh) AHB alumina was contacted with phosphate solutions containing from 0.04 to 7.5 mg P/l in borosilicate erlenmeyer flasks kept in a constant temperature bath maintained at 70° F (21° C). The samples were allowed to reach equilibrium over a period of 30 to 35 days, occasionally being subjected to manual agitation. Both "as received" and acid-treated aluminas were evaluated; the latter was prepared by contacting a preweighed quantity of alumina with a nitric acid solution (0.25, 0.5, and 1.0N) for 24 hr, washing the alumina with distilled water, and drying it by rolling in cheesecloth. The equilibration studies with the small (270 mesh) F-1 alumina and fly ash consisted of contacting the fine particles with phosphate solutions at concentrations varying from 0.03 to 16.6 mg P/l in baffled florence flasks equipped with magnetic stirrers. Equilibration was reached within 2 hr contact time at room temperature (24° C). The effect of the pretreatment of the fly ash was also investigated; a preweighed sample of the ash was contacted with standard (0.25 and 0.5N) solutions of nitric acid and hydrochloric acid and sodium hydroxide (0.25N), and the ash was then separated from the solution by filtration. Acid-treated F-1 alumina was not evaluated by Gangoli and Thodos, however, these authors have referred to the results previously presented in Winkler and Thodos (31) for comparative purposes. They concluded that the sorptive capacity for phosphates was greatest when the 3 sorbents were used without any pretreatment, and that the AHB alumina possessed the lowest capacity for the removal of phosphate, while the F-1 alumina and fly ash seemed to have comparable capacities.

Ames and Dean (32,33) have investigated the sorption of phosphorus on activated alumina using a synthetic secondary sewage plant effluent and effluent from the Richland, WA, trickling filter plant. Several 76-ml columns (1.1 cm diam, 8.0 cm high) packed with different aluminas were used in a series of tests with synthetic secondary effluent containing 3.5 to 10.3 mg P/l to study the effects of the particle surface area and size, presence of calcium and magnesium ions, and phosphorus concentration on the sorptive capacity of these materials. The small columns were operated at a flow rate ranging from 30 to 35 cv/hr [0.98 to 1.18 gpm/sq ft (39.9 to 48.0 l/min/sq m) rate; 2 to 1.7 min detention], and no information was given on the type of flow employed. The exhausted beds were used for regeneration and subsequent phosphorus reloading studies. In order to verify the findings obtained from the small columns using the synthetic secondary effluent and to evaluate the effect of the elution method on the subsequent reloading of phosphorus, Ames and Dean fed Richland trickling filter plant effluent to a 1000-ml column (1.5 cm diam, 49 cm high) packed with 28-48 mesh alumina. The plant effluent, which contained an average of 10 mg P/l, was pumped through a 7.6-cm diam, 60-cm high granulated charcoal column before passing to the alumina column at flow rates of 15 to 5 cv/hr [3 and 1 gpm/sq ft (122.1 and 40.7 l/min/sq m) rate; 4 and 12 min detention]. Ames and Dean reported that from 95 to more than 99 percent of the phosphorus was removed from the synthetic secondary sewage effluent by the alumina beds, providing an effluent concentration of 0.03 mg P/l or less.

The same phosphorus removal results were obtained with up to 500 cv of Richland plant effluent. The exhausted alumina beds could be satisfactorily regenerated with 8 cv of 2M sodium hydroxide solution, and the spent regenerant solution could be restored by the addition of a small amount of lime to precipitate the phosphorus as hydroxyapatite and the carbonate as calcite, producing only a small amount of solid waste. Alumina losses of about 0.1 percent/elution cycle were reported. Their data have also indicated that the presence of 60 mg/l calcium ions and 25 mg/l magnesium ions in the influent waste increased the phosphorus capacity of the column, while sulfate ion concentrations up to 4,800 mg/l showed little effect.

Purushothaman and Yue (34,35) have conducted studies which were primarily concerned with the capacity and efficiency of activated alumina to sorb phosphorus, and with the regeneration of the used alumina. The studies were conducted in 2 phases: batch tests undertaken to determine the sorptive capacity of the alumina and the chemical characteristics of the treated water, and continuous flow column studies to evaluate the effect of flow rate and ionic concentration on the sorptive process and verify the quality of the treated water. The upflow, 174-ml columns (3.8 cm diam, 15.3 cm high) were packed with 160 g activated alumina and were operated at flow rates of 8, 16, and 33 ml/min [0.17, 0.34, and 0.71 gpm/sq ft (7.0, 14.0, and 28.9 l/min/sq m) rate; 21.8, 10.9, and 5.3 min detention]. Three types of ALCOA aluminas, F-1 (28-48 mesh), ALCOA F-1 (-100 mesh), and ALCOA XM (-325 mesh), were investigated in the batch tests, while column studies were performed with only the F-1 (28-48 mesh) material. Three types of water containing phosphorus were tested; deionized and tap water to which potassium dihydrogen phosphate had been added at concentrations varying from 10 to 30 mg P/l, and secondary effluent from a bench-scale activated sludge unit which was operated for this purpose in the laboratory. The exhausted alumina column was regenerated with 2M sodium hydroxide solution. Typical results obtained in the batch and column studies are shown in Figure 1. Purushothaman and Yue found that under a given contact period, the sorptive capacity for phosphorus of the XM (-325 mesh) alumina was the best, and was followed by the F-1 (-100 mesh) and F-1 (28-48 mesh) aluminas. When the XM (-325 mesh) and F-1 (-100 mesh) aluminas were employed in column tests, some operational difficulties, such as clogging of the columns or forming a stream line through the beds, were encountered; these greatly reduced the effective use of the bed. The F-1 (28-48 mesh) alumina column was found capable of processing before breakthrough 130 l (corresponding to 750 cv) of secondary effluent containing 9.4 mg P/l, while effecting 100 percent removal of phosphorus. The treated water in the batch studies showed a marked change in quality, as measured in terms of pH, total alkalinity, total and calcium hardness; the effluent in the column studies initially exhibited a slight change in quality, but gradually returned to the characteristics of the influent as breakthrough occurred. It should be mentioned that this finding was contrary to that presented by Yee (29,30) who reported that activated alumina did not alter the chemical composition of the treated water.

B. REMOVAL OF NITROGEN AND PHOSPHORUS BY ION EXCHANGE

Eliassen, et al. (43) conducted a laboratory study to determine the ability of Duolite A-102D,* a strong-base anion resin, to remove

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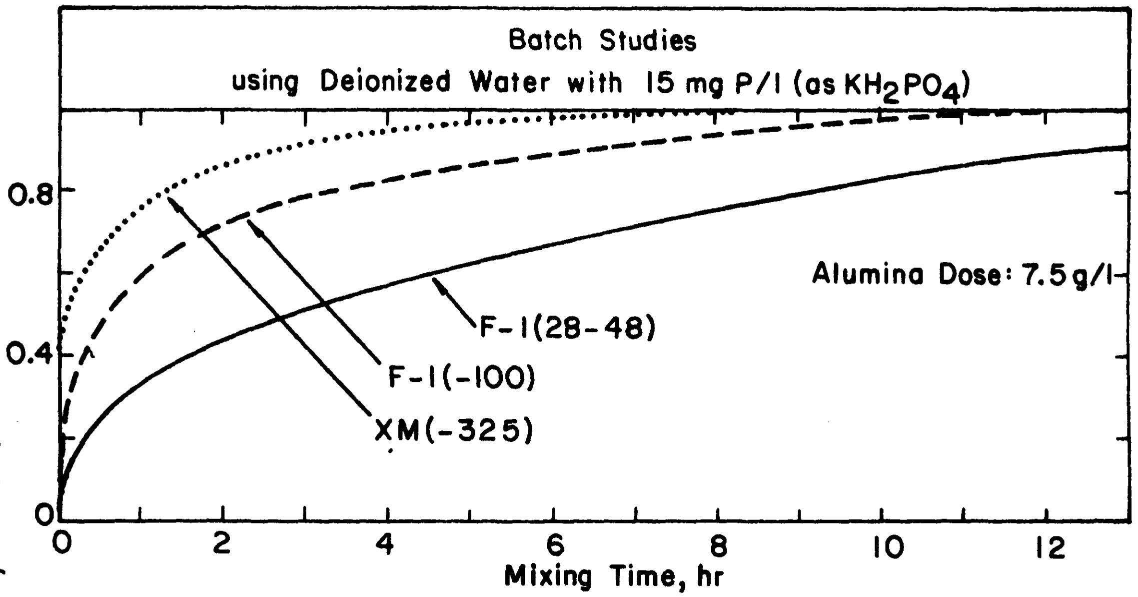
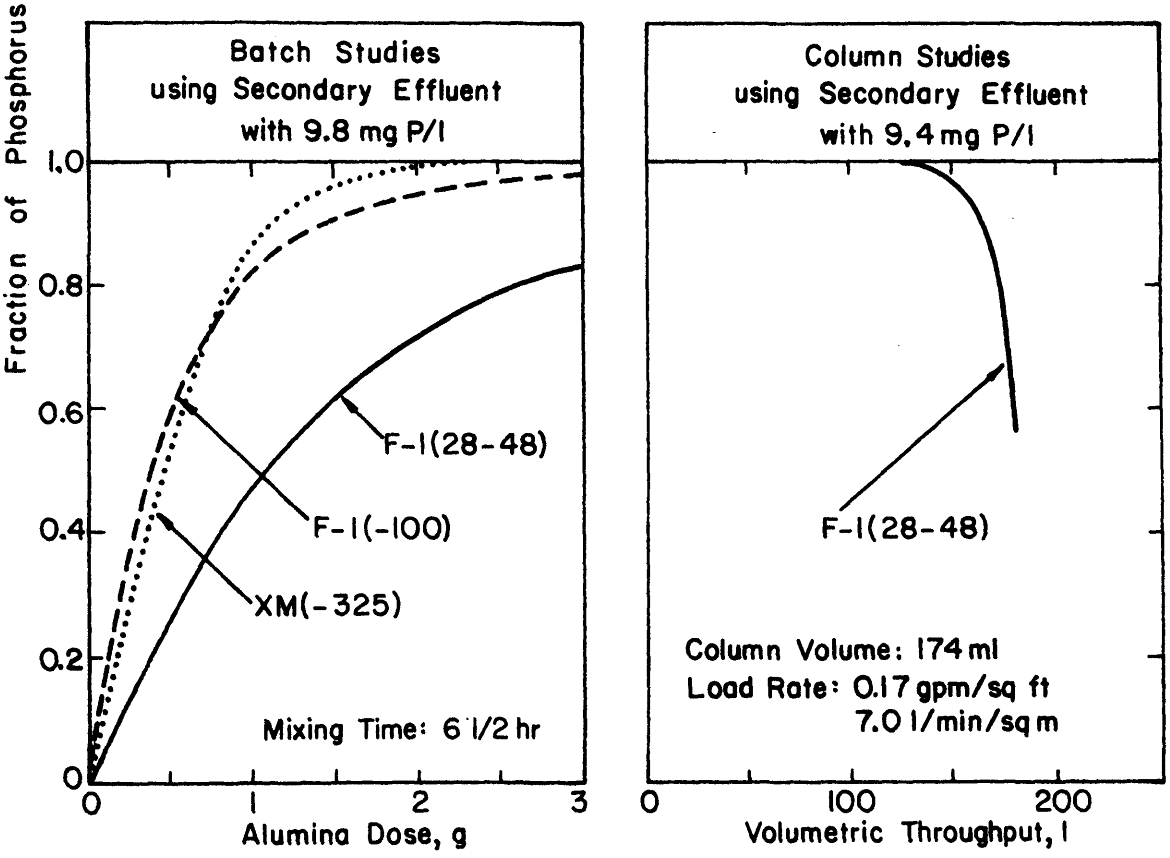
*A product of the Diamond Alkali Co., Western Division, Redwood City, CA.



a. Rate of Sorption of Phosphorus by Alumina



b. Sorptive Capacity of Alumina

c. Phosphorus Removal by Alumina

FIGURE 1. PHOSPHORUS REMOVAL BY ACTIVATED ALUMINA [After Yue (34)]

both phosphates and nitrates from secondary sewage treatment plant effluent. They employed batch and continuous flow tests using a 15-in. (38-cm) long glass column which was fed sand-pretreated effluent from the Palo Alto, CA, activated sludge treatment plant; the column diameter and the flow rate were not given. The batch system could produce 200 cv of treated effluent with a residual phosphate concentration of 0.2 mg P/l and nitrate concentration of 1.8 mg N/l from an influent containing 7.6 mg P/l and 18.4 mg N/l; the corresponding removals were 97 and 90 percent, respectively. Significant removal of organic matter, in terms of COD, ABS, and color, was also observed. Chlorides increased as the other anions were exchanged for them, but their concentration decreased during the run as the resin bed became exhausted. Regeneration was accomplished using 2 cv of 10 percent sodium chloride solution. In the continuous flow tests, each run was continued to the point of bed exhaustion, or to about 300 cv of throughput. The average phosphate and nitrate removals in the first 200 cv were approximately 95 and 84 percent, and were lower than those obtained with the batch system. The removal of COD was about the same as in the batch tests, but the color and ABS removals were not as great, indicating some resin fouling. The exhausted beds could be regenerated by recirculating 2 cv of a 10 percent sodium chloride solution for a period of 20 min. However, because of the fouling problem, Eliassen, _et_ _al_. investigated the restoration of the resin by other chemical and physical means. Chemical restoration consisted of passing through the bed either 4 cv of 1M sodium hydroxide at a flow rate of 3.4 cv/hr or 10 cv of equal parts of 1M hydrochloric acid and methanol at a flow rate of 4.4 cv/hr. The sodium hydroxide treatment was effective in removing silica, which was not removed by the chloride solution, while the acid-methanol treatment was effective in removing ABS, and both treatments were effective in restoring resin capacity. Physical restoration involved the addition of bentonite clay in the backwash; the clay scrubbed the resin particles and removed organic material that might have been present on the surface of the resin, thereby keeping the bed in good condition. These investigators recommended that the 2 chemical restoration treatments be used in an alternating manner, and that bentonite treatment be occasionally employed.

The feasibility of using ion exchange to remove nitrates and phosphates from water and wastewater has also been investigated by Midkiff and Weber (45) who undertook laboratory studies to determine the operating characteristics, selectivity, hydraulic loading, and required depth of the resin bed. The experiments were conducted in a 1-in. (2.54-cm) diam, 4-ft (1.2-m) long plexiglas column with the resin depth ranging from 3 in. to 3 ft (7.6 cm to 0.9 m). The resin selected for use was Dowex 21K, type 1,* a strong-base, 20-50 mesh resin which could be regenerated with sodium chloride in the presence of organic fouling substances. The synthetic feed solution consisted of distilled water containing 0.003M bicarbonates, 0.001M sulfates, 0.00025M phosphates, and 0.0005M nitrates, and was pumped downward through the column. For scale-up demonstrations, an additional column of 3 in. (7.6 cm) diam was operated in parallel with the 1-in. (2.54-cm) column. No significant difference in performance

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*A product of the Nalco Chemical Company, Chicago, IL.

was found between the 2 columns, although the surface area of the larger column was 9 times greater, and the authors concluded that information obtained relative to the operating characteristics of the 1-in. (2.54-cm) column could be directly extrapolateable to resin beds of greater surface areas.

Frontal analysis of typical breakthrough profiles revealed that chloride and bicarbonate had selectivities of similar magnitude, as both appeared in the effluent immediately; chloride, being on the resin in high concentration, was initially the ion displaced in the greatest quantity, and bicarbonate was forced ahead of the remaining 3 ions because of its low selectivity. The sulfate ion was the last to break through which would indicate that the column was most selective for this ion. Nitrate and phosphate broke through at the same time (at 240 cv) and at the same rate, however, the phosphate curve indicated greater magnitude of reverse exchange and thereby greater selectivity. Midkiff and Weber (45) concluded that the order of preference of the strong-base resin for ions in the solution tested was

$$SO_4^{=} > HPO_4^{=} > NO_3^{-} > HCO_3^{-}$$

and pointed out that the selectivity was not constant, but was dependent to some extent on the ion concentration in solution. No information was given on the operating conditions employed in this study. To evaluate the effect of hydraulic loading, 5 column runs were conducted under indentical conditions, except the loading rate which ranged from 6.5 to 59 gpm/sq ft (265 to 2,401 l/min/sq m); the colomn depth was not given. No significant difference in the breakthrough curves could be attributed to the change in flow rate;

nitrate and phosphate broke through at a throughput of 200 cv and sulfate at 400 cv. However, the authors pointed out that the strong-base anion exchange resin used had a very rapid rate of reaction, and suggested that sorption processes in which the rate of reaction is significantly slower will no doubt be considerably affected by changing the flow velocity in columnar operation. The effect of bed depth was investigated using columns containing from 12.5 to 150 g of resin (the resulting column depth ranged from 7 to 34 cm) with all other operating conditions being constant. Incipient leakage occurred for each of the 3 ionic species (nitrates, phosphates, and sulfates; bicarbonates were not determined) in the 7-cm beds; no initial break-through of the sulfate or nitrate ions was noted for the 14-cm bed, but a slight leakage was observed for phosphate. Midkiff and Weber considered the depth of 14 cm to be the approximate length of the reaction zone and suggested that use of a longer column would permit a higher percentage of the bed to be utilized to complete exhaustion, with a resulting higher efficiency of resin utilization. They defined the length of the reaction zone as the region between 5 and 95 percent breakthrough, and proposed that it could be determined by multiplying the total bed depth by the ratio of the corresponding volumetric throughputs.

A natural zeolite, clinoptilolite, has recently received considerable attention as a selective ion exchange resin for the removal of ammonium ions from wastewater. Mercer, et al. (15,49) chose this material for study on the basis of its good ammonium ion selectivity in the presence of magnesium, calcium, and sodium ions, and its potential low cost. Laboratory experiments were conducted with 2-in. (5.1-cm) diam, 24-in. (61-cm) high column beds containing 20-50 mesh granular clinoptilolite. Effluent from the Richland, WA, trickling filter plant containing 10.9 mg N/l NH_3-N was pumped upflow through the bed at a flow rate of 16.6 cv/hr [4.1 gpm/sq ft (168.6 l/min/sq m) rate; 3.6 min detention]. Channelling was observed throughout the bed, resulting in some loss in efficiency. The bed produced only 120 cv of effluent with an average 90 percent removal of ammonia. Further studies were conducted with pretreated secondary effluent. Pretreatment involved lime clarification [with 200 to 300 mg/l as $Ca(OH)_2$], addition of polyelectrolyte (8 mg/l nonionic polyacrylamide), filtration through an anthracite-sand filter and a granular activated carbon column, and was employed in order to remove suspended and dissolved organic matter; the filtrate was neutralized to pH 6.5 before it was pumped through the zeolite bed. The columns were operated in a downflow mode at a flow rate of 20 cv/hr [5.0 gpm/sq ft (203 l/min/sq m) rate; 3 min detention], and no plugging problems due to the suspended matter in the feed were experienced. Ammonia breakthrough curves presented by Mercer, _et_ _al_. show that the clinoptilolite columns receiving preclarified effluent containing 10.4 mg N/l NH_3-N could produce 170 cv with more than 90 percent ammonia removal. The exhausted clinoptilolite beds were regenerated with either a lime slurry containing 4.5 g/l [$Ca(OH)_2$] or a 0.1N sodium chloride solution containing 4.5 g/l lime at an upflow rate of 30 cv/hr [7.5 gpm/sq ft (304.7 l/min/sq m)]. The presence of sodium ions increased the ammonia capacity of the bed by 24 percent and sharpened the ammonia elution curve. The spent regenerant could be recovered in the laboratory by means of a 3-in. (7.62-cm) diam, 10-ft (3.05-m) high air-stripping column packed with 0.5-in. (1.27-cm) saddles. The regenerant was introduced at the top of the stripping column at 25 ml/min, while air was introduced at the bottom at 120 l/min, giving an air/liquid ratio of 640 cu ft/gal (4.74 cu m/l); the temperature of the influent air and liquid was 25±2° C. The ammonia concentration was reduced to less than 1 mg N/l and the regenerant could be reused.

Pilot plant studies were conducted with 3, 750-gal (2,840-l) ion exchange columns, 39 in. (99 cm) diam, packed with 20-50 mesh clinoptilolite. Chemical pretreatment for the Richland secondary effluent consisted of: powdered activated carbon, 70 mg/l; lime, 56 mg/l; alum, 240 mg/l; and polyelectrolyte, 2.5 mg/l. The lime was added to maintain the pH near 7. The exhausted bed was regenerated with lime solution containing 0.1 eq/l of calcium chloride and sodium chloride and the spent regenerant was recovered using a 43-in. (109.2-cm) diam air-stripping tower, packed with approximately 7 ft (2.13 m) of 1.5-in. (3.81-cm) porcelain saddles. The pilot plant was operated either with 500 gal (1,893 l) clinoptilolite beds at a 70,000-gpd (265,000-l/day) rate using clarified secondary effluent or with 330 gal (1,250 l) clinoptilolite beds at a 100,000-gpd (378,500-l/day) rate using chemically unclarified, but filtered, effluent. The influent stream was pumped downflow through either 1 bed or 2 beds in series. When the 2, 500-gal (1,893-l) columns were operated in series, the 1st bed was used alone until ammonia breakthrough was detected at a throughput of 75,000 gal (290,000 l); at that time the 2nd bed was added. The ammonia removal averaged 97 percent for the 154,000 gal (582,000 l) processed, with the average effluent ammonia concentration being 0.53 mg N/l. The 2, 330-gal (1,250-l) beds in series could process 138,250 gal (532,000 l) of product water with an average ammonia concentration of 1.1 mg N/l and a corresponding removal of 93 percent. No data were given for the recovery of the spent regenerant.

McLaren and Farquhar (50) used laboratory columns to determine the effect of temperature, flow rate, and ammonium ion concentration on the capacity and effluent breakthrough characteristics of clinoptilolite. The study consisted of 9 runs conducted with 3 columns operated under constant flow conditions; 2 of these columns were linked in series, while the 3rd was operated singly. The columns were constructed from 2-in. (5.08-cm) diam plexiglas and were packed with 750 g of 20-50 mesh clinoptilolite; they were operated in the downflow mode at rates of 6.67 and 13.33 cv/hr [1.2 and 2.4 gpm/sq ft (48.8 and 97.6 l/min/sq m) rate; 9 and 4.5 min detention] and temperatures of 2 and 12° C. A synthetic feed solution containing ammonium ion concentrations of 14 and 70 mg N/l was used. The authors concluded that the initial ammonium ion concentration and the flow rate had a significant effect on the ammonia capacity of clinoptilolite, while column operation was not affected by low temperature.

The removal of nitrates from wastewater using the so-called DUCOL process has been recently reported by Evans (46). The process involved 2 columns operated in series; the 1st column was a bed of strong-acid resin and the 2nd was a bed of weak-base resin: cations and anions were removed in the 1st and 2nd bed, respectively, during a demineralization cycle. The exhausted columns could be then additionally used in a softening cycle during which loosely bound sodium ions on the acid resin were replaced by calcium and magnesium ions, and chloride ions on the weak-base resin were replaced by nitrate and sulfate; there was no net change in equivalents during this cycle. Regeneration could be accomplished with hydrochloric acid (acid resin) and lime (weak-base resin). Evans employed 45-mm diam beds containing either 1,000 ml of acid resin* or 900 ml of weak-base resin,** and tested Beersheba, Israel, tap water fortified with sodium nitrate to give a nitrate concentration of 15.8 mg N/l; the TDS concentration was 970 mg/l. He reported that in the demineralization cycle, the system processed 32.5 gal (123 l) product water containing 0.02 mg N/l NO_3-N and 118 mg/l TDS, and in the softening cycle it produced 13.2 gal (50 l) of water containing 0.16 mg N/l NO_3-N and 842 mg/l TDS.

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*Srafion C-10, a product of the Ayalon Co., Israel.

**Amberlite IR-45, a product of the Rohm and Haas Co., Philadelphia, PA.

III. EXPERIMENTAL DETERMINATIONS

The main analytical parameters employed in this research study were phosphorus (Poly+ortho-P) and nitrogen (NH_3-N, Org-N, NO_3-N,and NO_2-N); other parameters used were COD, TSS, turbidity, and pH. All determinations were made in accordance with the procedures recommended by Standard Methods for the Examination of Water and Wastewater (51).

A. PHOSPHORUS

Acid-hydrolyzable phosphorus (Poly+ortho-P) was primarily measured. Phosphorus occurs in wastewaters in the form of orthophosphates, condensed (pyro-, meta-, and poly-) phosphates, and organically-bound phosphates; these may exist in solution, on particles of detritus, or in the bodies of aquatic organisms. Phosphorus determinations involve 2 procedural steps, conversion of the form of interest to soluble orthophosphate and colorimetric measurement of the orthophosphate; the type of phosphorus measured will depend on the conversion method used. Orthophosphate is measured directly on an untreated sample, while acid-hydrolyzable phosphorus and total phosphorus (Total-P) are determined in samples which have been subjected to mild acid hydrolysis and rigorous digestion, respectively. Acid hydrolysis converts the soluble and particulate condensed phosphates to dissolved orthophosphate, and digestion releases orthophosphate from both condensed phosphates, soluble and insoluble, and organically-bound phosphates. Three digestion technics are presented in Standard Methods (51, p.524), and in order of decreasing strength, these are digestion with perchloric acid, sulfuric-nitric acid, and persulfate; the required rigor of digestion will depend on the type of sample tested.

At the beginning of this investigation both Total-P and Poly+ortho-P were measured; however, preliminary data showed that in samples of the Rolla Southwest Sewage Treatment Plant effluent the concentration of Poly+ortho-P was consistently greater than that of Total-P (Table II). The reason for this is not known. It was thought initially that the amount of potassium persulfate used might have interfered with the development of the blue-colored sol in the samples; an excess residual persulfate was anticipated because of the low organic content of the plant effluent. Two tests were conducted with the persulfate dosage ranging from 0.5 to the 15 ml/sample suggested by Standard Methods (51) and the color development time was set at either 35 or 75 min; no significant difference was found in the phosphorus concentration (Table II). Another possibility might have been the presence of some saline particulates in the secondary effluent; according to Standard Methods (51, p.520), these particulates might precipitate some forms of phosphate during the digestion stage, especially when digestion drastically reduces the volume of sample. At any rate, little if any organically-bound phosphate was expected in the biologically-treated effluent.

The acid-hydrolyzable phosphate method (51, p.523) was therefore selected for this study because it was simpler and faster, required less chemicals, and was subject to less interference by suspended particulates. The method involved the formation, under acidic conditions, of an ammonium phosphomolybdate complex, the reduction of this complex with ascorbic acid to give a blue-colored sol, and the measurement of the color intensity on a spectrophotometer.

TABLE II. EVALUATION OF PHOSPHORUS DETERMINATION METHODS

a. Effect of Pretreatment Method

Sampling			Total Phosphorus			Filtrable Phosphorus		
Date	Time	Location	Sulfuric & Nitric Acid Digestion	Persulfate Digestion	Acid Hydrolysis	Sulfuric & Nitric Acid Digestion	Persulfate Digestion	Acid Hydrolysis
			Phosphorus, mg P/1					
1/23/72	2:30 PM	Rolla SW Sewage Treatment Plant Effluent	4.9	5.1	5.7	4.2	3.8	3.7
1/25/72	9:50 AM		3.2	3.8	4.3	2.6	3.0	2.9
	11:47 AM		3.8	4.0	5.0	3.7	2.5	3.5
1/26/72	9:00 AM		5.3	6.4	6.3	4.2	4.6	4.0
	12:05 PM		4.3	5.9	6.2	3.7	4.0	3.2
	2:20 PM		7.1	8.1	8.3	6.2	5.3	5.9

b. Effect of Potassium Persulfate Dose and Color Development Time

Sampling			Potassium Persulfate		Color Development Time, min	
Date	Time	Location	Strength g/1	Volume ml	35	75
					Phosphorus, mg P/1	
2/2/72	9:10 AM	Rolla SW Sewage Treatment Plant Effluent	50	0.5	2.8	2.9
				1.0	3.2	3.2
				2.0	2.5	2.5
				3.0	3.0	3.2
				4.0	2.8	3.1
				10.0	3.2	3.2
				15.0	3.2	3.2
	2:05 PM			0.5	5.7	5.6
				1.0	5.4	5.7
				2.0	4.6	4.8
				3.0	5.9	5.7
				4.0	5.9	5.7
				10.0	5.6	5.6
				15.0	5.2	5.3

One ml acid solution * was added to a 125-ml erlenmeyer flask containing 100 ml sample or aliquot diluted to 100 ml, as needed in order to obtain a spectrophotometric absorbance in the range of 0.1 to 0.7. The mixture was heated for 30 min in an autoclave under 15 psi (1.05 kg/sq cm) pressure; it was then cooled and restored to the original 100-ml volume with distilled water. Fifty ml pretreated sample were transferred to a nessler tube and 2.5 ml ethyl alcohol were added, followed by 2.5 ml combined reagent.** The mixture was mixed thoroughly and allowed to stand 10 min for color development; the color intensity was then measured on a spectrophotometer# at 880 mμ, verified to be the appropriate wavelength, and the Poly+ortho-P concentration was determined from a calibration curve.

B. NITROGEN

Four forms of nitrogen, NH_3-N, Org-N, NO_3-N and NO_2-N, were measured in this study.

1. Ammonia Nitrogen

Ammonia nitrogen (NH_3-N) was measured by means of the direct nesslerization method (51, p.226). Five procedures are given in Standard Methods (51) for the measurement of NH_3-N: the direct phenate and direct nesslerization methods, and distillation with either nessler finish, phenate finish, or titrimetric finish. The detectable range of NH_3-N concentration varies depending upon the method used; the

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*Prepared by diluting 300 ml sulfuric acid and 4.0 ml nitric acid to 1 l.

**Prepared by mixing 50 ml 5N sulfuric acid, 5 ml antimony potassium tartrate solution (2.194 g/100 ml), 15 ml ammonium molybdate solution (40 g/l), and 30 ml 0.1M ascorbic acid solution to produce 100 ml combined reagent; the reagent was stable for at least 1 wk if stored at 4° C.

#Spectronic 70, a product of Bausch & Lomb, Inc., Rochester, NY.

phenate method is suitable in the 0.01 to 0.5 mg N/l range, direct nesslerization is sensitive in the 0.2 to 5 mg N/l range, and distillation with titrimetric finish is useful for concentrations greater than 5 mg N/l but is equally applicable in lower ranges. According to Standard Methods (51, p.231), when synthetic samples containing various concentrations of chloride, NO_3-N, Org-N, phosphate, and silica were tested for NH_3-N, the lowest relative error was obtained by direct nesslerization. An evaluation of the various methods was undertaken and the results are shown in Table III; the phenate procedure was not included in this study because it is sensitive at concentrations which were not anticipated in the plant effluent. Test samples consisted of primary and secondary effluent, raw sewage, and a standard ammonium chloride solution. On the basis of these findings and the information presented in Standard Methods, the direct nesslerization procedure was selected for this research.

One hundred ml samples were first treated with 1 ml zinc sulfate solution (100 g/l) and 0.4 to 0.5 ml 6N sodium hydroxide were added to obtain a pH of 10.5; this pretreatment was used to precipitate calcium, iron, magnesium and sulfide, which would have formed turbidity when treated with the nessler reagent, and to remove suspended and colored matter (51, p.226). The treated sample was allowed to stand for approximately 10 min; a heavy flocculent precipitate settled, leaving a clear and colorless supernatant which was further clarified by centrifuging* at about 560G for 15 min. The clarified sample was

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*A Model CL clinical centrifuge was used; it was a product of the International Equipment Co., Needham Heights, MA.

TABLE III. EVALUATION OF AMMONIA NITROGEN DETERMINATION METHODS

Date	Type of Sample	Distillation with		Direct Nesslerization
		Titrimetric Finish	Nessler Finish	
		Nitrogen, mg N/l		
10/25/72	Secondary effluent	0	-	0.7
	NH_4Cl solution, 2.5 mg N/l	2.3	-	2.4
10/31/72	Secondary effluent	0	0.6	0.8
	NH_4Cl solution, 2.5 mg N/l	2.5	-	2.6
11/2/72	Secondary effluent	4.2	5.9	6.8
	Secondary effluent with 0.2 mg N/l added as NH_4Cl	4.5	6.8	7.2
11/4/72	Primary effluent	4.6	5.5	7.4
	NH_4Cl solution, 2.5 mg N/l	2.5	2.6	2.7
	Secondary effluent	-	-	0.9
	Secondary effluent with 1.0 mg N/l added as NH_4Cl	-	-	1.5
11/7/72	Raw sewage	10.1	11.5	7.8
	Primary effluent	8.8	11.0	9.3
	Secondary effluent	3.5	4.6	5.1
	NH_4Cl solution, 2.5 mg N/l	2.3	2.5	2.4

diluted, if necessary, with ammonia-free water* to obtain a spectrophotometric absorbance in the range of 0.1 to 0.7, and 50 ml sample or aliquot were placed in a nessler tube; 1 drop (0.05 ml) EDTA reagent** was added and mixed, and then 2.0 ml nessler reagent# were introduced for color development. The resulting color intensity was read on the spectrophotometer at 389 mμ, verified to be the appropriate wavelength, and the NH_3-N concentration was determined from a calibration curve.

2. Organic Nitrogen

Organic nitrogen (Org-N) was computed as the difference between the total kjeldahl nitrogen (Total kjeldahl-N) and NH_3-N (51, p.244). Total kjeldahl-N was determined (51, p.469) by converting organically-bound nitrogen to ammonium bisulfate using sulfuric acid and potassium sulfate as the oxidizing agents in the presence of a mercuric sulfate catalyst. The mercury ammonium complex is decomposed by sodium thiosulfate, and the ammonia is steam-distilled from an alkaline medium and absorbed in boric acid; its concentration is then determined colorimetrically or by titration with a standard mineral acid depending on the Org-N content of the sample. According to Standard Methods (51, p.244) the sensitivity of the colorimetric method makes it useful for the determination of nitrogen levels below 1 mg N/l, while the titrimetric method is suitable for the determination of nitrogen in a

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*Prepared by contacting distilled water with ANGC-101 specialty inorganic resin; the resin was a product of the J.T. Baker Chemical Co., Phillipsburg, NJ.

**Prepared by dissolving 50 g disodium ethylenediamine tetraacetate dihydrate in 60 ml water containing 10 g sodium hydroxide; the mixture was then diluted to 100 ml.

#Prepared by dissolving 100 g mercuric iodide and 70 g potassium iodide in a small quantity of water, and adding this mixture slowly, with stirring, to a cool solution of 160 g sodium hydroxide in 500 ml water; the mixture was then diluted to 1 l.

wide range of concentrations, depending on the volume of boric acid absorbent used and the concentration of the standard acid titrant. Since more than 1 mg N/l Total kjeldahl-N was expected in the secondary effluent, the titrimetric finish was used.

A mixture of 100 ml sample, 50 ml digestion reagent,* and a few glass beads was added into an 800-ml kjeldahl flask. The flask was placed in the digestion rack of a kjeldahl unit,** and the sample was digested until at least 30 min after clearing from the formation of sulfur trioxide fumes (the total digestion time was on the order of 3 hr). The flask and its contents were allowed to cool, and 300 ml ammonia-free distilled water, 0.5 ml phenolphthalein indicator solution, and 50 ml hydroxide-thiosulfate reagent# were added and mixed. The flask was then connected to the presteamed distillation rack of the kjeldahl unit and approximately 200 ml distillate were collected below the surface of 50 ml boric acid solution (20 g/l) containing a mixed indicator solution.## The NH_3-N concentration in the distillate was measured by titrating with standard 0.02N sulfuric acid.

3. Nitrate Nitrogen

Several tentative methods for the determination of nitrate nitrogen (NO_3-N) in wastewater are listed in the Standard Methods (51, p.454), and each method would eliminate certain interferences

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*Prepared by mixing a solution containing 134 g potassium sulfate and 200 ml concentrated sulfuric acid with a solution containing 2 g red mercuric oxide and 25 ml 6N sulfuric acid; the mixture was then diluted to 1 l.

**A 12-place digestion and distillation unit was used; it was a product of the Labconco Corporation, Kansas City, MO.

#Prepared by dissolving 500 g sodium hydroxide and 25 g sodium thiosulfate in 1 l ammonia-free water.

##Prepared by dissolving 200 mg methyl red and 100 mg methylene blue in 150 ml ethyl alcohol.

but would be subject to others. Thus the choice of method would depend on the sample being tested and the equipment available in the laboratory. The brucine method, which is subject to few interferences, works well in waters containing salinity, and does not require special equipment, was selected.

The sample was diluted with distilled water as needed to obtain a spectrophotometric absorbance in the range of 0.1 to 0.7; 10 ml diluted sample containing between 0.1 and 8 μg NO_3-N were transferred to a test tube, and the tube, in a rack, was placed in a cool water bath. Two ml sodium chloride solution (300 g/l) were added and mixed thoroughly; 10 ml sulfuric acid solution (400 ml/l) were then introduced and mixed, and the sample was allowed to cool. One-half ml brucine-sulfanilic acid reagent* was added and mixed thoroughly. The tube was transferred to a well-stirred boiling water bath that maintained a temperature of not less then 95° C and kept there for exactly 20 min in order to enable color development. The intensity of the resulting yellow color was read on the spectrophotometer at 412 mμ, verified to be the appropriate wavelength, and the NO_3-N concentration was determined from a calibration curve.

4. Nitrite Nitrogen

Nitrite nitrogen (NO_2-N) was determined (51, p.240) through the formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by the coupling of diazotized sulfanilic acid with naphthylamine hydrochloride. If the sample contained suspended matter, it was first clarified by centrifuging at 560G for 15 min. One ml EDTA solution (500 mg/ml)

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*Prepared by mixing 3 ml concentrated hydrochloric acid and 70 ml distilled water containing 1 g brucine sulfate and 0.1 g sulfanilic acid; the mixture was diluted to 100 ml.

and 1.0 ml sulfanilic acid reagent* were added to 50 ml clear sample or aliquot, which had been neutralized if necessary to pH 7, and mixed thoroughly. The reaction was allowed to proceed for 3 to 10 min and then 1.0 ml naphthylamine hydrochloride reagent** and 1.0 ml 2M sodium acetate buffer solution were introduced and mixed well; after 10 to 30 min the reddish purple color was measured on the spectrophotometer at 520 mμ, verified to be the appropriate wavelength, and the concentration of NO_2-N was determined from a calibration curve.

C. OTHER DETERMINATIONS

Other determinations included COD, TSS, turbidity, and pH and were employed to study the effect of activated alumina on the plant effluent.

1. Chemical Oxygen Demand

Chemical oxygen demand (COD) was used to investigate the possibility of the activated alumina removing organic matter. It was determined in accordance with Standard Methods (51, p.495), except that the concentrated sulfuric acid-silver sulfate reagent was added to the sample before the flask was placed on the reflux condenser. Twenty ml sample were added to a refluxing flask already containing 0.4 g mercuric sulfate and a few glass beads, and were followed by 10.0 ml 0.25N potassium dichromate solution and 30 ml sulfuric acid-silver sulfate reagent.# The mixture was refluxed for 2 hr, cooled, diluted

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*Prepared by dissolving 600 mg sulfanilic acid in 60 ml distilled water containing 20 ml concentrated hydrochloric acid; the mixture was then diluted to 100 ml.

**Prepared by dissolving 600 mg 1-naphthylamine hydrochloride in 70 ml distilled water containing 1.0 ml concentrated hydrochloric acid; the mixture was then diluted to 100 ml.

#Prepared by adding 22 g silver sulfate to a 9-lb (4.1-kg) bottle concentrated sulfuric acid.

to approximately 140 ml, and titrated with a 0.1N ferrous ammonium sulfate solution using ferroin as an indicator to determine the amount of dichromate remaining. A blank containing 20 ml distilled water was also run concurrently with each set of samples.

2. Total Suspended Matter

Total suspended matter (total suspended solids, TSS) was determined primarily in order to evaluate the loss of alumina in the rapid mix-sedimentation system. It was measured (51, p.537) by filtering an appropriate volume of sample through a predried and tared 0.45-μ membrane filter. The filter and retained solids were dried at 103° C in an oven* for 1 hr and the increase in weight was used to compute the TSS concentration.

3. Turbidity

Turbidity was measured in order to determine the effect of the activated alumina treatment on the processed effluent. It was determined (51, p.577) using a turbidimeter,** which was a nephelometer and photometrically measured the amount of light reflected at right angles to the incident light beam by the turbidity-causing particles. The instrument was calibrated in Jackson candle turbidity units and was standardized with a standard turbidity rod supplied by the manufacturer.

4. pH

The pH was determined using a pH meter.#

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*Thelco Model 28, a product of Precision Scientific, Chicago, IL.

**Model 1860 laboratory turbidimeter, a product of the Hach Chemical Company, Ames, IA.

#Fisher Accumet Model 210 pH meter, a product of Fisher Scientific, Pittsburgh, PA.

IV. MATERIALS

Materials used in this investigation included 3 activated aluminas and secondary wastewater treatment plant effluent.

A. ACTIVATED ALUMINA

Activated alumina is a porous form of aluminum oxide which has a high surface area, is resistant to shock and abrasion, and has the capacity to absorb liquids, vapors, and gases, without any change in its form or properties. Three sizes of ALCOA F-1 series activated alumina,* -325 mesh /F-1 (-325)/, -100 mesh /F-1 (-100)/, and 28-48 mesh /F-1 (28-48)/, were employed as sorbents in both the laboratory study and the field pilot plant evaluation. The following typical properties have been reported by the manufacturer (52) for these aluminas.

Property	Value/Description
Composition, %	
Al_2O_3	92.0
Na_2O	0.9
Fe_2O_3	0.08
SiO_2	0.09
Loss on ignition at 1,100° C (after reactivation), %	6.5
Form	Granular
Surface area, sq m/g	210
Bulk density, lb/cu ft (kg/cu m)	
Loose	52(832)
Packed	55(880)
Specific gravity	3.3
Static sorption at 60 % relative humidity, %	14-16
Crushing strength, %**	55

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*Products of the Aluminum Company of America, Pittsburgh, PA.

**Determined by pressing 60 g 0.25 to 0.125-in. (0.64 to 0.32-cm) alumina at 200 psi (14.06 kg/sq cm) and placing the crushed material on a 28 mesh screen; crushing strength reflects the percentage of material retained on the screen (53).

Because the aluminas could absorb moisture and the drying conditions in the laboratory were not the same with those used in the factory, the weight change after varying periods of drying was evaluated and the results are given in Table IV. Tests conducted included: the drying of duplicate 5-g samples of "as received" alumina material in an oven* at 104° C or in a controlled temperature room** at 59° C; wetting 20 g of "as received" alumina with 20 ml distilled water and then drying in the oven at 104° C or mixing 200 g of alumina with 200 ml distilled water and drying in a controlled temperature room at 59° C; and drying 200 g of wet exhausted alumina (obtained from a field column) in the oven at 104° C. The data presented in Table IV enable the computation of the sorptive capacity of new and regenerated aluminas on an equivalent weight basis.

B. WASTEWATER TREATMENT PLANT EFFLUENT

Secondary effluent was obtained from the manhole at the discharge end of the Rolla Southwest Sewage Treatment Plant, a contact stabilization activated sludge plant, by means of a 0.75-hp (0.56-kw) centrifugal pump,# and was either directly supplied to the field units or carried to the laboratory in 5-gal (18.9-l) polyethylene carboys and stored at room temperature in 2, 30-gal (113.6-l) epoxy-coated steel drums. The drums served as a feed reservoir as well as a complete mixing tank so that a homogeneous effluent could be obtained to feed the laboratory system. Normally the contents of a drum were sufficient for a complete run, except for the small column tests

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*Thelco Model 28, a product of Precision Scientific, Chicago, IL.

**No. 751A-X, a product of Lab-Line Instruments Inc., Melrose Park, IL.

#No. 390,208, a product of Sears, Roebuck and Company, Kansas City, MO.

TABLE IV. WEIGHT CHANGE OF THE ACTIVATED ALUMINAS BY DRYING

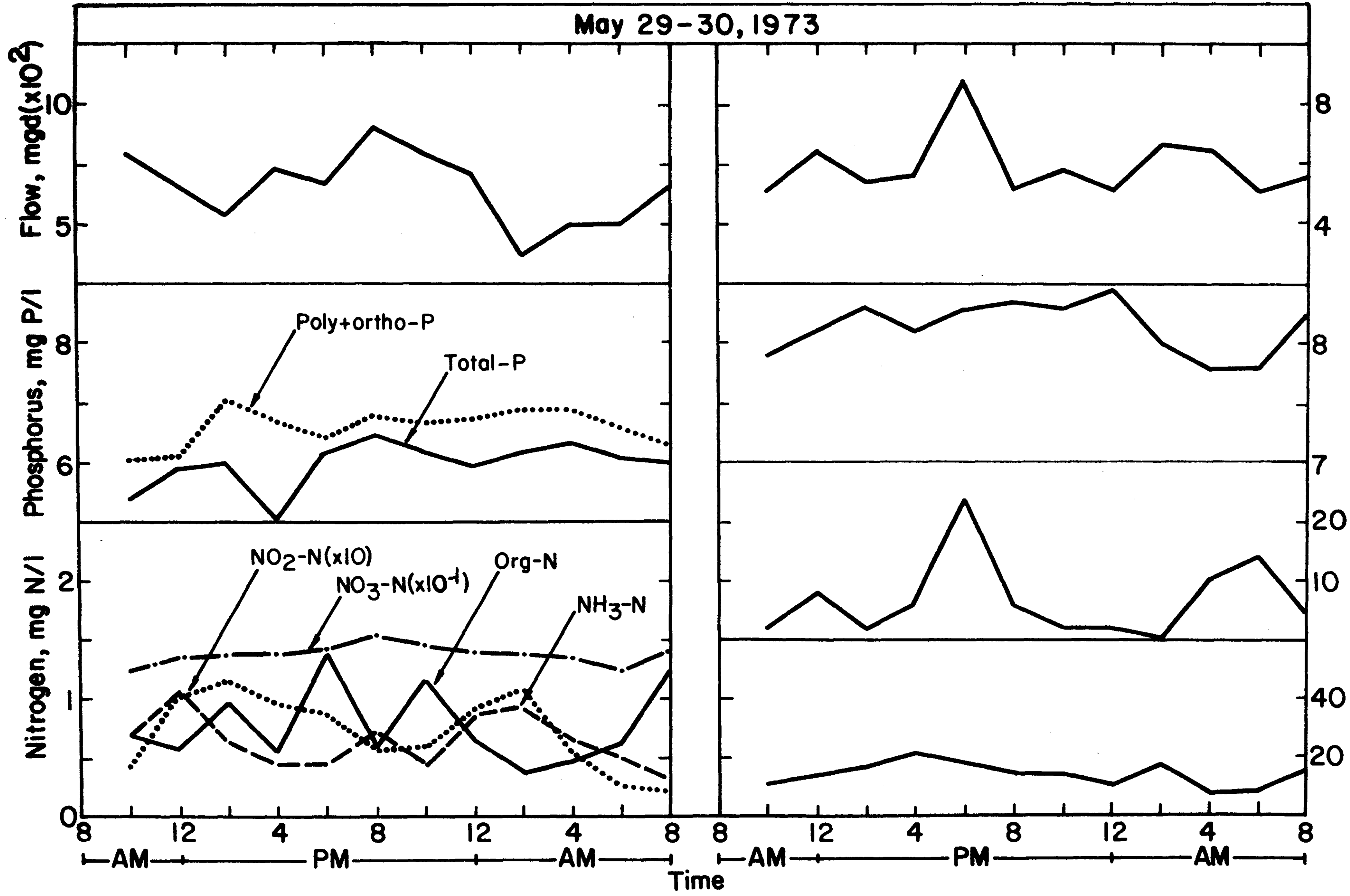
Drying Time*		Type of Alumina						
		As-received			Pre-wetted			Exhausted
		F-1(-325)	F-1(-100)	F-1(28-48)	F-1(-325)	F-1(-100)	F-1(28-48)	
hr	days	Weight Loss, %						
0.5		2.72	1.94	0.95				
1		2.58	2.05	0.96				
1.5		3.09	2.45	1.47				
2		3.03	2.32	1.20				
3		3.09	2.44	1.26				
4					-5.24	3.38	1.75	
5		2.57	1.89	0.82				
9		2.98	2.32	1.28				
16		2.57	2.00	0.87				
40		3.02	2.38	1.08				
47								23.58
	3				-4.77	3.73	2.03	
	7	0.98**	0.62**	0.41**	-17.75**	-0.65**		
	60				-5.11	4.57	1.37	24.03
	152							24.40

*Dried at 104° C in an oven, unless otherwise indicated.
**Dried at 59° C in a controlled temperature room.

which occasionally required slightly more than 30 gal (113.6 l). In order to minimize quality changes in the secondary effluent, tests began immediately after a sufficient quantity had been collected; this usually required about 1 hr.

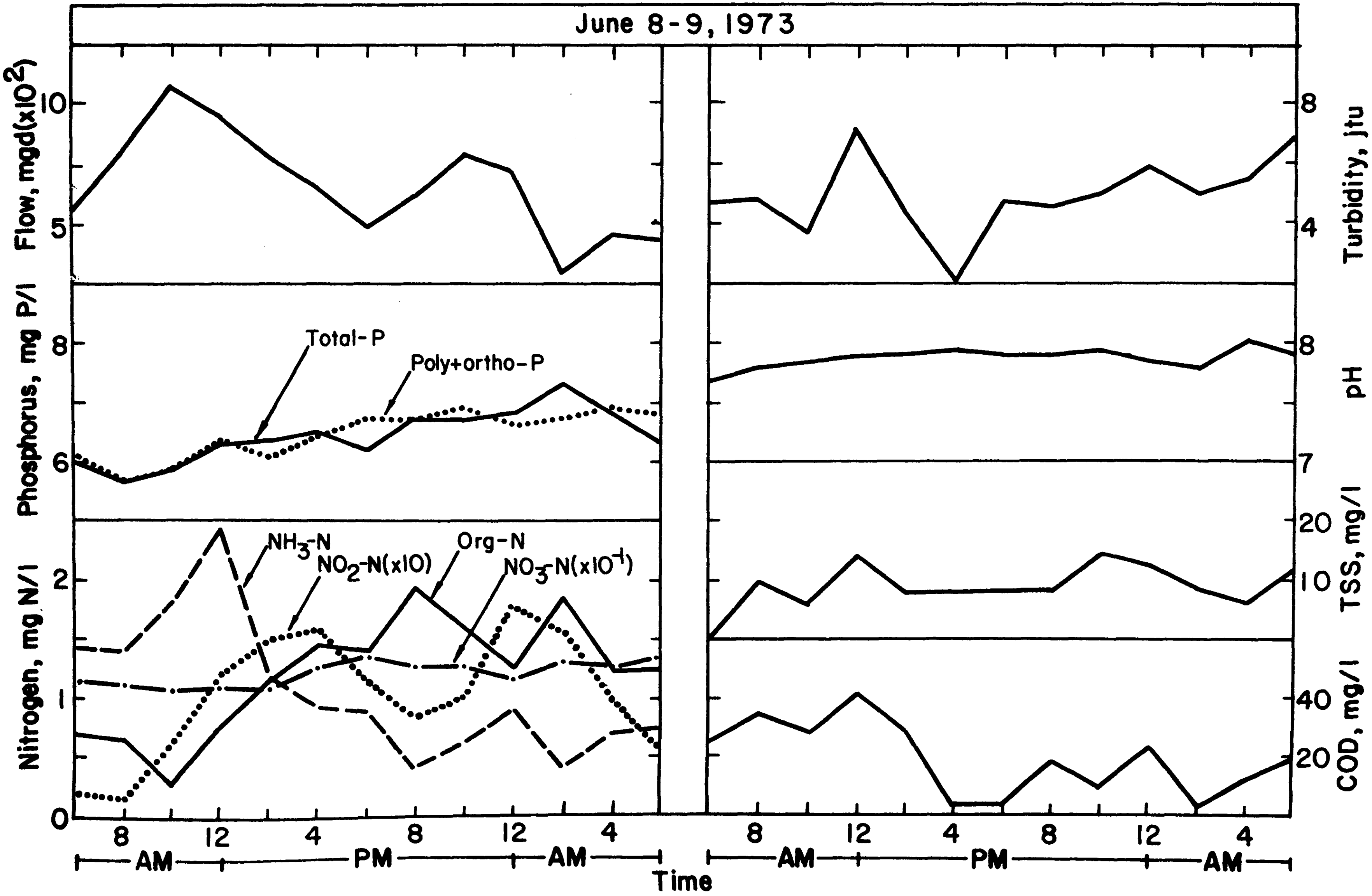
A diurnal record of the plant effluent characteristics was made on 3 different occasions in 1973: May 29-30, immediately following a long weekend; and June 8-9 and September 25-26, which were normal weekdays. Hourly samples were collected continuously for a period of 24 hr and composited every 2 hr; the composites were generally analyzed for Total-P, Poly+ortho-P, NH_3-N, Org-N, NO_3-N, NO_2-N, COD, TSS, turbidity, and pH; and the results are presented in Figure 2 together with the corresponding plant flow.

Because each laboratory run required from 6 to 24 hr to complete, background information on changes in the phosphorus and nitrogen content of the plant effluent was needed. A 3-l volume of effluent was placed in a 4-l pyrex glass bottle and exposed to the laboratory environment at approximately 25° C; a series of samples was withdrawn at different intervals from 0 to 24.5 hr and analyzed for NH_3-N, Org-N, NO_3-N, NO_2-N, and Total-P. The results of these analyses are reported in Figure 3.



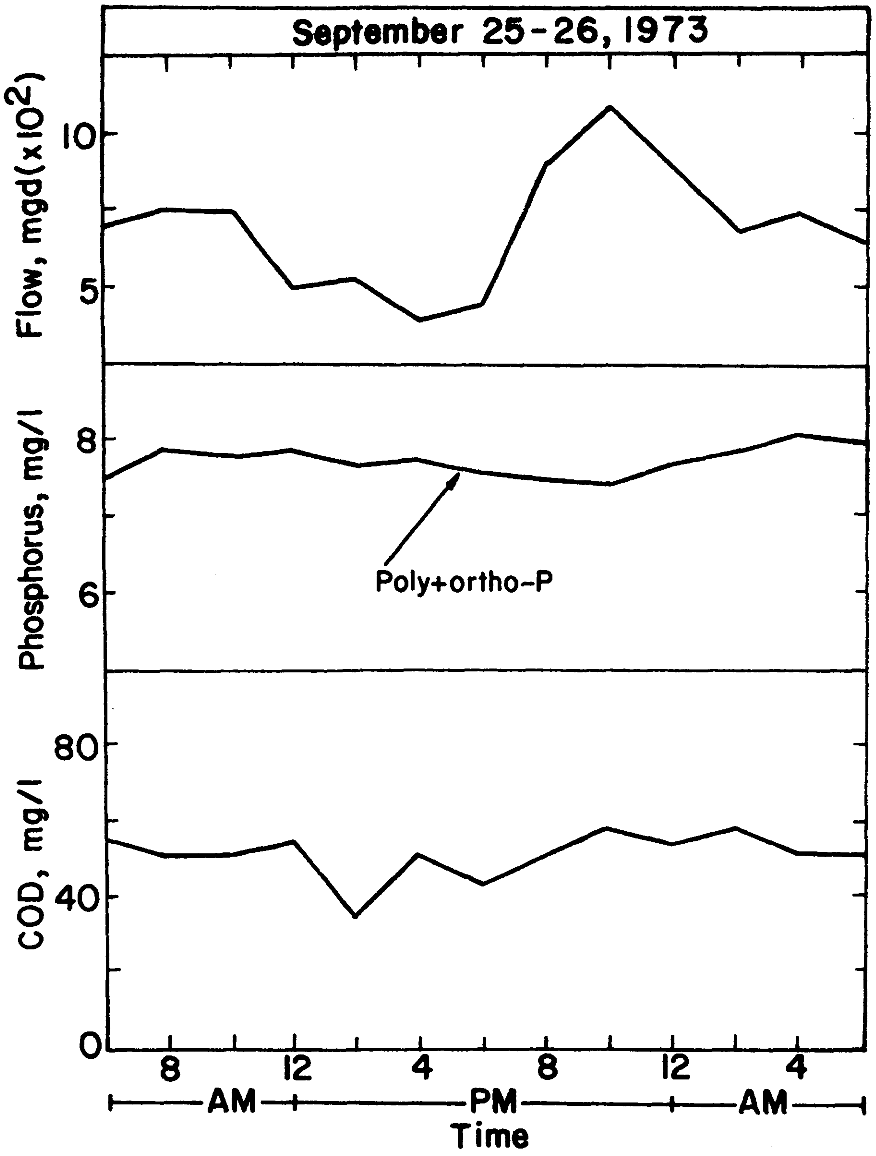
To convert mgd to cu m/day multiply by 3,785

FIGURE 2. CHARACTERISTICS OF THE SECONDARY WASTEWATER PLANT EFFLUENT



To convert mgd to cu m/day multiply by 3,785

FIGURE 2(cont.). CHARACTERISTICS OF THE SECONDARY WASTEWATER PLANT EFFLUENT



To convert mgd to cu m/day multiply by 3,785

FIGURE 2(cont.). CHARACTERISTICS OF THE SECONDARY WASTEWATER PLANT EFFLUENT

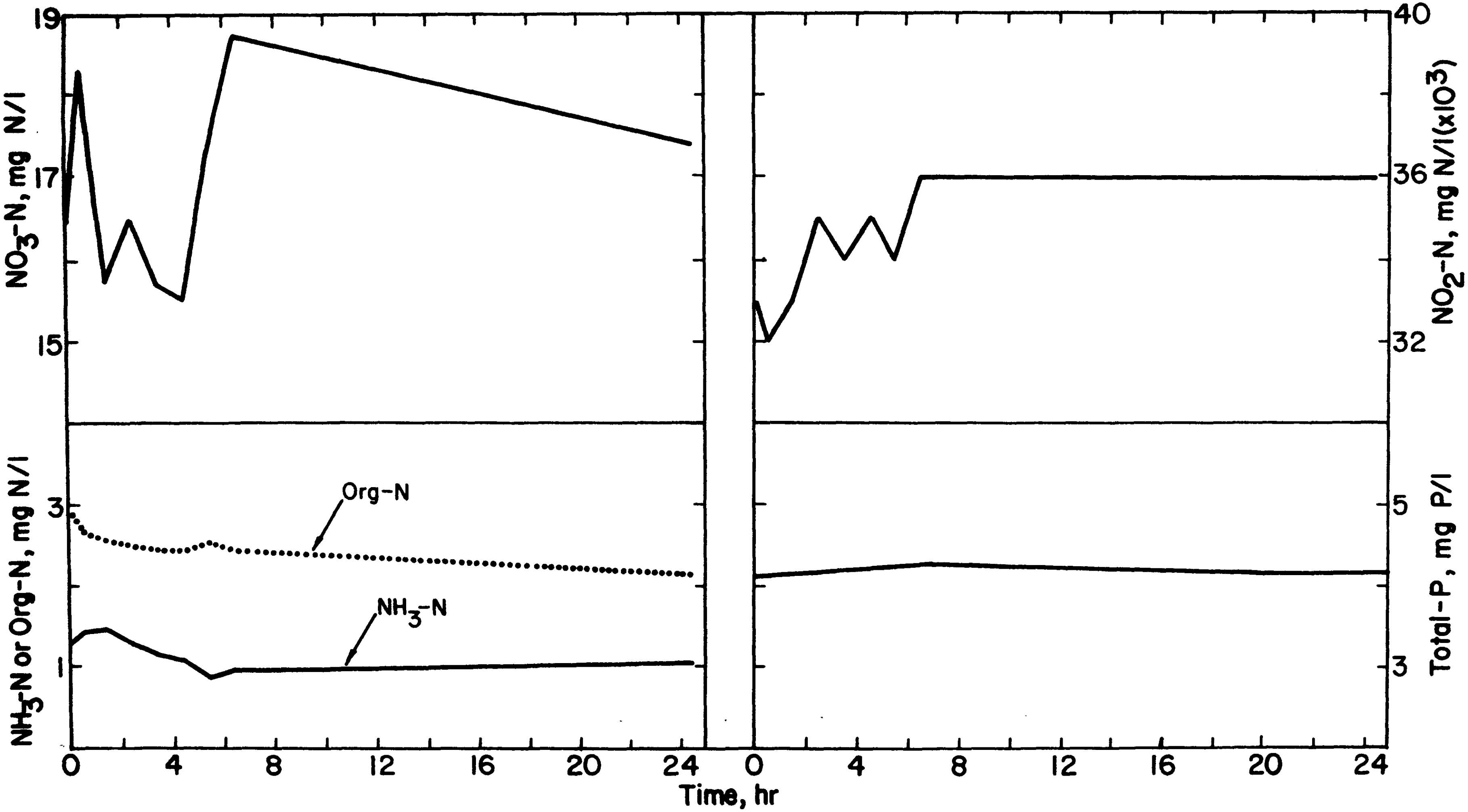


FIGURE 3. VARIATION IN THE NITROGEN AND PHOSPHORUS CONTENT OF STORED WASTEWATER PLANT EFFLUENT

V. DEVELOPMENT OF THE TEST SYSTEM

The development and construction of appropriate bench and field-scale pilot plant units utilizing the column and rapid mix-sedimentation operational modes, which was a necessary prerequisite to the study, required that appropriate design data be obtained on the sorptive and settling characteristics of the activated aluminas. The bench-scale system was first designed on the basis of data obtained from a batch study and its performance characteristics were evaluated before the design of the field system was completed.

A. DESIGN CRITERIA

Three characteristics of the activated aluminas were considered essential to the design of the rapid mix-sedimentation system: the sorptive rate, which governed the required detention time in the mixing unit; the sorptive capacity, which controlled the alumina dose; and the settling rate, which affected the design of the sedimentation unit. The sorptive rate also determined the bed depth of the column units, while the sorptive capacity governed the relative volume of wastewater effluent which could be processed before the bed was exhausted.

1. Sorptive Characteristics

A batch study was conducted to evaluate these characteristics. Nine g "as received" alumina was mixed* with 3 l of secondary effluent at 750 rpm in a 4-l pyrex glass bottle for periods up to 19 to 23.5 hr; 25-ml samples were withdrawn at appropriate intervals and analyzed for Total-P, and the corresponding data are shown in Figure 4. All 3

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*A variable speed cone-driven stirring motor equipped with a 1.75-in. (4.45-cm) diam polyethylene propeller was used; it was a product of the Sargent-Welch Scientific Co., Skokie, IL.

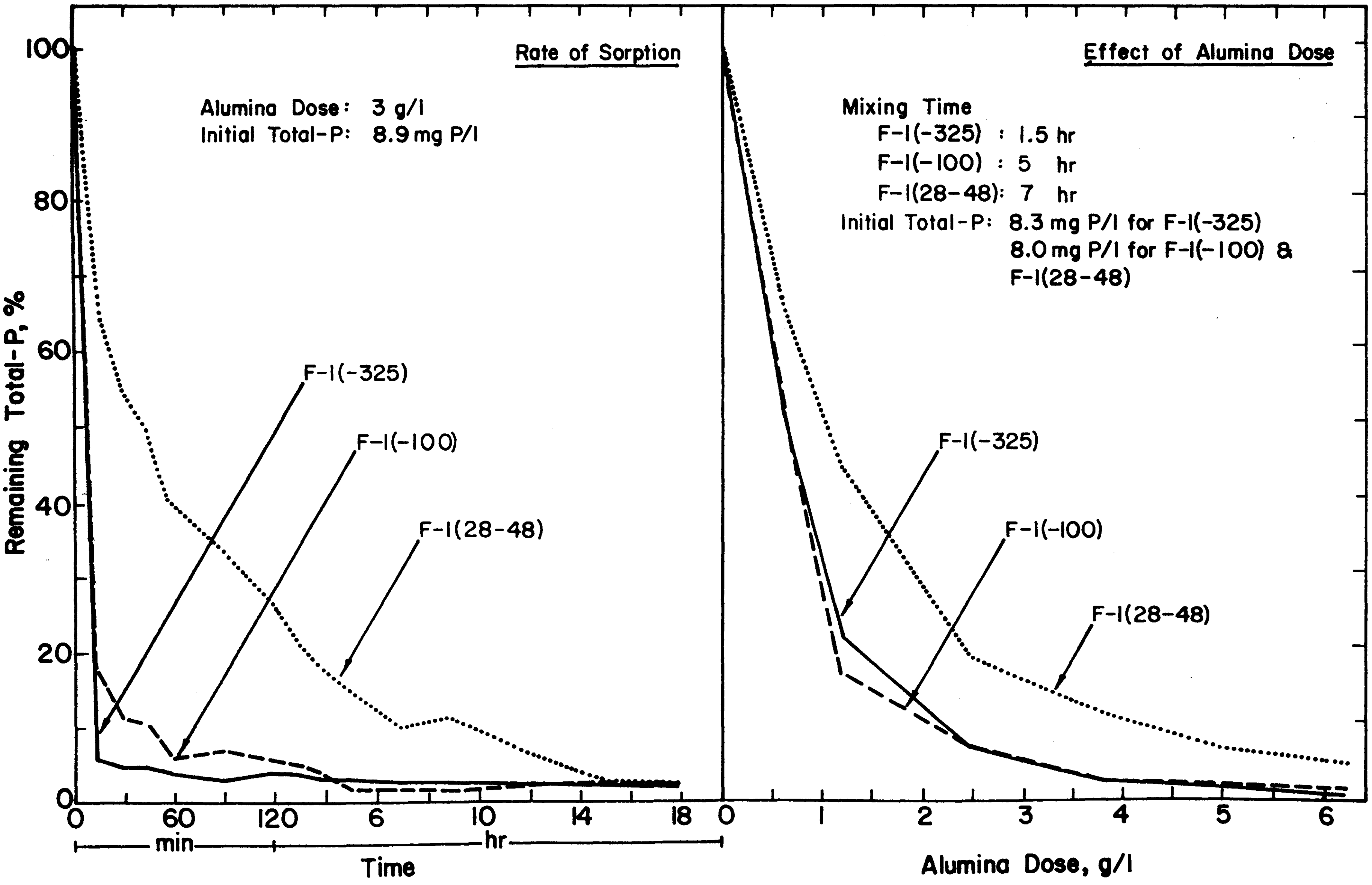

FIGURE 4. SORPTIVE CHARACTERISTICS OF THE ACTIVATED ALUMINAS - PHOSPHORUS DATA

aluminas could achieve a 98 percent removal of Total-P; however, the required mixing periods were different and varied from 1.5 hr for F-1 (-325) to 5 hr for F-1 (-100) to 15 hr for F-1 (28-48). A mixing time of 15 hr was considered to be too long for practical application and was reduced to 7 hr in subsequent laboratory studies; at the end of this period the F-1 (28-48) alumina removed (Figure 4) slightly in excess of 90 percent Total-P.

Sorptive capacity was determined using a 6-unit variable speed stirrer* operated at 100 rpm; 800-ml volumes of secondary effluent were placed in 1-l beakers and treated with varying doses of alumina ranging from 0.5 to 5 g for periods of 1.5, 5, and 7 hr for F-1 (-325), F-1 (-100), and F-1 (28-48), respectively. The mixture were then allowed to settle for 15 min and the supernatants were withdrawn and analyzed for Total-P; although some samples appeared to be turbid due to the presence of alumina particles, clarification was not attempted prior to analysis because this step was not expected in practical application. The effect of the alumina dose on phosphorus removal is reported in Figure 4 and Table V. It may be seen that given adequate contact time, the larger size alumina would have the same sorptive capacity for phosphorus as the smaller size material. This is exemplified best by the results in Table V which indicate that by allowing different contact times, the F-1 (-325) and F-1 (-100) aluminas produced comparable capacities; this was not true for the F-1 (28-48) alumina, however, the detention time had been decreased for this material.

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*Model 77-903, a product of Phipps & Bird, Inc., Richmond, VA.

TABLE V. SORPTIVE CHARACTERISTICS OF THE ACTIVATED ALUMINAS-PHOSPHORUS DATA

Alumina Dose g/l	F-1(-325)			F-1(-100)			F-1(28-48)		
	Mixing Time, hr								
	1.5			5			7		
	Total-P Removed*		Sorptive Capacity mg P/g	Total-P Removed**		Sorptive Capacity mg P/g	Total-P Removed**		Sorptive Capacity mg P/g
	mg P/l	%		mg P/l	%		mg P/l	%	
0.63	3.98	48	6.37	3.80	48	6.08	2.72	34	4.35
1.25	6.47	78	5.18	6.64	83	5.31	4.48	56	3.58
2.50	7.72	93	3.09	7.74	93	2.98	6.48	81	2.59
3.75	8.05	97	2.15	7.78	97	2.07	7.04	88	1.88
5.00	8.13	98	1.63	7.76	98	1.55	7.44	93	1.49
6.25	8.22	99	1.32	7.92	99	1.27	7.60	95	1.22

*Initial Total-P concentration in secondary effluent: 8.3 mg P/l.
**Initial Total-P concentration in secondary effluent: 8.0 mg P/l.

The effect of the activated alumina treatment on a broader range of secondary effluent characteristics was studied by mixing 15 g "as received" alumina with 3 l effluent in a 4-l bottle using the cone-driven stirrer at 750 rpm. At the end of the previously selected mixing times, a 15-min settling period was provided; the supernatant was siphoned off and analyzed for Total-P, NH_3-N, Org-N, NO_3-N and COD, and the results are given in Table VI. A significant reduction in the Org-N and COD concentrations generally accompanied the removal of Total-P, especially when the finer size aluminas were used; the reduction in NO_3-N was relatively low, while the removal of NH_3-N was inconsistent.

2. Settling Characteristics

The settling characteristics of the activated alumina particles in secondary wastewater effluent were determined by means of a 3-in. (7.62-cm) diam, 4.4-ft (1.34-m) high settling column. The column was made of a clear cast acrylic tubing* with 4 sampling ports at 12-in. (30.5-cm) intervals from the top; the ports were inserted into the column wall and extended to the center of the column in an effort to minimize the wall-effect on the settling particles. Ten-l volumes of secondary effluent containing varying alumina doses (19.5, 13.0, and 6.5 g), were first mixed for 22 min and were then introduced into the column. At predetermined time intervals, samples were withdrawn from the ports and analyzed for TSS and turbidity, and the data obtained are reported in Table A-1, Appendix A. Percent removal values for TSS are given in Table VII and TSS isoremoval curves are

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*A product of Cope Plastics Inc., Godfrey, IL.

TABLE VI. SORPTIVE CHARACTERISTICS OF THE ACTIVATED ALUMINAS

Test No.	Secondary Effluent		Dose g/l	Mixing Time hr	Total-P		NH_3-N		Org-N		NO_3-N		COD	
					Conc mg P/l	Remov %	Conc mg N/l	Remov %	Conc mg N/l	Remov %	Conc mg N/l	Remov %	Conc mg/l	Remov %
1	Initial				8.05		0.67		0.79					
	Treated by	F-1(-325)	5	1.5	0.03	99.6	0.78	-16.4	0.45	43.0				
		F-1(-100)		5	0.07	99.1	0.78	-16.4	0.68	13.9				
		F-1(28-48)		7	0.25	96.9	0.56	16.4	1.01	-27.8				
2	Initial				12.10		1.90		2.36					
	Treated by	F-1(-325)	5	1.5	0.15	98.8	2.35	-23.7	0.61	74.2				
		F-1(-100)		5	0.23	98.1	2.02	-6.2	1.12	52.5				
		F-1(28-48)		7	0.55	95.5	1.96	-3.2	1.62	31.4				
3	Initial				6.80		7.45		1.59		1.8			
	Treated by	F-1(-325)	5	1.5	0.05	99.3	7.00	6.0	0.49	69.2	1.5	16.7		
		F-1(-100)		5	0.14	97.9	6.94	6.8	1.00	37.1	1.7	5.6		
		F-1(28-48)		7	0.31	95.4	6.89	7.5	1.47	7.5	1.6	11.1		
4	Initial				3.00		5.60		1.68		2.0		29	
	Treated by	F-1(-325)	5	1.5	0.02	99.3	4.48	20.0	0.56	66.7	1.6	20.0	6	79.3
		F-1(-100)		5	0.06	98.0	4.76	15.0	1.12	33.3	1.8	10.0	18	37.9
		F-1(28-48)		7	0.13	95.7	4.20	25.0	1.12	33.3	1.8	10.0	23	20.7

*NH_3-N was measured by distillation with titrimetric finish.

TABLE VII. SETTLING CHARACTERISTICS OF THE ACTIVATED ALUMINAS*

Alumina		Settling Time min	Column Depth, ft							
			1		2		3		4	
Type	Dose g/l		Avg TSS mg/l	Removal %	Avg TSS mg/l	Removal %	Avg TSS mg/l	Removal %	Avg TSS mg/l	Removal %
F-1 (-325)	1.95	0	1808							
		10	770	57.4	710	60.7	716	60.4	692	61.7
		30	310	82.9	346	80.9	332	81.6	378	79.1
		60	158	91.3	256	85.8	210	88.4	220	87.8
		120	52	97.1	110	93.9	134	92.6	142	92.1
	1.30	0	1174							
		10	682	41.9	724	38.3	703	40.1	650	44.7
		30	301	74.4	345	70.6	347	70.4	366	68.8
		60	128	89.1	204	82.6	221	81.2	235	80.0
		120	60	94.9	121	89.7	155	86.8	159	86.5
	0.65	0	602							
		10	468	22.3	504	16.3	532	11.6	544	9.6
		30	234	61.1	288	52.2	302	49.8	330	45.2
		60	126	79.1	166	72.4	200	66.8	208	65.4
		120	46	92.4	88	85.4	112	81.4	152	74.8
F-1 (-100)	1.95	0	580							
		10	170	70.7	228	60.7	254	56.2	236	59.3
		30	106	81.7	120	79.3	130	77.6	144	75.2
		60	80	86.2	86	85.2	84	85.5	96	83.4
		120	62	89.3	64	89.0	68	88.3	76	86.9
	1.30	0	479							
		10	94	80.3	122	74.4	143	70.1	168	64.9
		30	40	91.6	56	88.3	65	86.4	78	83.7
		60	17	96.4	42	91.2	43	91.0	54	88.7
		120	11	97.6	11	97.6	19	96.0	32	93.3
	0.65	0	258							
		10	66	74.4	100	61.2	120	53.5	140	45.7
		30	38	85.3	50	80.6	54	97.1	62	76.0
		60	36	86.0	26	89.9	36	86.0	38	85.3
		120	22	91.0	24	90.7	28	89.1	22	91.5
F-1 (28-48)	1.95	0	18							
		10	18	0	17	5.6	22	-22.2	15	16.7
		30	17	5.5	12	33.3	18	0	15	16.7
		60	10	44.0	15	16.7	13	27.8	13	27.8
		120	9	50.0	9	50.0	13	27.8	12	33.3
	1.30	0	34							
		10	19	44.1	21	38.2	18	47.1	18	47.1
		30	12	64.7	12	64.7	12	64.7	12	64.7
		60	18	47.1	16	52.9	8	76.5	8	76.5
		120	7	79.4	5	82.3	6	82.4	10	70.6
	0.65	0	14							
		10	13	7.1	14	0	16	-14.3	18	-28.6
		30	15	-7.1	13	7.1	16	-14.3	14	0
		60	12	14.3	9	35.7	12	14.3	11	21.4
		120	6	57.1	9	35.7	10	28.6	11	21.4

***In secondary effluent.**

plotted in Figure 5.

An analysis of the sedimentation column data (54, p.289) indicated that at the end of 1 hr the 4.0-ft (1.22-m) column would have removed 85 and 94 percent TSS when 1.3 g/l of F-1 (-325) and F-1 (-100) aluminas were used, respectively; the corresponding settling velocity would have been 4.0 ft/hr (1.22 m/hr). Considering appropriate adjustment factors to relate column data to sedimentation basin performance (54, p.289), the following design values were selected.

Detention time	2 hr
Settling velocity	2.6 ft/hr (0.79 m/hr)
Overflow rate (surface loading)	460 gpd/sq ft (18.8 cu m/day/sq m)

B. BENCH TEST SYSTEM

The bench rapid mix-sedimentation test system developed in this study (Figure 6) consisted of 2 parallel test units each of which was composed of a mixing tank equipped with a propeller stirrer, a sedimentation tank, a chemical feeder, a pumping system with flow regulating device, and a secondary effluent feeding reservoir. One of the units was provided with a dry feeding system, while the other employed a wet feeding system. Each unit was designed for a test flow of 1 gph (3.78 l/hr) which was the maximum that could be reasonably handled in the laboratory.

The rapid mix and sedimentation tanks were made of 0.25-in. (0.64-cm) thick clear plexiglas sheets,* and the dimensions and construction details of each are shown in Figure 7. The 2 tanks were bolted together to form a single unit; a rubber gasket (not shown)

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*A product of Cope Plastics Inc., Godfrey, IL.

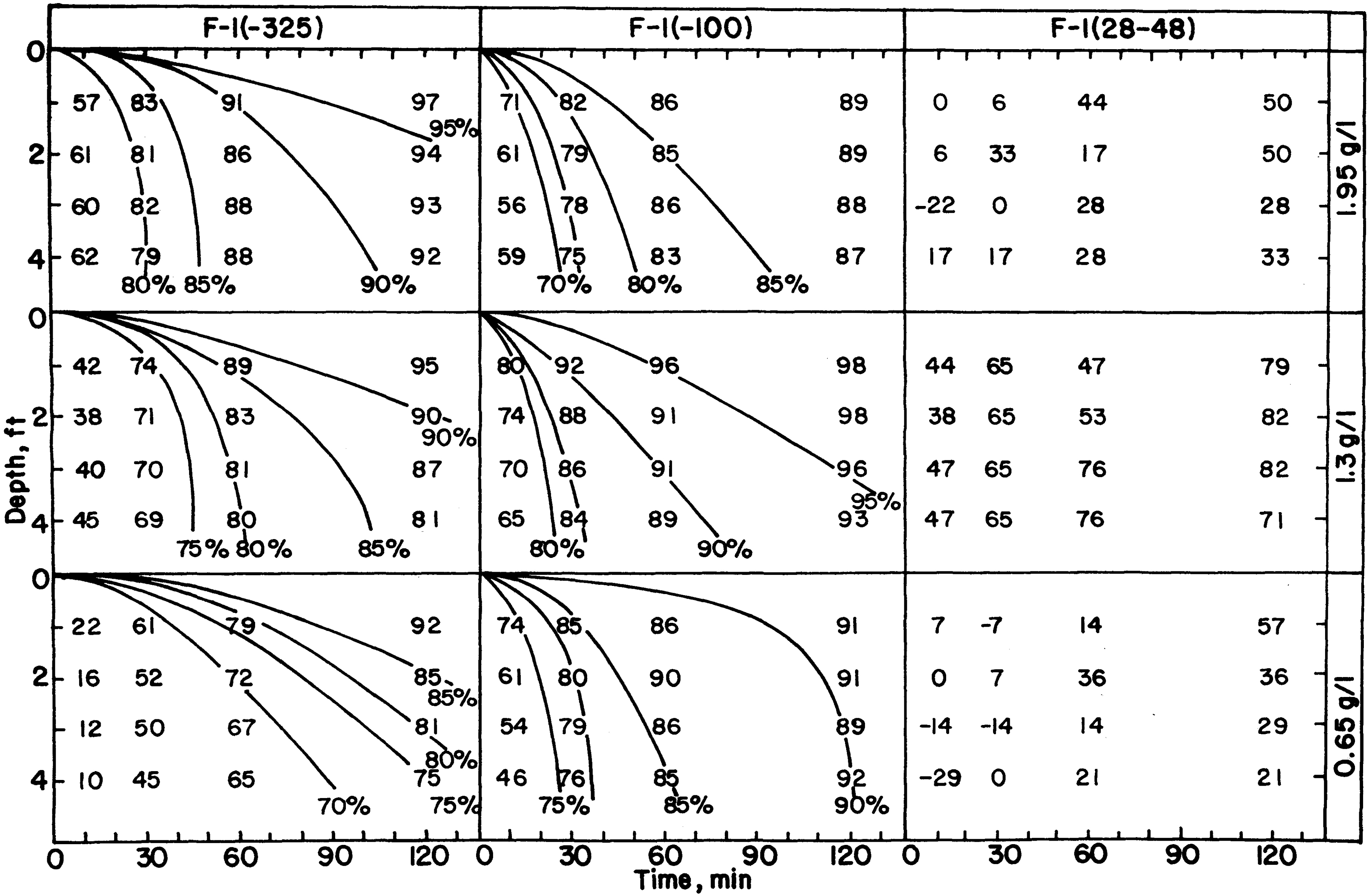
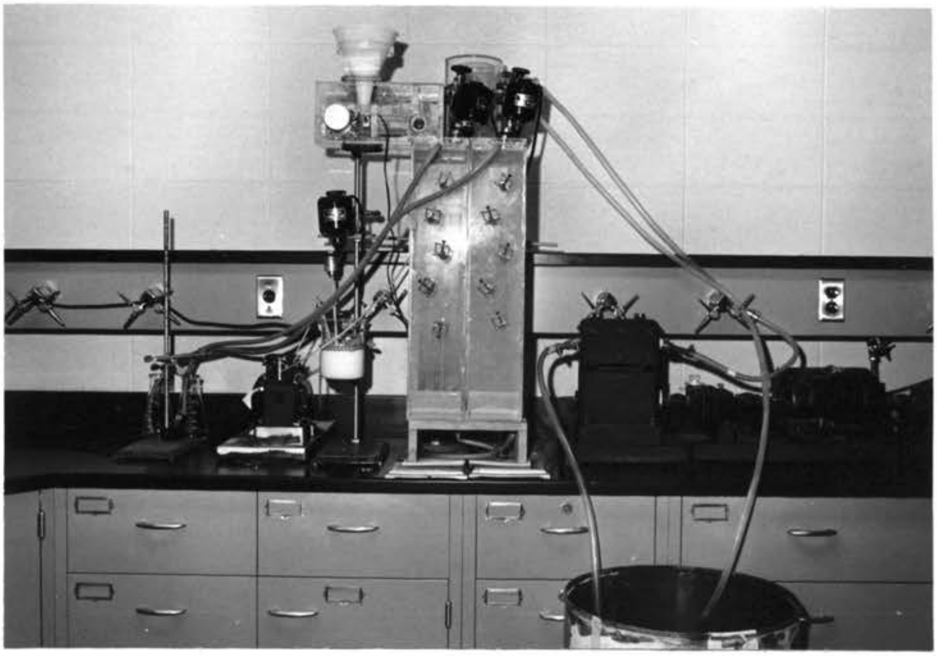
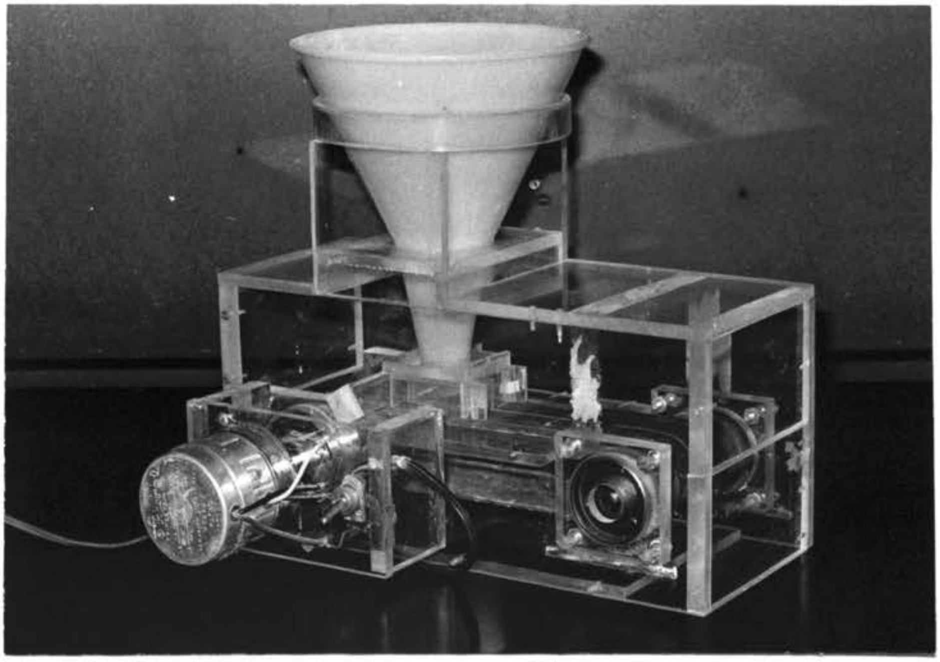


FIGURE 5. SETTLING CHARACTERISTICS OF THE ACTIVATED ALUMINAS



Rapid Mix-Sedimentation Test System



Chemical Dry Feeder

FIGURE 6. BENCH RAPID MIX-SEDIMENTATION TEST SYSTEM

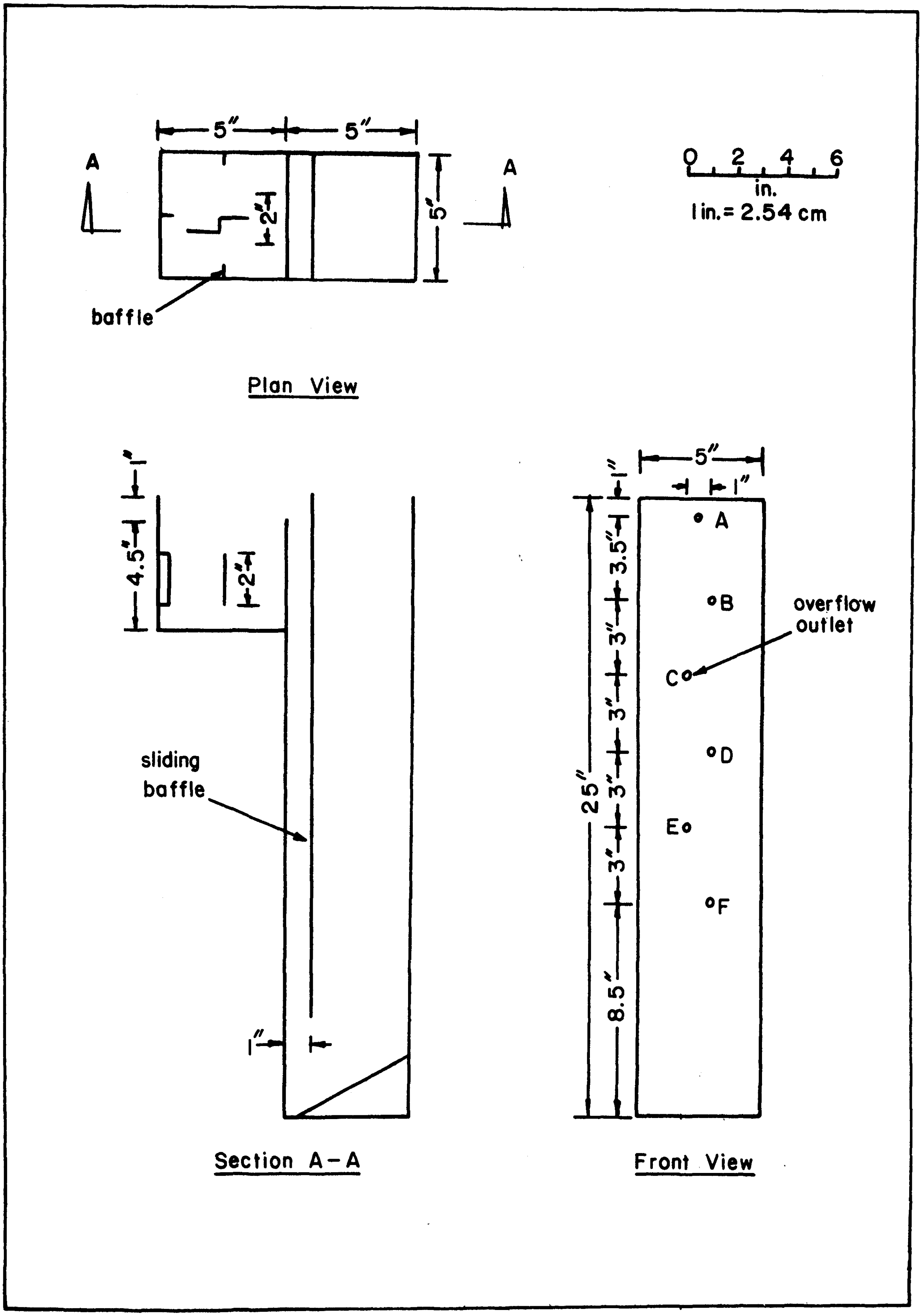


FIGURE 7. BENCH MIXING AND SEDIMENTATION TANKS

was inserted between the 2 tank walls in order to prevent leakage. The mixing tanks were designed to provide a contact period of 15 min, which had been found (Figure 4) to enable a high rate of phosphorus removal [97 and 83 percent of Total-P were removed by the F-1 (-325) and F-1 (-100) aluminas during this period]. The corresponding theoretical tank volume was 57.7 cu in. (946 cu cm), however, in order to compensate for volume loss when the stirrer was working, the design volume was increased to 86.0 cu in. (1,410 cu cm). The actual operational volume of the constructed units was measured and found to be 60.0 cu in. (984 cu cm) for Unit 1 and 61.7 cu in. (1,011 cu cm) for Unit 2; the corresponding liquid detention times were 15.6 and 16.0 min, respectively. One-in. (2.54-cm) wide and 2-in. (5.08-cm) high baffles were installed at mid depth on the 3 sides of the tank in order to prevent rotation of the water in the tank.

Considering a detention time of 2 hr, an overflow rate of 460 gpd/sq ft (18.8 cu m/day/sq m), and a design flow rate of 1 gph (3.78 l/hr), the sedimentation basin volume was computed to be 0.267 cu ft (0.00748 cu m), the area 0.052 sq ft (0.00483 sq m), and the depth 5.14 ft (1.57 m). Because the tank in effect would have been a column and there was concern over wall-effects, the overflow rate was reduced to 170 gpd/sq ft (6.94 cu m/day/sq m) [and correspondingly the area was increased to 0.141 sq ft (0.0131 sq m)] and the depth was decreased to 1.89 ft (0.58 m). Several outlets (Figure 7) were installed to permit operation at different depths and the corresponding tank volumes and theoretical detention times are shown on the following page.

Outlet	Tank Depth in.*	Unit 1 Volume l	Unit 1 Detention Time hr	Unit 2 Volume l	Unit 2 Detention Time hr
A	24.0	7.29	1.93	7.21	1.90
B	20.5	6.25	1.65	6.17	1.63
C	17.5	5.27	1.39	5.23	1.38
D	14.5	4.30	1.14	4.26	1.13
E	11.5	3.34	0.88	3.32	0.88
F	8.5	2.39	0.63	2.37	0.63

*To convert in. to cm multiply by 2.54.

A dry chemical feeder (Figure 6) was designed using the principle of the commercial belt-type feeders and was constructed of 0.25-in. (0.64-cm) thick clear plexiglas and rollerskate wheels as bearings. A 2-in. (5.1-cm) wide belt was made of black rubber gasket material and was supported on 2, 1.5-in. (3.8-cm) diam wheels at a wheelbase of 7.5 in. (19.1 cm); the wheels were made of 1.5-in. (3.8-cm) diam clear cast acrylic tubing and the axle was of 0.375-in. (0.95-cm) steel rod. One of the wheels was driven by a motor* rotating at a constant speed of 0.34 rpm, and the belt travelled at a speed which resulted to 1 full turn/11.5 min. The alumina was stored in a plastic funnel, located above the belt, which functioned as a hopper and discharged to a dosing box. Chemical dosing was controlled by adjusting the opening of the gate on the box and/or the width of the dosing outlet. Dosing rates ranging from 25 to 6,000 mg/min could be obtained by this arrangement and were suitable for operation both in the laboratory and in the field. When the feeder was tested with the smaller size alumina /F-1 (-325)/, a "bridge" was formed across the bottom of the hopper and prevented the free discharge of the

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*Model CA, a product of the Hurst MFG Corp., Princeton, IN.

chemical onto the belt. Consequently, a wet feeding system was especially designed for this alumina and consisted of a continuously mixed* feeding tank holding a suspension of the alumina in distilled water and a variable speed, multi-channel finger pump.**

A 30-gal (113.6-l) epoxy-coated steel drum served as a holding reservoir for the influent waste, and a large stirrer# was used to mix the secondary effluent for 10 min prior to feeding it to the test system. The waste was raised by means of a large multi-channel finger pump## to a constant head feeding reservoir and thereafter supplied by gravity flow to the 2 units; the excess waste was returned to the holding reservoir through an overflow outlet. The advantage of this arrangement was that the flow was independent of the speed of the motor, which varied with the voltage fluctuation in the power line.

The flow rate was initially adjusted by using tap water and a graduated cylinder and stopwatch, and was verified by running the regulating device with tap water for 4 hr and measuring the total amount passed to obtain an average rate. The flow was frequently checked during a test run.

The bench column test system (Figure 8) consisted of 3 glass columns which had been used by Yue and Purushothaman (34,35) in a previous related study. Each column was made of a 2-ft (0.61-m) long piece of 1.5-in. (3.8-cm) ID heavy walled pyrex glass pipe+

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*A variable speed cone-driven stirrer was used.
**Model T-8, a product of Sigmamotor Inc., Middleport, NY.
#Lightnin Model 10, a product of the Mixing Equipment Co., Rochester, NY.
##Model TM-1, a product of Sigmamotor Inc., Middleport, NY.
+No. P7110, a product of the Corning Glass Works, Corning, NY.

FIGURE 8. BENCH COLUMN TEST SYSTEM

which had flared conical ends capable of taking a specially designed metal flange.* The ends of the pipe were plugged with single-hole rubber stoppers kept in position by the 2 metal flanges bolted together; a glass tube was inserted into each rubber stopper and was connected with the outlet or inlet tubing. The bottom of each column was packed with a 2-in. (5.1-cm) layer of 6-mm diam hollow glass beads used to dissipate the velocity head of the feed water. Wastewater was fed to the columns in an upflow mode, and since the alumina bed was much shorter than the height of the column and it was undesirable to trap excessive effluent on top of the bed, the glass tube connecting to the outlet tubing was extended to the surface of the alumina bed. Sample collection ports were provided at the inlet and outlet ends of the column.

The 30-gal (113.6-l) epoxy-coated steel drum served as a feeding reservoir, and the secondary effluent was pumped to the columns by means of the variable speed multi-channel finger pump. The columns were operated at a flow rate of 0.3 gpm/sq ft (12.2 l/min/sq m), and the corresponding detention time was 7 min.

The rapid mix-sedimentation test system was evaluated in 10 different runs using the F-1 (-325) (wet chemical feeding) and F-1 (-100) (dry chemical feeding) aluminas. The purpose of this work was to verify under continuous flow conditions the design data which were obtained in the batch tests in order to get adequate information for the design of the field test system and to gain

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*Type 2 cast iron flange, No. P9653, equipped with a molded insert gasket, a product of the Corning Glass Works, Corning, NY.

enough experience for field operation. Flow rates ranging from 0.4 to 2.3 gph (1.5 to 8.7 l/hr) and alumina doses varying from 4.4 to 7.9 g/gal (1.2 to 2.1 g/l) were employed. The volume of the sedimentation tanks was also varied by using Outlet A for Runs No. 1,2,3 and 8, Outlet B for Runs No. 4,5,7,9 and 10, and Outlet E for Run No. 6; this enabled the system to be operated in a wide range of detention times and overflow rates. Samples were taken from the influent and effluent of the units at predetermined time intervals and analyzed for Total-P, Poly+ortho-P, NH_3-N, Org-N, NO_3-N, NO_2-N, COD, TSS, turbidity, and pH. The operational characteristics and test results are presented in Table VIII, and the sorptive capacity of the aluminas for phosphorus in the secondary effluent is given below.

	Sorptive Capacity, mg P/g			
	Unit 1 - F-1(-325)		Unit 2 - F-1(-100)	
Run No.	Total-P	Poly+ortho-P	Total-P	Poly+ortho-P
1	4.3	4.2	3.5	3.4
2	3.3	3.1	2.2	2.1
3	4.1	4.2	2.3	2.5
4	1.7	1.7	1.7	1.7
5	3.0	2.7	2.8	2.6
6	2.9	3.3	2.7	1.3
7	3.3	3.1	2.9	2.7
8	2.2	3.0	0.9	1.7
9	1.2	1.3	1.0	1.1
10	1.3	1.4	1.1	1.2

The aluminas showed the highest sorptive capacity for both Total and Poly+ortho-P in Run No. 1, and this resulted from the high influent phosphorus concentration and the low alumina dose used; however, the corresponding phosphorus removal was in the range of 48 to 56 percent, which was considered to be too low for field operation. The next highest sorptive capacities were observed in Runs No. 3, and 2 or 7 for Unit 1 and Runs No. 7 and 5 for Unit 2, and the corresponding phosphorus

TABLE VIII. BENCH RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES

Unit 1 - F-1(-325) Alumina

Run No.	Date	Run Duration	Operational Characteristics					Value	Quality Characteristics									
			Detention Time		Flow Rate	O/F* Rate	Alumina Dose		Phosphorus mg P/l		Nitrogen, mg N/l				COD	TSS	Turb	pH
		hr	Mix min	Sed hr	gph#	gpd/sq ft+	g/gal#		Total	Poly+ortho	NH3	Org	NO3	NO2	mg/l	mg/l	jtu	
1	8/23 1972	4.8	20	1.7	1.1	188	4.4	Influent Avg	9.2	8.8	1.5	1.7	20.2	0.60	46			
								Range	0.2	0			1.0	0	0			
								Effluent Avg	4.2	3.9	0.3	2.3	19.8	0.60	43			
								Range	0.2	0	0.7	1.0	0.1	0	0			
								Removal, % (2 samples)	54.3	55.7	80.0	-35.3	2.0	0	7.5			
2	9/4 1972	23.5	26	2.2	0.9	154	8.0	Influent Avg	7.5	7.1	4.0	1.4	17.1	0.60	69	3	10	7.7
								Range	1.4	1.6	2.5	0.4	5.8	0.20	44	6	10	0.5
								Effluent Avg	0.7	0.6	4.1	0.7	16.0	0.60	60	46	45	8.0
								Range	0.8	0.8	2.5	0.5	4.6	0.20	79	23	16	0.1
								Removal, % (8 samples)	90.7	91.5	-2.5	50.0	6.4	0	13.1			
3	9/29 1972	10.8	18	2.2	0.9	154	6.5	Influent Avg	8.1	8.3	5.6	2.5	4.9	0.20	69	12	10	7.7
								Range	0.9	0.6	3.2	0.9	3.4	0.10	24	12	4	0.2
								Effluent Avg	1.2	1.1	6.6	1.6	5.0	0.20	46	64	44	8.0
								Range	0.5	0.4	2.7	0.1	3.8	0.10	24	44	25	0.3
								Removal, % (11 samples)	85.2	86.7	-17.9	36.0	-2.0	0	33.0			
4	11/28 1972	11.0	22	2.75	0.7	119	6.5	Influent Avg	3.9	3.8	0.6	3.3	6.2	0.02	42			
								Range	0.2	0.3	1.0	0.3	2.0	0	9			
								Effluent Avg	1.0	0.9	1.4	2.2	6.2	0.02	43			
								Range	0.4	0.5	1.5	1.1	2.1	0.01	14			
								Removal, % (9 samples)	74.4	76.3	-133.3	33.3	0	0	-4.3			
5	12/16 1972	9.2	24	2.50	0.7	119	6.3	Influent Avg	6.5	6.1	6.9	11.2	3.8	0.04	63	1	7	7.8
								Range	0.7	1.1	5.1	7.3	1.2	0	3	2	2	0.3
								Effluent Avg	1.4	1.5	7.7	7.3	4.4	0.03	37	86	129	8.2
								Range	1.2	1.0	4.3	4.2	2.0	0.01	18	76	81	0.3
								Removal, % (9 samples)	78.5	75.4	37.7	34.3	-15.8	0.30	40.9			
6	12/19 1972	11.9	43	2.4	0.4	68	5.6	Influent Avg	6.0	6.4	9.7	8.0	2.9	0.05	82	18	13	7.8
								Range	1.7	1.0	8.3	10.2	0.3	0	0	0	3	0.2
								Effluent Avg	1.7	1.5	8.2	7.7	2.8	0.04	55	49	35	8.2
								Range	0.7	0.7	8.0	7.9	1.4	0.01	35	174	23	0.1
								Removal, % (9 samples)	71.7	76.6	15.4	3.8	3.4	20.00	33.3			
7	1/10 1973	10.2	14	1.5	1.1	188	6.5	Influent Avg	6.4	6.1	8.2	3.0	2.8	0.06	57	18	10	8.2
								Range	0	1.2	0	6.0	0.5	0.01	7	0	0	0.1
								Effluent Avg	0.8	0.8	6.4	4.3	3.2	0.05	29	68	53	8.3
								Range	0.2	0.2	6.0	6.0	1.4	0.02	18	50	30	0.3
								Removal, % (9 samples)	87.5	86.9	22.0	-43.3	-14.3	16.70	47.5			
8	1/17 1973	6.0	7	0.86	2.2	375	6.4	Influent Avg	6.5	7.4					98	22	19	8.1
								Range	1.2	1.5					11	0	2	0.1
								Effluent Avg	2.8	2.3					68	208	176	8.2
								Range	2.0	1.8					18	114	50	0.1
								Removal, % (7 samples)	56.9	68.9					30.4			
9	1/20 1973	7.0	14	1.7	1.1	188	6.6	Influent Avg	3.2	4.1					40	2	4	8.1
								Range	0.7	0.1					2	4	2	0.1
								Effluent Avg	1.1	1.8					34	118	119	8.2
								Range	0.6	0.4					15	248	134	0.1
								Removal, % (7 samples)	65.6	56.1					15.1			
10	1/27 1973	6.7	12	1.3	1.3	222	7.4	Influent Avg	2.9	3.1					48	10	12	8.2
								Range	0.1	0.1					19	5	7	0.1
								Effluent Avg	0.4	0.4					31	89	81	8.3
								Range	0.3	0.2					19	49	30	0.1
								Removal, % (7 samples)	86.2	87.1					36.1			

*Overflow rate or surface loading.

#To convert gal to l multiply by 3.785.

+To convert gpd/sq ft to cu m/day/sq m multiply by 0.0408.

TABLE VIII (cont.). BENCH RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES

Unit 2 - F-1(-100) Alumina

Run No.	Date	Run Duration hr	Operational Characteristics: Detention Time Mix min	Detention Time Sed hr	Flow Rate gph#	O/F* Rate gpd/sq ft+	Alumina Dose g/gal#	Value	Quality Characteristics: Phosphorus mg P/1 Total	Phosphorus mg P/1 Poly+ortho	Nitrogen, mg N/1 NH3	Nitrogen Org	Nitrogen NO3	Nitrogen NO2	COD mg/1	TSS mg/1	Turb jtu	pH
1	8/23 1972	4.8	21	1.8	1.0	171	4.8	Influent Avg	9.2	8.8	1.5	1.7	20.2	0.60	46			
								Range	0.2	0			1.0	0	0			
								Effluent Avg	4.8	4.5	0.9	2.3	20.6	0.60	43			
								Range	0	0.1	0.5	0.1	0.8	0	0			
								Removal, %	47.8	48.9	40.0	-35.3	-1.5	0	7.5			
								(2 samples)										
2	9/4 1972	23.5	23	2.0	1.0	171	7.5	Influent Avg	7.5	7.1	4.0	1.4	17.1	0.60	69	3	10	7.7
								Range	1.4	1.6	2.5	0.4	5.8	0.20	44	6	10	0.5
								Effluent Avg	3.1	2.9	4.0	1.2	15.9	0.60	65	40	32	7.9
								Range	1.5	1.2	2.4	0.3	4.0	0.20	96	44	24	0.2
								Removal, %	58.7	59.2	0	14.3	7.0	0	6.3			
								(8 samples)										
3	9/29 1972	10.8	18	2.2	0.9	154	6.2	Influent Avg	8.1	8.3	5.6	2.5	4.9	0.20	70	12	10	7.7
								Range	0.9	0.6	3.2	0.9	4.7	0	24	12	4	0.2
								Effluent Avg	4.3	4.2	6.7	2.3	5.9	0.20	56	39	22	7.7
								Range	0.7	0.5	2.2	0.3	3.8	0.10	22	18	10	0.4
								Removal, %	46.9	49.4	-19.6	8.0	-20.4	0	20.2			
								(11 samples)										
4	11/28 1972	11.0	23	2.8	0.7	119	6.8	Influent Avg	3.9	3.8	0.6	3.3	6.2	0.02	42			
								Range	0.2	0.3	1.0	0.3	2.0	0	9			
								Effluent Avg	0.8	0.8	1.1	2.1	7.4	0.02	56			
								Range	0.6	0.7	0.8	1.9	2.6	0	10			
								Removal, %	79.5	78.9	-83.0	36.4	-19.4	0	-25.4			
								(9 samples)										
5	12/16 1972	9.2	25	2.5	0.6	102	6.9	Influent Avg	6.5	6.1	6.9	11.2	3.8	0.04	64	1	7	7.8
								Range	0.7	1.1	5.1	7.3	1.2	0	3	2	2	0.3
								Effluent Avg	1.4	1.3	7.9	7.9	3.7	0.04	51	8	24	8.1
								Range	0.6	0.3	5.8	8.7	1.0	0	29	24	31	0.5
								Removal, %	78.5	78.7	15.5	29.5	2.6	0	20.1			
								(9 samples)										
6	12/19 1972	11.9	46	2.5	0.4	68	4.9	Influent Avg	6.0	6.4	9.7	8.0	2.9	0.05	82	18	13	7.8
								Range	1.7	1.0	8.3	10.2	0.3	0	0	0	3	0.2
								Effluent Avg	2.5	2.3	5.5	7.6	2.2	0.04	72	17	17	7.7
								Range	0.5	0.3	7.9	8.5	1.3	0.01	47	6	4	0.3
								Removal, %	58.3	64.1	43.3	5.0	24.1	20.00	12.0			
								(9 samples)										
7	1/10 1973	10.2	15	1.5	1.1	188	6.2	Influent Avg	6.4	6.1	8.2	3.0	2.8	0.06	57	18	10	8.2
								Range	0	1.2	0	6.0	0.5	0.01	7	0	0	0.1
								Effluent Avg	1.6	1.7	6.4	4.3	2.8	0.05	49	42	29	8.2
								Range	0.3	0.3	6.0	6.0	0.7	0.01	22	20	11	0.2
								Removal, %	75.0	72.1	22.0	-43.3	0	16.70	13.3			
								(9 samples)										
8	1/17 1973	6.0	7	0.8	2.3	392	6.4	Influent Avg	6.5	7.4					98	22	19	8.1
								Range	1.2	1.5					11	0	2	0.1
								Effluent Avg	4.9	4.4					76	75	41	8.1
								Range	0.9	0.8					14	108	19	0.2
								Removal, %	24.6	40.5					22.4			
								(7 samples)										
9	1/20 1973	7.0	13	1.3	1.2	205	7.0	Influent Avg	3.2	4.1					40	2	4	8.1
								Range	0.7	0.1					2	4	2	0.1
								Effluent Avg	1.4	2.1					38	144	68	8.1
								Range	1.3	0.4					15	368	127	0.1
								Removal, %	56.3	48.8					4.0			
								(7 samples)										
10	1/27 1973	6.7	12	1.2	1.3	222	7.4	Influent Avg	2.9	3.1					48	10	12	8.2
								Range	0.1	0.1					19	5	7	0.1
								Effluent Avg	0.7	0.8					41	42	36	8.3
								Range	0.2	0.2					15	23	22	0
								Removal, %	75.9	74.2					15.6			
								(7 samples)										

*Overflow rate or surface loading.
#To convert gal to l multiply by 3.785.
+To convert gpd/sq ft to cu m/day/sq m multiply by 0.0408.

removals ranged from 85 to 92 percent for Unit 1 and 72 to 79 percent for Unit 2. Taking into consideration the operational characteristics of these runs, the following design values were selected for the field units.

Detention time	
Rapid mix	25 min
Sedimentation	2 hr
Overflow rate (surface loading)	
Sedimentation	190 gpd/sq ft (7.75 cu m/day/sq m)
Sorptive capacity	
F-1 (-325)	4.1 mg P/g
F-1 (-100)	2.9 mg P/g

C. FIELD TEST SYSTEM

The field test system (Figure 9) consisted of 2 rapid mix-sedimentation units operated in parallel using F-1 (-325) (wet chemical feeding) and F-1 (-100) (dry chemical feeding) aluminas, and 4 column units operated in series using F-1 (28-48) alumina. Secondary effluent was supplied to the system from the manhole at the discharge end of the Rolla Southwest Sewage Treatment Plant by means of a 0.75-hp (0.56-kw) centrifugal pump* on a 115-v hook-up. The pump capacity was greater than required and provisions were made for bypassing the excess flow. The intake facility consisted of a vertical 1-in. (2.54-cm) PVC pipe connected to an especially designed screen which was attached to a wooden, inverted "T" frame; this frame, functioning as a dam, raised the wastewater level in order to facilitate pumping. A water meter** was placed ahead of the 1st column and was used to measure the total volume of wastewater passed

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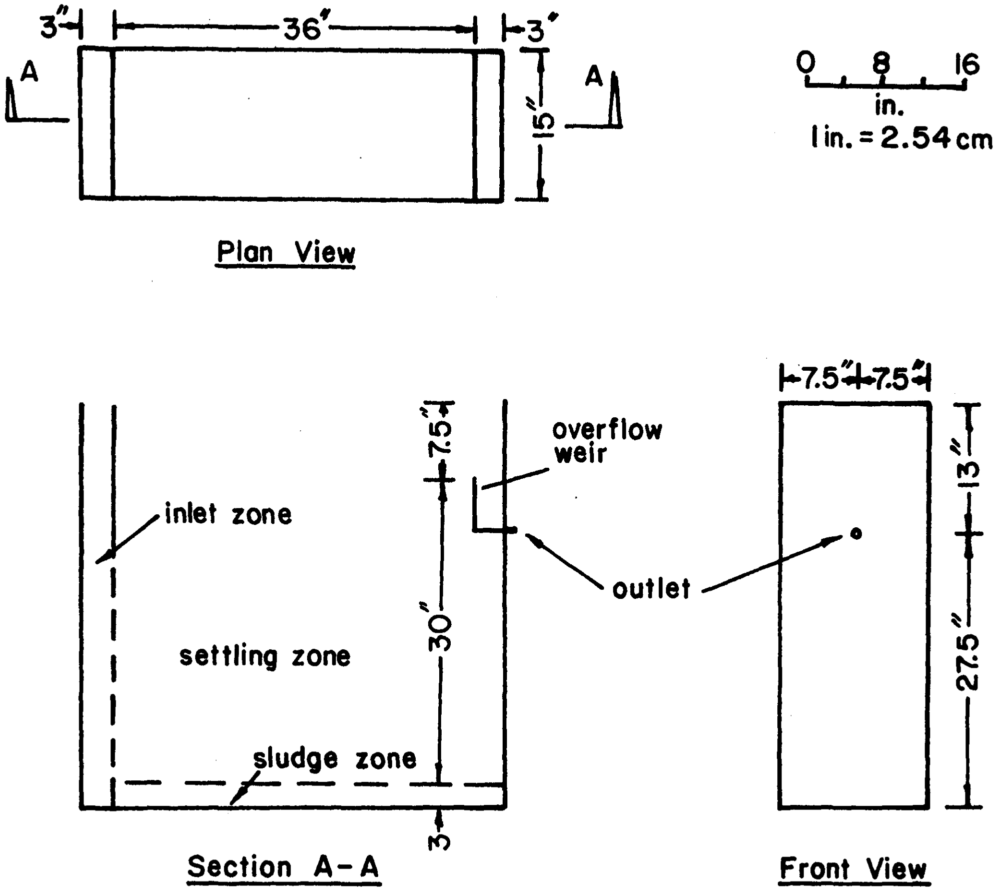
*Model 390.208, a product of Sears, Roebuck & Co., Kansas City, MO.

**A Trident, Triseal, Neptune Style No. 3 meter was used; it was purchased from the Rolla Municipal Utilities, Rolla, MO.

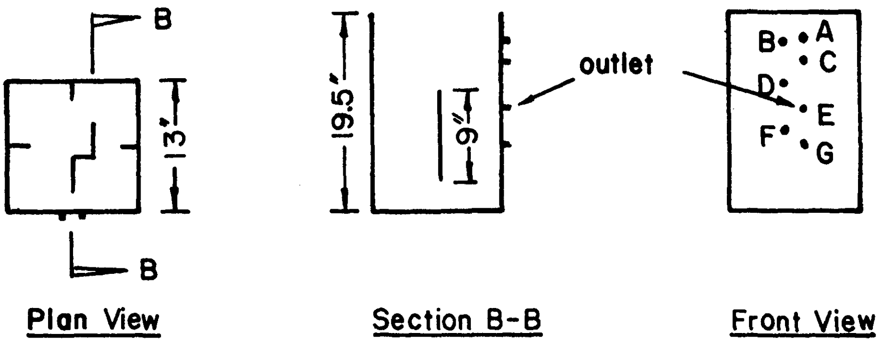
FIGURE 9. FIELD TEST SYSTEM

through the beds, and a pressure gage was installed in front of the meter to control the pressure in the column test system. A 30-ft (9.14-m) long piece of 1.25-in. (3.18-cm) ID PVC pipe was provided to collect the effluent from both the rapid mix-sedimentation and column units and to discharge it into the manhole at the downstream side of the dam.

The rapid mix-sedimentation units consisted of a mixing tank equipped with a propeller stirrer, a sedimentation tank, an alumina feeding system, and a flow regulating device. The alumina feeders were those used with the bench-scale system, except that the chemical storage capacity was enlarged to accommodate round-the-clock continuous operation between each refill. To accomplish this purpose a 12-in. (30.5-cm) section of 6-in. (15.2-cm) diam clear cast acrylic tubing was installed on top of the plastic funnel used with the dry feeder [F-1 (-100) alumina], while a 5-gal (18.9-l) polyethylene container was used to hold the alumina suspension in the wet feeder [F-1 (-325)]. The rapid mix and sedimentation tanks were designed for a test flow of 0.5 gpm (1.9 l/min), and to increase the flexibility of operation, both tanks were built to be capable of providing a range of detention times without changing the influent flow rate. The tanks were made of 0.25-in. (0.64-cm) thick clear plexiglas sheets, and their dimensions and construction details are shown in Figure 10. The volume of the mixing tanks and corresponding detention time could be changed by selecting a suitable outlet, and based on the 0.5 gpm (1.9 l/min) flow the following relationships held.



SETTLING TANK



MIXING TANK

FIGURE 10. FIELD MIXING AND SEDIMENTATION TANKS

Outlet	Mixing Tank Volume l	Detention Time min
A	47.1	25
B	45.7	24
C	41.5	22
D	34.6	18
E	26.3	14
F	22.9	12
G	18.7	10

The sedimentation tanks were designed on the basis of an overflow rate of 190 gpd/sq ft (7.75 cu m/day/sq m) and a detention time of 2 hr. The tanks provided a 10-cu ft (0.28-cu m) settling zone and a 0.93-cu ft (0.026-cu m) sludge zone; the height of the overflow weir could be easily changed by replacing the weir plate and correspondingly the volume of the tank could be varied. The cone-driven stirrer (operating at 2,800 rpm) was retained with Unit 1, however, a higher speed (3,200 rpm) stirrer* was employed with Unit 2 to assure adequate mixing of the larger alumina. The flow regulating device was the same as used in the laboratory, except that appropriate adjustments were made to permit the higher flow.

The design of the 4 field columns was based on the operational characteristics of the small bench-scale columns; these had been developed by Yue and Purushothaman (34,35) who had employed flow rates ranging from 0.7 to 0.2 gpm/sq ft (28.5 to 8.1 l/min/sq m) and corresponding detention times varying from 5 to 22 min. The field columns were designed to provide 20 min detention at a flow rate of 1.4 gpm/sq ft (57 l/min/sq m). They were constructed using 6-in. (15.2-cm) diam clear acrylic tubing, 42 in. (106.6 cm) in length, and

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*Dyna-mix model 143, a product of Fisher Scientific, Pittsburgh, PA.

flange joints at both ends. The joints were made of a 0.5-in. (1.3-cm) thick clear plexiglas sheet and a 0.0625-in. (0.16-cm) thick red rubber gasket. A 3-in. (7.6-cm) section of 5.5-in. (14-cm) diam clear acrylic tubing, covered with 50 mesh stainless steel screen and filled with 6-mm diam glass beads, was placed at each end of each column, and the space between the column wall and this section was filled with glass wool in order to prevent the leakage of alumina. The section functioned as a filter as well as a dissipator of the flow. The columns were packed with 25 lb (11.4 kg) of F-1 (28-48) alumina between the 2 filters. Two sampling ports were initially designed for each column, however, the ports clogged with alumina shortly after a run began and were not used. The dimensions and construction details of each column are shown in Figure 11.

D. REGENERATION SYSTEM

Regeneration of the exhausted alumina from the bench rapid mix-sedimentation system was accomplished using 2, 6-unit variable speed (20 to 100-rpm) stirrers, usually employed for water coagulation studies, and a series of 1-l beakers. Exhausted alumina from the field rapid mix-sedimentation units was regenerated in the laboratory using 4, 30-gal (113.6-l) epoxy-coated steel drums using 2 pilot plant stirrers,* and liquid transfer between the drums was facilitated by 2 self-priming pumps.** An arrangement of the system is shown in Figure 12. The regenerated alumina was then placed in aluminum baking

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*Lightnin Models 10 and 10X, products of the Mixing Equipment Co., Rochester, NY.

**Model PE4-M6, a product of ITT Jabsco Inc., Costa Mesa, CA.

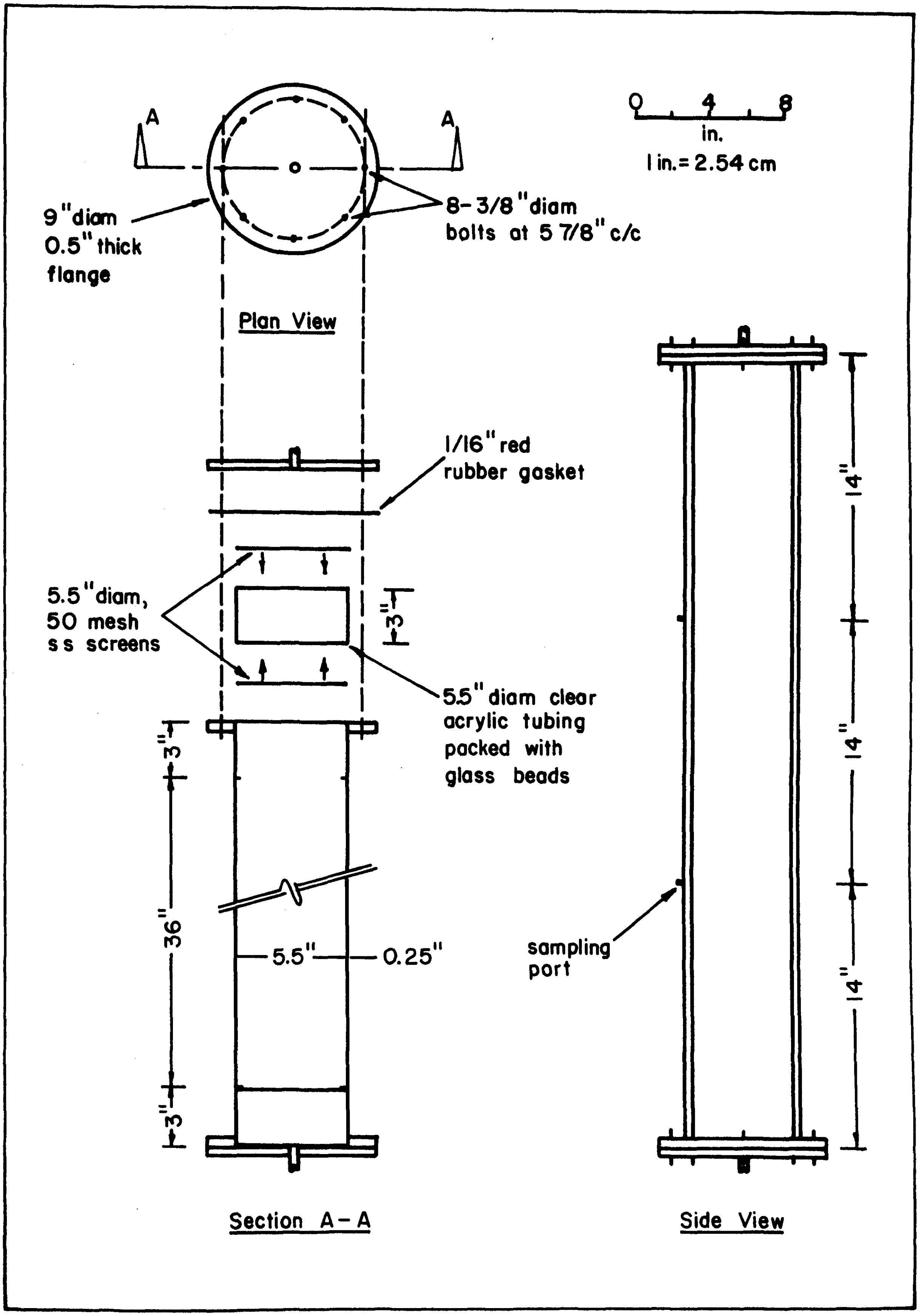

FIGURE 11. FIELD COLUMN UNIT

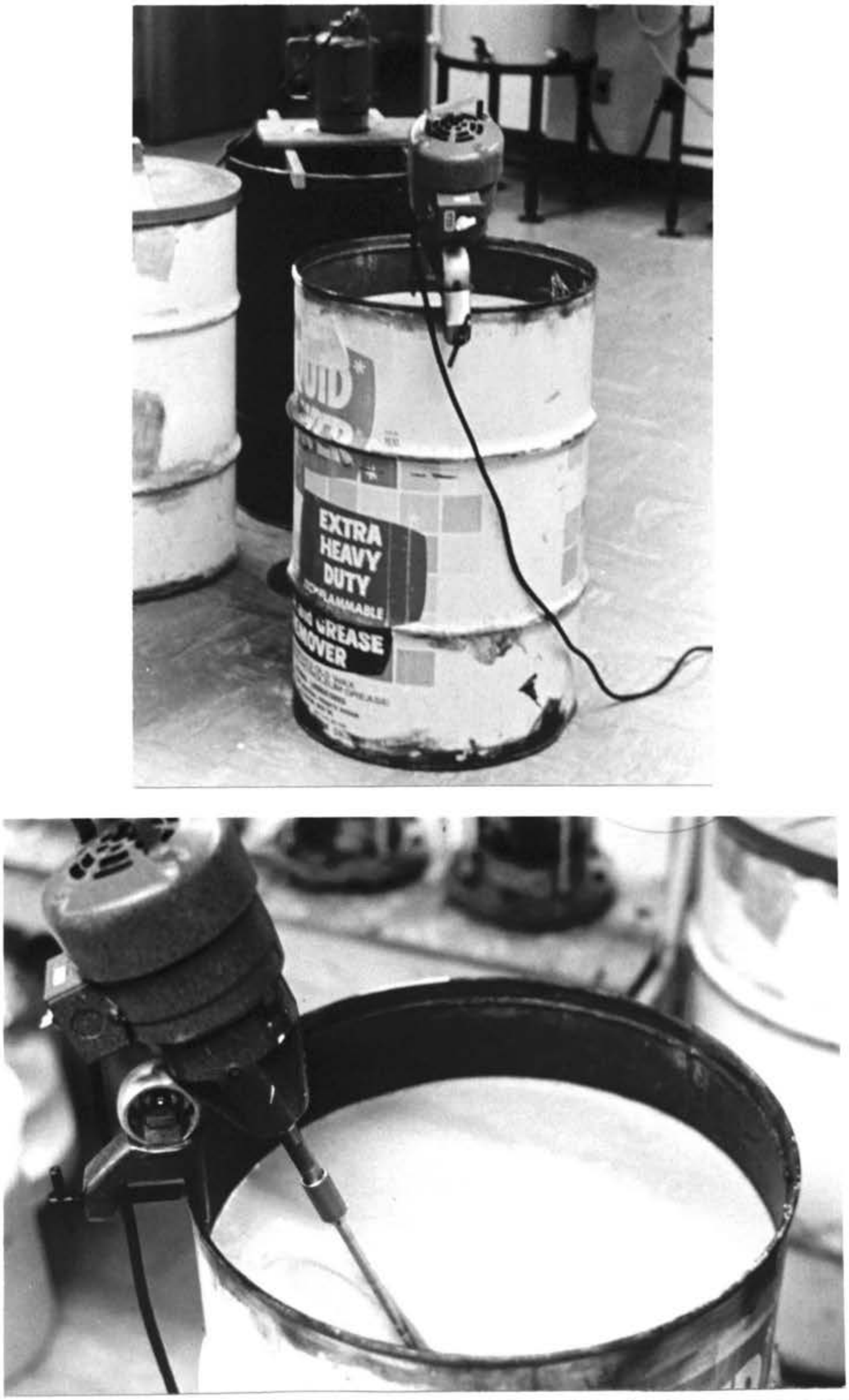

FIGURE 12. LARGE SCALE ACTIVATED ALUMINA REGENERATION SYSTEM

pans,[*] and was dried at 59° C[**] for a period of 1 wk. Alumina in the exhausted bench and field columns was treated in the columns, which if necessary were brought to the laboratory. The large multi-channel finger pump was used to circulate the regenerant and subsequent wash water through each column in the upflow mode.

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[*] Eight 18 x 24-in. (45.7 x 61-cm) pans were used; they were purchased from the State Agency for Surplus Property, Jefferson City, MO.

[**] No. 751A-X, a product of Lab-Line Instruments, Inc., Melrose Park IL.

VI. EXPERIMENTAL STUDIES AND RESULTS

Studies were undertaken during a 9-month period (June 1973 to March 1974) to evaluate the ability of 3 activated aluminas to remove nutrients from wastewater treatment plant effluent and to investigate the regeneration characteristics of the spent aluminas. Two test runs (S-1 and S-2) were made in the field utilizing concurrently the rapid mix-sedimentation and column operational modes; Run S-1, a 1-month test conducted in June and July 1973, employed fresh aluminas and Run S-2, a 2-wk test performed in September and October 1973, investigated regenerated aluminas. A final run (S-3) was then made in the laboratory using aluminas which had been regenerated twice; the column study was performed over a 6-day period in February 1974, while the rapid mix-sedimentation study was run on March 3, 1974. Aluminas used in the rapid mix-sedimentation system were removed from the sedimentation basins and were regenerated (in a batch system) with 1M sodium hydroxide, washed with distilled water, dried at 59° C for 7 days, and crushed with a cement trowel to individual particles for reuse; the alumina in the columns was treated in place with 1M sodium hydroxide and distilled water, and was not dried prior to reuse. The studies performed and their time sequence are outlined in Figure 13, and a summary of the experimental conditions employed is given in Table IX; to facilitate presentation, the results are not reported in sequence but have been grouped into 2 sections, sorption and regeneration studies.

A. SORPTION STUDIES

Field work was conducted at the Rolla Southwest Sewage Treatment Plant and effluent from this plant was used in the laboratory investigations. The plant was located approximately 2 miles southwest of the

Study	Date	Test System	
		Rapid Mix-Sedimentation (RMS) F-1(-325) (Unit 1) F-1(-100) (Unit 2)	Column (CTS) F-1(28-48)
Run S-1 Sorption study using fresh alumina	6/18/73 to 7/18/73	Field RMS	Field CTS
Regeneration Study Development/evaluation of regeneration procedure	RMS 7/26/73 to 8/17/73 CTS 8/19/73 to 9/1/73 11/27/73 to 12/14/73	Laboratory Batch Regeneration Bench RMS	Laboratory Column Regeneration Bench CTS
Run R-1 1st regeneration of used alumina	RMS 8/18/73 to 10/5/73 CTS 9/19/73 to 9/24/73	Batch Regeneration	Column Regeneration
Run S-2 Sorption study using regenerated alumina	9/28/73 to 10/10/73	Field RMS	Field CTS
Run R-2 2nd regeneration of used alumina	RMS 2/1/74 to 3/2/74 CTS 1/31/74 to 2/4/74	Batch Regeneration	Column Regeneration
Run S-3 Sorption study using regenerated alumina	RMS 3/3/74 CTS 2/5/74 to 2/11/74	Bench RMS Exhausted Alumina	Bench CTS Exhausted Alumina

FIGURE 13. TYPE AND SEQUENCE OF STUDIES

TABLE IX. SUMMARY OF EXPERIMENTAL CONDITIONS

Sorption Studies

Run No.	Unit 1 - F-1(-325)				Unit 2 - F-1(-100)				Column - F-1(28-48)			
	Flow Rate gph*	Detention Time		Alumina	Flow Rate gph	Detention Time		Alumina	Column Volume l	Alumina lb##	Rate gpm/sq ft#	Det Time min
		Mix min	Sed hr	g/gal**		Mix min	Sed hr	g/gal				
S-1	30.8+	24+	2.4+	5.6+	30.7+	24+	2.4+	7.1+	13.6	25	1.3	23
S-2	31.2	24	2.4	9.3	31.4	24	2.4	9.4	13.6	25	1.5	16
S-3	1.0	16	2.0	7.7	1.0	17	2.0	7.8	0.1	0.22	0.3	7

Regeneration Studies

Run No.	Unit 1 - F-1(-325) & Unit 2 - F-1(-100)							Column - F-1(28-48)						
	1M NaOH Wash++			Water Wash			Dry Time hr	Rate gpm/sq ft#	1M NaOH Wash++			Water Wash		
	Wash Volume gal*	Alumina lb##	Mix Time hr	No. of Cycles	Volume/Cycle gal	Mix Time min			No. of Cycles	Volume/Cycle gal	Recirc Time hr	No. of Cycles	Volume/Cycle gal	Recirc Time hr
R-1	18	30	4.5	2	18	30	168	0.12	2	10 6.5	6 5	2	14	5
R-2	0.13	0.22	4.5	2	0.18	1	74.5	0.12	1	0.12	21.2	3	0.16 0.08 0.08	19.5 4.8 6.0

*To convert gph to l/hr & gal to l multiply by 3.785.

**To convert g/gal to g/l multiply by 0.264.

#To convert gpm/sq ft to cu m/day/sq m multiply by 0.408.

##To convert lb to kg multiply by 0.454.

+Average values during July 4-18 period.

++The corresponding hydroxyl ion to alumina weight ratios, in gOH^-/g alumina, were 0.085 for F-1(-325) and F-1(-100) and 0.094 for F-1(28-48).

city limits on the South Outer road. It employed the contact stabilization activated sludge process and had a design flow of 0.4 mgd (1,514 cu m/day); however, it was operating only at about 20 percent of its design capacity, serving an area of approximately 72.6 acres (29.4 ha) at the southwest corner of the city. Located in this area were mainly motels, restaurants and service stations, and a few single-family dwellings; more than 90 percent of the flow was contributed by the commerical activities. It was estimated* that wastewater generated within the area would have taken between 1.25 and 2.5 hr to reach the plant. A layout of the collection system and a block diagram of the plant are shown in Figure 14; also indicated on this figure is the relative position of the field test system. The character of the contributing area and the fact that the plant was operating well below design capacity affected the quality of both the influent raw waste and the plant effluent. Unfortunately, the other 2 Rolla plants were being upgraded at that time and the ongoing construction activities precluded any field work.

1. Field Studies

An 8.0x6.5x6.0-ft (2.4x2.0x1.8-m) high wooden frame was constructed and was covered by a 9.5x11.5-ft (2.9x3.5-m) cotton duck tarps** to form a protective housing for the test equipment (see Figure 9, p.66). A mobile laboratory was parked nearby to facilitate field work and

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*On the basis of the diameter, slope, and length of the sewers serving the area, it was computed that at full flow the time of travel to the plant would have been 30 to 60 min; however, because of the relationship of actual to full flow, the actual velocity would have been only 35 to 45 percent of the value at full flow, and correspondingly the time of travel estimate was increased to 75 to 150 min.

**No. 6B7645C, a product of Sears, Roebuck and Co., Kansas City, MO.

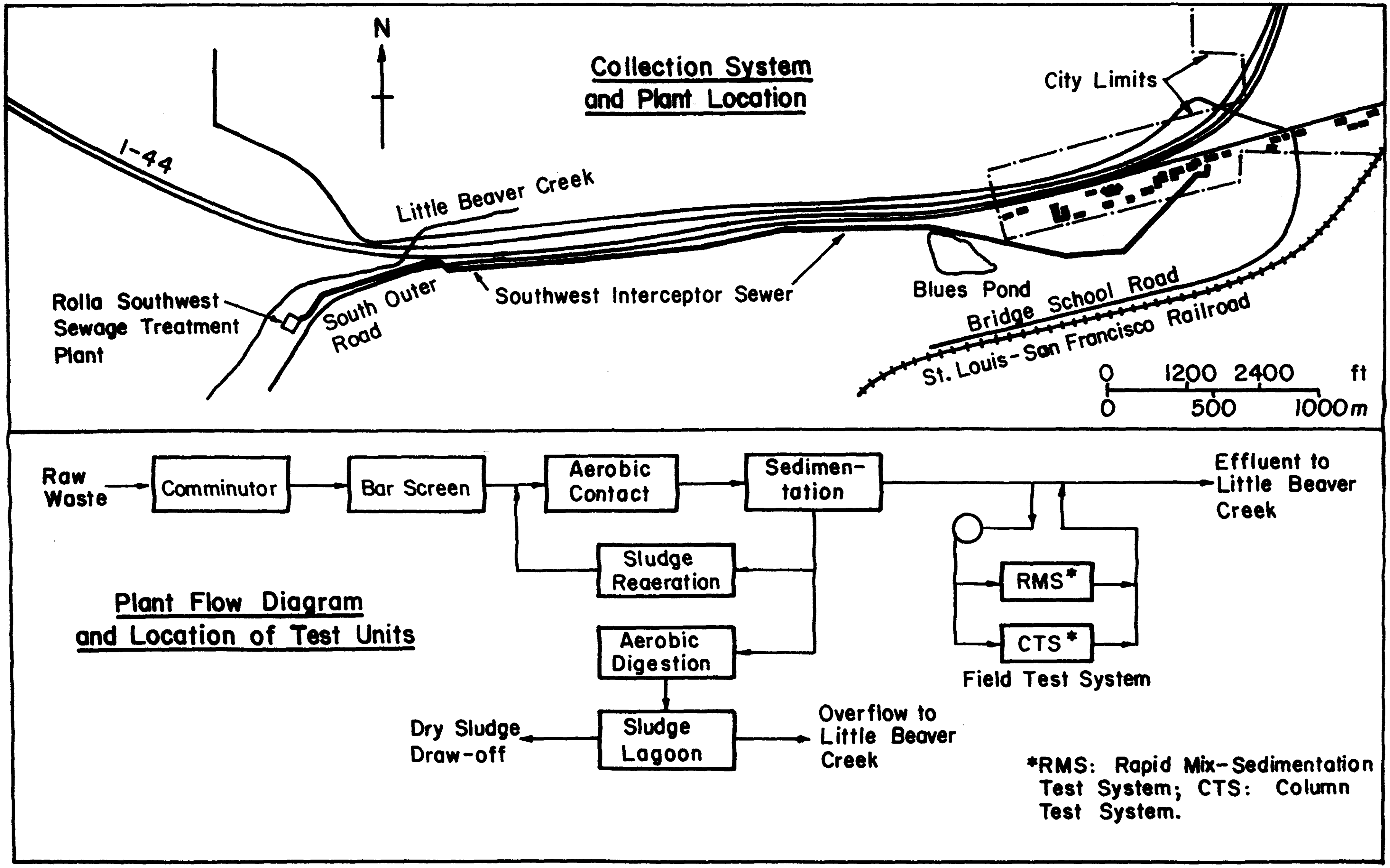

FIGURE 14. ROLLA SOUTHWEST SEWAGE TREATMENT PLANT AND LOCATION OF FIELD TEST SYSTEM

provide storage for materials and tools and overnight shelter during 24-hr sampling tests.

The rapid mix-sedimentation test equipment was thoroughly cleaned and assembled in the laboratory, and was then transported to the field location where the pump, flow controlling devices, and inlet and outlet tubing were connected. The flow controlling devices and chemical feeding systems were initially adjusted in the laboratory and were checked on a daily basis. The alumina feeding reservoirs were refilled each morning, and used aluminas were withdrawn from the sedimentation basins by siphoning every 3 or 4 days and placed into plastic containers which were then carried to the laboratory for regeneration. The 4 columns were packed with alumina in the laboratory and were transported to the field completely assembled; 2 of the columns were connected in series and tied to the inlet pump so as to allow upflow operation. The flow through and pressure in the columns were controlled by adjusting appropriate valves in the system, and the total amount of secondary effluent passing through the columns was automatically recorded on the flow meter. Samples were collected in the morning (10:00 AM) and in the afternoon (6:00 PM) and were obtained from 5 different points: influent to the 2 systems and effluents from Unit 1 [dosed with F-1 (-325) alumina], Unit 2 [supplied with F-1 (-100) alumina], and Columns 1 and 2 [both loaded with F-1 (28-48) alumina]. The morning samples were stored at 4° C until they were composited on an equal volume basis with the afternoon samples. The composites were analyzed on the same day for Poly+ortho-P, NH_3-N, Org-N, NO_3-N, NO_2-N, COD, TSS, turbidity, and pH.

The 2 sampling times (10:00 AM and 6:00 PM) were selected to reflect the average daily quality of both the influent and effluent samples. In order to arrive at these 2 times, the characteristics of the Rolla treatment plant effluent were monitored on a 24-hr basis on 3 different occasions (May 29-30, June 8-9, and September 25-26, 1973), and the results have been presented in Figure 2 (p.42-44); the May and June dates preceded Run S-1 and the September date preceded Run S-2. The phosphorus data are summarized in Figure 15, together with the corresponding plant flow. Because the diurnal fluctuation in the concentration of phosphorus was relatively small, consideration was also given in selecting the sampling times to the plant maintenance schedule and the need to complete the analyses within the same day, while avoiding conflict with other students utilizing the same analytical equipment in the laboratory.

Two test runs were conducted in the field and the daily operational characteristics are given in Table X and summarized in Table IX (p.76). Run S-1 employed fresh alumina, while Run S-2 used the same alumina after it had been treated with 1M sodium hydroxide to restore its sorptive capacity as outlined in Table IX (Run R-1). Quality characteristics are presented in Table XI (influent to the system), XII (effluent from the rapid mix-sedimentation units), and XIII (effluent from the columns).

The rapid mix-sedimentation system performed satisfactorily throughout Run S-1 with only a few minor difficulties which caused the leakage of phosphorus from the units (Figure 16); these resulted from the failure of the alumina feeding system in Unit 1 and of the mixing stirrer in Unit 2. The dosing rate of the wet feeding system employed

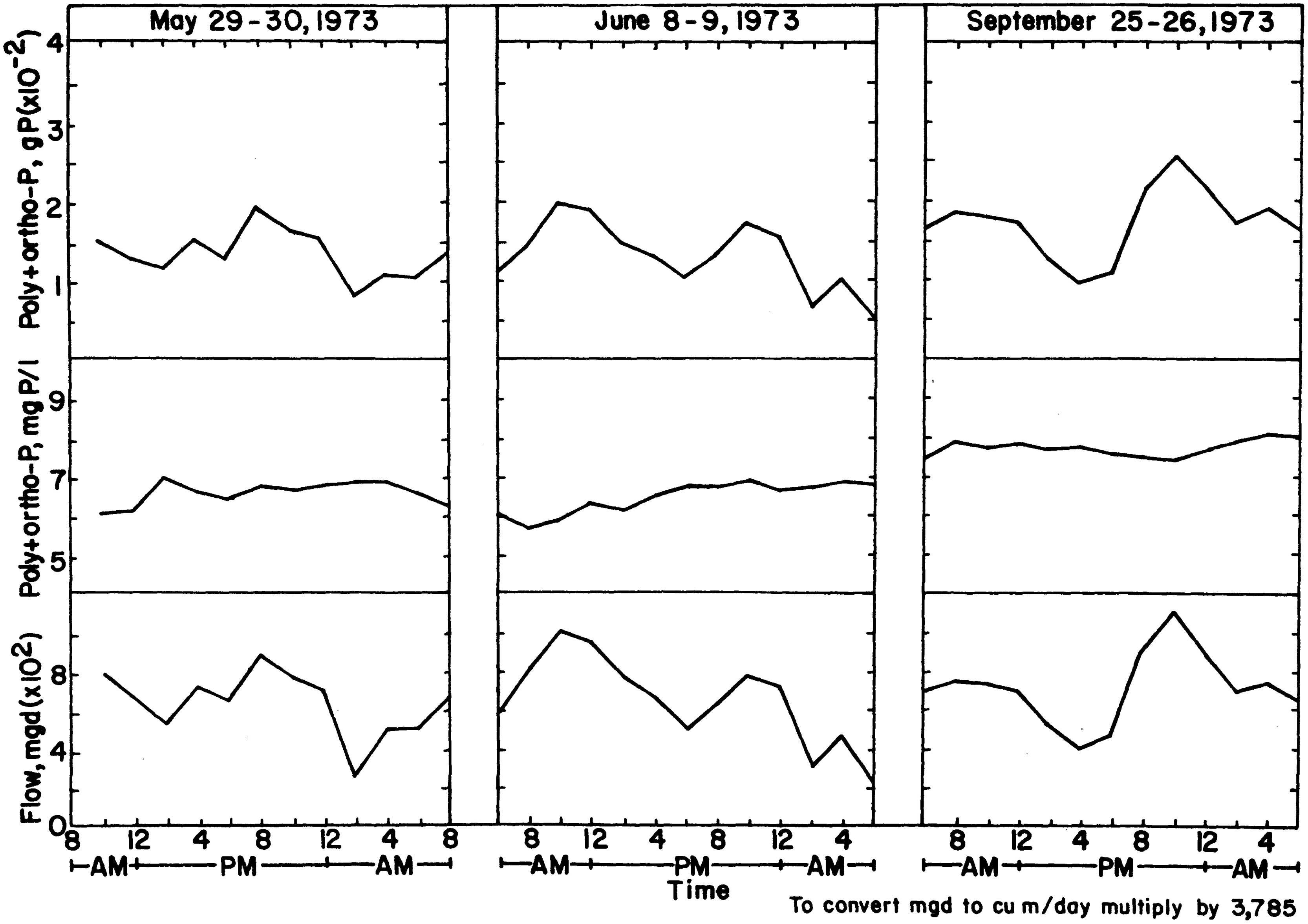

FIGURE 15. DIURNAL PHOSPHORUS AND FLOW VARIATION OF SECONDARY PLANT EFFLUENT

TABLE X. FIELD TEST SYSTEM STUDIES - OPERATIONAL CHARACTERISTICS

Day of Operation	Date	Unit 1 - F-1(-325)				Unit 2 - F-1(-100)				Columns - F-1(28-48)		
		Flow Rate	Detention Time		Alumina Dose	Flow Rate	Detention Time		Alumina Dose	Thru-Put Volume	Load Rate	Det Time
		gph*	Mix min	Sed hr	g/gal#	gph	Mix min	Sed hr	g/gal	gal*	gpm/sq ft+	min/column
Run S-1 - Fresh Alumina												
1	6/18	29.7	25	2.5	5.2	29.8	25	2.5	6.7	68	0.6	36
2	6/19	30.8	24	2.4	5.0	30.9	24	2.4	6.5	190	0.5	44
3	6/20	30.9	24	2.4	5.0	31.4	24	2.4	6.4	279	0.4	55
4	6/21	31.1	24	2.4	5.0	31.2	24	2.4	6.4	664	1.6	14
5	6/22	30.9	24	2.4	5.0	31.5	24	2.4	6.4	969	1.3	17
6	6/23	31.5	24	2.4	4.9	31.6	24	2.4	6.4	1,351	1.6	14
7	6/24	29.5	25	2.5	5.2	28.7	26	2.6	7.0	1,821	2.0	11
8	6/25	26.7	28	2.8	5.8	27.8	27	2.7	7.2	2,129	1.3	17
9	6/26	25.8	29	2.9	6.0	26.6	28	2.8	7.5	2,225	0.4	55
10	6/27	25.5	29	2.9	6.0	24.7	30	3.0	8.1	2,365	0.6	36
11	6/28	23.1	32	3.2	6.7	23.0	32	3.2	8.7	2,621	1.1	20
12	6/29	22.8	33	3.3	6.8	21.6	34	3.5	9.3	2,865	1.0	22
13	6/30	22.0	34	3.4	7.0	20.8	36	3.6	9.7	3,208	1.5	15
14	7/1	21.4	35	3.5	7.2	20.0	37	3.7	10.0	3,482	1.1	20
15	7/2	19.7	38	3.8	7.8	19.0	39	3.9	10.5	3,869	1.6	14
16	7/3	18.7	40	4.0	8.2	17.8	42	4.2	11.3	4,289	1.7	13
17	7/4	29.6	25	2.5	5.2	30.9	24	2.4	6.5	4,328	2.5	9
										1st column removed; 2nd column became 1st & new column added.		
										4,701	1.7	13
18	7/5	30.3	25	2.5	5.1	30.9	24	2.4	6.5	4,747	0.2	109
19	7/6	28.5	26	2.6	5.4	29.6	25	2.5	6.8	5,125	1.6	14
20	7/7	31.1	24	2.4	5.0	29.5	25	2.5	6.8	5,575	1.9	12

*To convert gph to l/hr or gal to l multiply by 3.785.
#To convert g/gal to g/l multiply by 0.264.
+To convert gpm/sq ft to l/min/sq m multiply by 40.7.

TABLE X(cont.). FIELD TEST SYSTEM STUDIES - OPERATIONAL CHARACTERISTICS

Day of Operation	Date	Unit 1 - F-1(-325)				Unit 2 - F-1(-100)				Columns - F-1(28-48)		
		Flow Rate gph*	Detention Time Mix min	Detention Time Sed hr	Alumina Dose g/gal#	Flow Rate gph	Detention Time Mix min	Detention Time Sed hr	Alumina Dose g/gal	Thru-Put Volume gal*	Load Rate gpm/sq ft+	Det Time min/column
Run S-1 - Fresh Alumina (cont.)												
21	7/8	30.9	24	2.4	5.0	30.6	24	2.4	6.6	6,089	2.2	10
22	7/9	30.1	25	2.5	5.1	30.8	24	2.4	6.5	6,484	1.7	13
23	7/10	31.4	24	2.4	4.9	30.9	24	2.4	6.5	6,907	1.8	12
24	7/11	30.5	25	2.4	5.0	30.1	25	2.5	6.6	7,339	1.8	12
25	7/12	31.1	24	2.4	5.0	31.2	24	2.4	6.4	7,629	1.2	18
26	7/13	31.2	24	2.4	4.9	30.9	24	2.4	6.5	8,031	1.7	13
27	7/14	31.7	23	2.4	4.9	30.8	24	2.4	6.5	8,416	1.6	14
28	7/15	31.7	23	2.4	4.9	31.2	24	2.4	6.4	8,756	1.4	16
29	7/16	31.1	24	2.4	5.0	31.2	24	2.4	6.4	9,073	1.3	17
30	7/17	30.9	24	2.4	5.0	31.1	24	2.4	6.4	9,307	1.0	22
31	7/18	31.4	24	2.4	4.9	30.8	24	2.4	6.5	9,385	1.0	22
Run S-2 - Regenerated Alumina												
1	9/28	30.9	24	2.4	9.4	31.9	23	2.3	9.3	71	0.7	31
2	9/29	31.4	24	2.4	9.2	31.4	24	2.4	9.4	555	2.1	10
3	9/30	31.7	23	2.4	9.1	31.6	24	2.4	9.4	939	1.6	14
4	10/1	31.7	23	2.4	9.1	31.4	24	2.4	9.4	1,176	1.0	22
5	10/2	31.7	24	2.4	9.3	31.1	24	2.4	9.5	1,472	1.3	17
6	10/3	31.6	23	2.4	9.1	31.7	23	2.4	9.3	1,959	2.2	10
7	10/4	31.1	24	2.4	9.3	31.4	24	2.4	9.4	2,549	2.4	9
8	10/5	30.1	25	2.5	9.6	30.9	24	2.4	9.6	2,992	1.8	12
9	10/6	31.7	23	2.4	9.1	32.0	23	2.4	9.2	3,408	1.8	12
10	10/7	31.1	24	2.4	9.3	31.1	24	2.4	9.5	3,850	1.8	12
11	10/8	31.1	24	2.4	9.3	31.1	24	2.4	9.5	4,081	1.0	22
12	10/9	30.9	24	2.4	9.4	31.2	24	2.4	9.5	4,288	0.9	24
13	10/10	30.9	24	2.4	9.4	31.2	24	2.4	9.5	4,312	1.2	18

*To convert gph to l/hr or gal to l multiply by 3.785.
#To convert g/gal to g/l multiply by 0.264.
+To convert gpm/sq ft to l/min/sq m multiply by 40.7.

TABLE XI. QUALITY OF SECONDARY TREATMENT PLANT EFFLUENT

Day of Oper-ation	Date	Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
			NH_3	Org	NO_3	NO_2				
		mg P/1	mg N/1				mg/1		jtu	
Run S-1 - Fresh Alumina										
1	6/18	6.70	0.80	0.46	8.0	0.24	32	8	5.5	7.5
2	6/19	7.70	1.13	0.90	8.3	0.15	32	16	5.0	7.8
3	6/20	7.10	0.49	1.19	11.4	0.07	16	10	3.5	7.9
4	6/21	7.30	1.40	0	12.2	0.11	20	18	4.6	7.9
5	6/22	8.00	1.45	0.23	13.9	0.12	24	2	3.8	7.4
6	6/23	7.30	1.20	1.04	13.7	0.15	68	12	12	7.1
7	6/24	7.30	1.78	0.18	14.2	0.21	32	4	4.2	6.9
8	6/25	8.10	0.99	0.41	15.8	0.13	43	14	11	7.5
9	6/26	7.30	1.55	0.13	13.7	0.14	51	20	6.2	7.1
10	6/27	7.70	1.40	0.56	12.5	0.14	23	2	6.5	7.5
11	6/28	6.50	1.28	0.40	13.0	0.13	51	22	6	7.6
12	6/29	6.40	0.95	0.59	15.5	0.14	23	22	4.7	7.7
13	6/30	6.40	0.80	0.60	15.7	0.21	39	18	3.1	7.5
14	7/1	8.60	1.67	0.22	14.5	0.22	20	8	4.3	7.6
15	7/2	7.80	1.48	0.06	13.3	0.16	23	8	2.7	7.5
16	7/3	8.30	1.55	0.13	12.7	0.17	24	16	3.3	7.7
17	7/4	8.00	0.52	0.88	13.5	0.08	28	0	4.8	7.6
18	7/5	7.70	0.95	0.03	12.7	0.06	16	14	3.5	7.6
19	7/6	6.30	0.78	1.32	15.3	0.16	43	16	9.8	7.6
20	7/7	8.90	1.53	0.30	13.7	0.22	20	28	4.5	7.6
21	7/8	8.10	2.09	0	16.1	0.22	23	4	3.3	7.5
22	7/9	8.10	1.50	0	15.5	0.15	24	0	2.8	7.6
23	7/10	7.50	4.40	0.90	8.3	0.51	47	0	6.8	7.6
24	7/11	6.80	2.55	0	12.6	0.18	20	0	3.8	7.6
25	7/12	6.10	1.73	0	12.7	0.14	31	0	6.1	7.5
26	7/13	7.90	1.05	1.05	13.0	0.15	23	0	3.2	7.5
27	7/14	9.00	1.78	0	14.0	0.12	24	0	2.5	7.6
28	7/15	8.80	1.90	0.62	15.5	0.17	16	0	2.4	7.6
29	7/16	8.90	0.98	0.14	15.7	0.08	24	0	1.9	7.6
30	7/17	8.90	2.15	0	16.1	0.14	15	6	4.3	7.6
31	7/18	8.60	2.48	0	14.0	0.21	27	0	2.7	7.6
Run S-2 - Regenerated Alumina										
1	9/28	7.50	0.55	0.29	10.7	0.02	47	0	2.8	8.1
2	9/29	7.20	0.70	0.42	8.8	0.03	47	0	3.4	7.3
3	9/30	5.50	0.78	0.76	11.0	0.03	8	0	2.6	7.3
4	10/1	6.50	0.53	0.45	10.8	0.02	16	0	5.8	7.7
5	10/2	6.90	0.15	0.55	11.0	0.02	20	0	28	7.3
6	10/3	7.20	0.52	0.18	12.8	0.03	24	0	3.5	7.7
7	10/4	5.80	0.40	0.44	11.7	0.04	12	0	4.1	7.3
8	10/5	5.80	0.20	0.92	9.7	0.07	54	0	3.4	7.3
9	10/6	5.80	1.47	0	10.9	0.08	16	42	4.1	7.2
10	10/7	5.40	1.00	0	11.1	0.08	12	18	3	7.2
11	10/8	6.10	0.15	0.69	11.7	0.03	12	32	2.5	7.2
12	10/9	6.10	0.65	1.17	11.7	0.06	28	30	11	7.2
13	10/10	7.00	1.45	0	12.2	0.15	24	16	3.6	7.2

TABLE XII. FIELD RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES - QUALITY CHARACTERISTICS

Day of Operation	Date	Unit 1 - F-1(-325)									Unit 2 - F-1(-100)								
		Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH	Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
			NH_3	Org	NO_3	NO_2						NH_3	Org	NO_3	NO_2				
		mg P/l	mg N/l				mg/l		jtu		mg P/l	mg N/l				mg/l		jtu	
Run S-1 - Fresh Alumina																			
1	6/18	1.70	0.82	0.86	8.0	0.19	28	54	6	8.2	1.30	1.05	0.07	8.2	0.22	36	24	13	8.0
2	6/19	1.70	0.94	0.18	8.5	0.20	12	36	80	8.1	1.10	1.55	0	7.7	0.16	24	14	10	8.1
3	6/20	1.20	1.16	0	10.4	0.14	12	74	70	8.0	1.10	1.12	0	9.2	0.09	20	10	10	7.7
4	6/21	1.76	1.05	0	11.9	0.13	16	68	65	8.0	3.90	0.65	0.47	12.7	0.10	16	18	9	8.0
5	6/22	2.16	1.12	0	12.9	0.15	20	74	80	7.7	2.20	0.98	0.42	13.5	0.11	16	18	14	7.6
6	6/23	2.14	0.76	0.08	13.7	0.16	20	68	85	7.9	2.10	1.05	0	13.0	0.17	20	14	14	7.8
7	6/24	2.22	2.36	0	12.7	0.27	20	60	70	7.1	2.20	1.80	0	13.0	0.24	24	2	13	7.1
8	6/25	3.86	0.79	0	13.0	0.14	28	46	50	8.1	2.30	0.71	0.27	12.8	0.11	24	12	11	8.0
9	6/26	2.87	1.28	0	12.8	0.17	27	62	50	7.9	2.00	0.99	0	13.3	0.16	39	26	12	7.9
10	6/27	1.62	1.10	0	12.1	0.17	8	62	80	8.1	1.60	1.00	0.12	12.5	0.14	19	8	10	8.3
11	6/28	1.28	0.65	0.19	14.5	0.18	66	114	120	8.0	1.50	0.64	0.76	15.0	0.15	47	24	14	8.0
12	6/29	1.34	0.96	0	14.9	0.19	20	112	120	8.2	1.30	1.00	0.26	14.9	0.17	20	32	16	8.2
13	6/30	1.24	1.12	0	14.2	0.21	12	114	130	8.2	1.20	1.02	0.10	13.0	0.24	28	28	12	8.2
14	7/1	1.28	1.20	0	14.3	0.29	4	170	160	8.1	0.90	1.83	0	13.7	0.33	4	38	28	8.2
15	7/2	0.86	1.12	0	13.5	0.17	20	110	110	8.0	1.10	1.05	0.07	12.7	0.21	12	34	18	8.1
16	7/3	0.76	0.95	0.17	12.6	0.17	20	182	150	8.2	0.80	1.05	0.07	12.7	0.21	24	26	12	8.2
17	7/4	1.62	0.65	0.19	14.8	0.13	24	0	85	8.1	1.50	0.33	0.79	14.0	0.15	16	8	18	8.1
18	7/5	1.42	0.90	0	13.8	0.08	16	118	110	8.2	2.50	0.80	0.04	13.3	0.08	28	26	14	8.0
19	7/6	1.17	0.61	0.37	15.3	0.17	16	90	100	8.2	1.90	0.61	0.23	14.8	0.18	0	18	15	8.1
20	7/7	1.24	1.52	0	12.7	0.22	8	108	8	8.1	3.40	1.34	0	12.0	0.24	0	20	12	8.0
21	7/8	1.28	1.87	0	14.9	0.26	8	56	6	8.1	0.52	1.77	0	15.8	0.31	4	4	12	8.1
22	7/9	1.42	1.54	0	15.5	0.18	8	26	75	8.0	0.80	1.45	0	15.7	0.21	16	0	3	8.1
23	7/10	1.60	4.70	0.60	8.9	0.24	24	0	38	8.2	1.61	4.50	0.82	8.3	0.42	31	4	16	8.3
24	7/11	1.69	1.89	0	12.3	0.20	16	34	90	8.1	1.24	3.15	0	11.7	0.27	12	0	23	8.0
25	7/12	1.52	1.03	0	12.5	0.15	16	34	70	8.0	0.54	1.00	0.12	12.2	0.16	27	0	12	8.1
26	7/13	4.26	0.93	0.65	12.8	0.18	27	44	65	7.9	1.96	1.03	0.37	13.3	0.22	20	0	13	8.0

TABLE XII(cont.). FIELD RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES - QUALITY CHARACTERISTICS

Day of Operation	Date	Unit 1 - F-1(-325)									Unit 2 - F-1(-100)								
		Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH	Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
			NH_3	Org	NO_3	NO_2						NH_3	Org	NO_3	NO_2				
		mg P/l	mg N/l				mg/l		jtu		mg P/l	mg N/l				mg/l		jtu	
Run S-1 - Fresh Alumina (cont.)																			
27	7/14	2.27	1.38	0	14.3	0.14	20	60	80	8.1	2.50	1.18	0	14.1	0.17	24	2	12	8.1
28	7/15	2.02	2.03	0	15.7	0.22	16	64	80	8.0	2.40	1.77	0	15.5	0.26	20	0	15	8.0
29	7/16	1.88	0.82	0	17.4	0.09	8	48	70	8.1	2.51	0.78	0	15.8	0.14	16	0	12	8.2
30	7/17	2.14	1.99	0	15.4	0.15	15	64	70	7.8	2.82	1.69	0	17.5	0.21	15	6	11	7.9
31	7/18	1.78	2.12	0	13.3	0.28	27	92	100	8.0	2.50	2.40	0	14.9	0.35	23	0	19	8.0
Run S-2 - Regenerated Alumina																			
1	9/28	3.60	0.20	1.48	10.4	0.04	36	350	210	8.4	2.80	0.70	0.70	11.7	0.03	43	78	64	8.3
2	9/29	1.50	0.72	0	9.8	0.06	43	92	95	8.0	2.00	0.50	0.34	9.7	0.04	31	0	18	8.2
3	9/30	0.90	0.45	0	12.2	0.09	16	40	70	8.3	1.60	0.49	0.07	12.2	0.06	8	0	17	8.1
4	10/1	1.50	0.23	0.05	11.3	0.12	0	140	130	8.5	1.60	0.22	0.90	10.6	0.03	12	16	27	8.4
5	10/2	1.20	0.35	0.07	10.2	0.12	12	118	140	8.4	1.10	0.52	0	11.0	0.05	24	0	11	8.1
6	10/3	1.50	0.63	0	11.7	0.05	24	104	120	8.6	1.40	0.48	0	11.8	0.05	35	28	23	8.4
7	10/4	1.30	0.98	0	13.2	0.08	12	26	60	8.3	1.40	0.72	0.12	12.7	0.09	12	0	18	8.0
8	10/5	1.30	1.07	0	10.7	0.07	54	0	120	8.3	1.60	1.18	0	10.3	0.08	46	0	18	8.1
9	10/6	1.10	0.80	0	10.7	0.09	8	86	80	8.3	1.40	1.02	0	10.6	0.09	8	26	14	8.0
10	10/7	1.30	0.90	0	12.7	0.09	8	110	100	8.2	1.40	0.72	0	11.7	0.11	8	40	19	8.0
11	10/8	1.40	0.50	0	10.9	0.02	8	78	70	8.2	2.10	0.52	0.18	11.2	0.04	16	28	15	8.0
12	10/9	1.30	0.38	0.38	12.9	0.05	16	100	90	8.4	1.30	0.40	0.16	12.9	0.06	20	36	18	8.2
13	10/10	1.60	1.15	0	11.7	0.06	0	124	120	8.3	1.70	1.12	0	8.6	0.07	4	48	40	8.1

TABLE XIII. FIELD COLUMN TEST SYSTEM STUDIES - QUALITY CHARACTERISTICS

Day of Operation	Date	Column 1 - F-1(28-48)									Column 2 - F-1(24-48)								
		Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH	Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
			NH_3	Org	NO_3	NO_2						NH_3	Org	NO_3	NO_2				
		mg P/l	mg N/l				mg/l		jtu		mg P/l	mg N/l				mg/l		jtu	
									Run S-1 - Fresh Alumina										
1	6/18	0	0.45	0.11	7.7	0.26	28	50	29	10.0	0	0.49	0.07	8.0	0.23	65	300	140	11.0
2	6/19	0	0.80	0.42	8.9	0.17	20	0	38	9.3	0	1.00	0	8.7	0.47	36	28	27	8.1
3	6/20	0	0.93	0	10.0	0.09	12	8	4.3	7.9	0	0.47	0.09	9.8	0.10	12	4	6.8	9.1
4	6/21	0	0.68	0	12.5	0.11	24	0	7.8	8.0	0	0.75	0	13.0	0.06	4	6	3.3	9.8
5	6/22	0.10	0.99	0	14.3	0.11	24	0	2.3	7.8	0	0.48	0	12.8	0.11	12	0	8	7.9
6	6/23	0.21	0.41	0.43	14.5	0.16	32	0	5.5	7.9	0	0.41	0.15	13.3	0.16	8	0	1	8.1
7	6/24	0.45	1.75	0	13.3	0.26	24	150	45	7.0	0	1.08	0	13.3	0.25	24	0	1.5	7.2
8	6/25	0.78	0.68	0.16	12.6	0.13	28	32	4.2	8.1	0	0.55	0	13.8	0.12	24	2	2.2	7.8
9	6/26	4.56	0.95	0.17	13.3	0.17	35	0	2	7.9	0	0.65	0.19	13.2	0.18	31	14	1.4	8.0
10	6/27	0.80	1.12	0.14	12.7	0.24	31	6	4	8.0	0	0.76	0.08	12.5	0.35	12	0	1.2	8.1
11	6/28	1.50	0.45	0.95	14.0	0.08	47	24	8.2	8.0	0	0.34	0.22	14.4	0.08	43	16	2	7.9
12	6/29	2.45	0.64	0.34	15.3	0.11	20	28	6.4	7.9	0	0.45	0.25	14.3	0.08	0	14	1.3	7.9
13	6/30	3.75	1.45	0	15.8	0.15	28	26	6.8	8.1	0	0.64	0.06	12.8	0.16	16	22	0.8	8.0
14	7/1	2.75	1.10	0	14.9	0.28	4	28	8.2	7.8	0.01	0.50	0	14.9	0.33	4	24	1.0	8.0
15	7/2	5.53	0.72	0.40	14.3	0.14	23	26	3.3	8.1	0.90	0.85	0	14.6	0.11	20	20	4.3	7.9
16	7/3	6.33	1.10	0.30	13.7	0.21	24	22	2.6	7.9	0.30	0.78	0.34	12.9	0.21	20	18	1.8	8.0
17	7/4	5.90	0.32	0.66	14.4	0.03	28	-	1.8	8.2	0.30	0.45	0.39	14.5	0.01	12	-	1.5	8.1
									1st column removed; 2nd column became 1st & new column added										
		0.10	0.38	0.18	16.4	0.01	24	2	4.7	8.1	0	0.10	0.46	14.1	0.02	16	0	2.3	9.8
18	7/5	0.80	0.98	0.14	13.3	0.04	16	8	12	8.1	0	1.26	0	14.8	0.03	8	24	1.7	8.0
19	7/6	0.75	0.51	0	13.7	0.52	31	22	8	8.2	0	0.45	0.81	15.7	0.34	20	8	1.8	8.3
20	7/7	1.98	1.19	0	12.7	0.32	16	38	11	8.0	0	1.04	0	14.2	0.26	12	12	2	8.0
21	7/8	2.60	0.80	0.60	15.7	0.37	12	20	12	7.9	0.06	0.77	0	15.7	0.36	16	0	1.8	8.0
22	7/9	4.33	0.84	0.14	15.8	0.15	16	0	5.6	7.8	0.03	0.86	0	16.3	0.10	24	0	1	7.9
23	7/10	5.25	4.55	0.21	9.2	0.38	24	0	12	8.0	0.03	4.50	0	8.9	0.42	28	0	2.1	8.0
24	7/11	5.68	1.25	0	13.0	0.36	20	0	5.2	7.8	0.02	1.65	0	13.5	0.39	12	0	1	7.1

TABLE XIII(cont.). FIELD COLUMN TEST SYSTEM STUDIES - QUALITY CHARACTERISTICS

Day of Operation	Date	Column 1 - F-1(28-48)										Column 2 - F-1(28-48)									
		Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH	Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
			NH_3	Org	NO_3	NO_2						NH_3	Org	NO_3	NO_2				
		mg P/l	mg N/l				mg/l		jtu		mg P/l	mg N/l				mg/l		jtu	
Run S-1 - Fresh Alumina (cont.)																					
25	7/12	5.20	0.38	0.18	13.7	0.08	31	0	1.2	7.8	0.26	0.53	0.31	14.0	0.08	32	0	1	7.9
26	7/13	5.68	0.78	0.84	14.4	0.12	20	0	3.8	7.6	0.50	0.80	0.46	15.5	0.03	32	0	6	7.7
27	7/14	7.95	0.98	0	15.8	0.09	24	0	8.2	7.8	1.16	0.56	0.42	15.0	0.04	20	0	2.6	7.9
28	7/15	7.23	0.71	0.13	15.9	0.04	20	0	5.3	7.9	1.23	1.16	0	16.7	0.04	16	0	2.1	7.8
29	7/16	7.57	0.47	0.37	15.2	0	0	0	3.6	7.7	1.24	0.50	0.06	16.1	0	12	0	1.6	8.0
30	7/17	7.92	0.32	0.52	16.7	0.11	15	8	1.2	7.7	1.66	0.68	0.30	17.1	0.03	15	0	1	7.7
31	7/18	7.77	1.34	0	15.3	0.32	30	28	2.3	7.8	1.87	1.52	0	16.1	0.39	23	2	2.1	7.7
Run S-2 - Regenerated Alumina																					
1	9/28	7.80	0.62	1.34	9.3	0.02	51	140	28	11.2	9.30	0.80	0.60	7.5	0.95	58	-	70	11.3
2	9/29	0.42	0.43	0.13	9.8	0.02	43	-	9	8.9	0.05	0.46	0.10	10.2	0.01	39	-	13	8.7
3	9/30	0.27	0.65	0	11.1	0.03	16	-	3.3	8.4	0.03	0.35	0	11.4	0.02	12	-	8	8.4
4	10/1	0.47	0.43	0.69	10.0	0.02	20	22	18	8.4	0.03	0.30	0	10.8	0.01	4	-	1	8.4
5	10/2	0.87	0.52	0	10.2	0.02	12	-	9.3	8.3	0.02	0.50	0	11.2	0.03	16	-	16	8.2
6	10/3	2.64	0.52	0.04	12.2	0.02	28	-	6.2	8.3	0.07	0.83	0	11.9	0.01	28	-	2.6	8.2
7	10/4	6.80	0.65	0.33	12.5	0.04	20	22	23	8.1	0.65	0.65	0.19	12.7	0.04	8	850	18	8.0
8	10/5	4.65	1.53	0	10.8	0.08	66	190	18	8.1	1.92	1.25	0	11.0	0.07	43	8	12	8.0
9	10/6	5.15	1.40	0	10.7	0.11	8	28	9	8.0	3.02	0.86	0	11.2	0.08	4	14	4	8.0
10	10/7	5.65	0.78	0	10.9	0.09	16	24	7.4	8.0	4.20	0.75	0	12.2	0.07	20	20	2.6	7.9
11	10/8	5.30	0.45	0.25	11.0	0.03	8	410	11	8.0	3.90	0.56	0	11.3	0.02	12	24	3.5	8.0
12	10/9	3.30	0.35	0	10.5	0.01	4	12	5.4	8.1	1.22	0.40	0	11.0	0.01	8	230	32	8.1
13	10/10	3.40	1.28	0	14.4	1.30	12	6	2.1	8.1	1.15	1.00	0	11.4	0.09	16	10	2.3	8.1

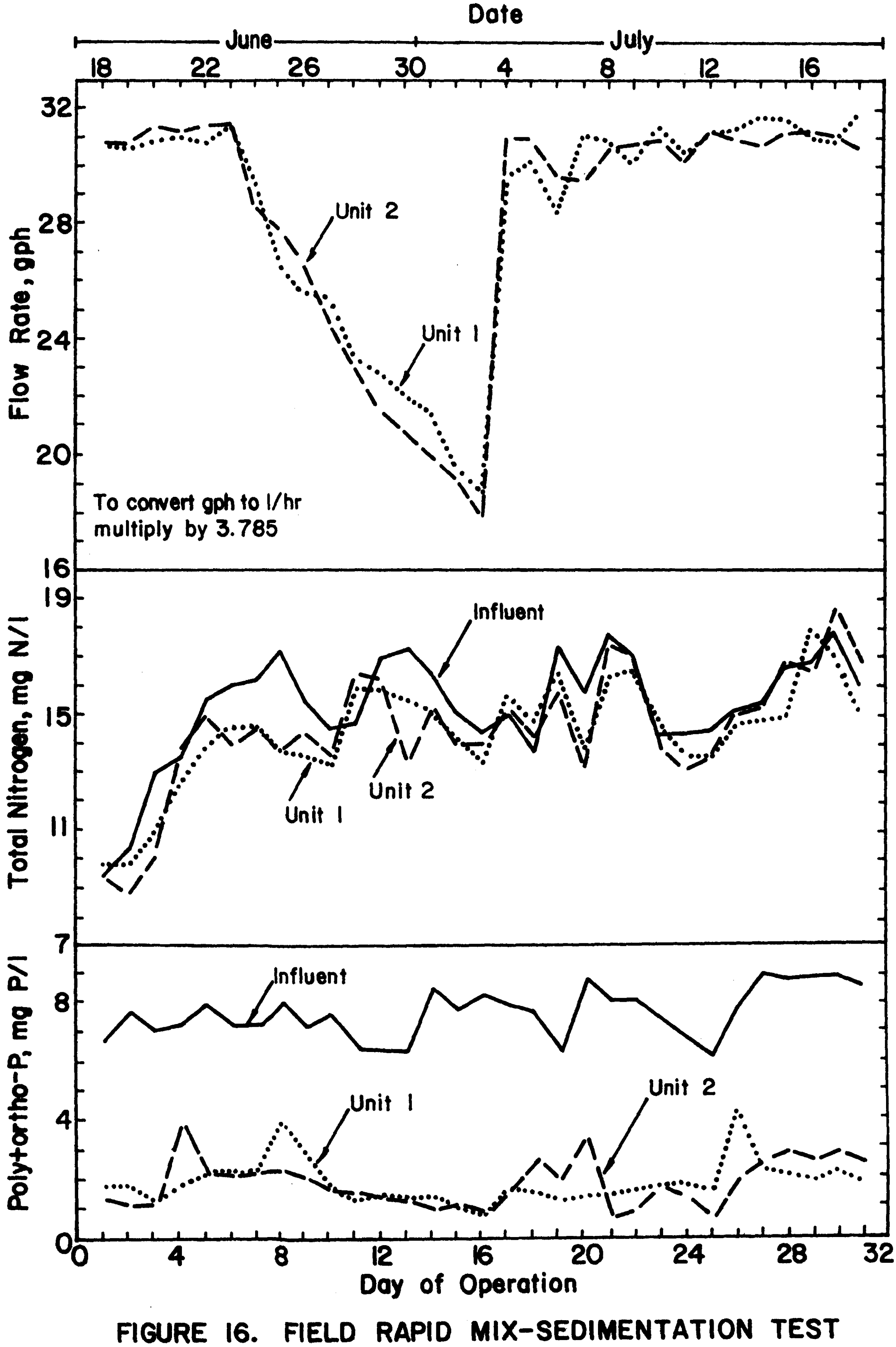

FIGURE 16. FIELD RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES - RUN S-1

in Unit 1 was controlled by means of a variable speed, multi-channel finger pump. Unfortunately, 1 of the 4 springs behind the pressure plate, which was used in conjunction with the fingers to press the tygon tubing during pumping, was broken on the 8th and 26th day of operation and as a consequence an insufficient amount of alumina was supplied to the unit. In Unit 2, the stirrer motor became overheated after it had operated for 4 days and caused its fuse to blow. When attempts to restore the motor operation failed (several fuses were blown in the process and the problem was later found to be related to the armature), the stirrer was replaced with a cone-driven unit. The new stirrer was not able to provide adequate agitation and auxiliary manual mixing was required periodically in order to remove excessive alumina from the mixing tank; however, the effectiveness of the system was not seriously affected. A new high-speed stirrer was procured and placed in operation on July 4 (the 17th day), however, it also failed after 5 days and was again replaced with the cone-driven unit.

The chemical dosing systems were initially adjusted to provide alumina doses* of 6.7 and 7.1 g/gal (1.8 and 1.9 g/l) to Units 1 and 2, respectively. The actual doses averaged 5.6 g/gal (1.5 g/l) for Unit 1 and 7.1 g/gal (1.9 g/l) for Unit 2 over the 31-day test period. The flow rate of the wet feeding system employed in Unit 1 had been adjusted in the laboratory with tap water and apparently this rate

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*These doses were based on the findings of the preliminary laboratory study shown in Table VIII (p.63-64). Considering both phosphorus removal efficiency and sorptive capacity, doses of 6.5 and 6.9 g/gal (1.7 and 1.8 g/l) were selected for the F-1 (-325) and F-1 (-100) aluminas; however, because the initial Poly+ortho-P concentration averaged 6.1 mg P/l in the laboratory study and was expected to average 6.3 mg P/l in the field study (Figure 15, June 8-9), the doses were adjusted to 6.7 and 7.1 g/gal (1.8 and 1.9 g/l).

could not be maintained with the mixture of alumina and distilled water, especially under the increased suction head which was required.

A flow rate of approximately 30 gph (114 l/hr) was employed with both units, however, when the system had been operated for about 6 days the rate was found to gradually decrease. The cause for this was not established until a microbial growth was observed in the inlet tubing; thereafter the tubes were cleaned daily and the flow rate was maintained at a relatively constant level. During the period of reduced flow, the residual Poly+ortho-P in the effluent from the units decreased by only a fraction of 1 mg P/l (Figure 16) despite the fact that the alumina dose was correspondingly significantly increased. By the end of the run an average of 21,053 gal (79,693 l) had passed through each unit, and 242.0 and 314.5 lb (109.8 and 142.8 kg) of F-1 (-325) and F-1 (-100) aluminas had been fed to Units 1 and 2, respectively.

Average values for each major parameter tested, computed from the data presented in Tables XII and XIII, are summarized below, together with the corresponding removal efficiency.

	Avg Concentration, mg/l*			Removal, %	
Parameter	Influent	Unit 1 F-1(-325)	Unit 2 F-1(-100)	Unit 1 F-1(-325)	Unit 2 F-1(-100)
Poly+ortho-P	7.68	1.78	1.78	76.8	76.8
NH_3-N	1.49	1.33	1.33	10.7	10.7
Org-N	0.40	0.11	0.16	72.5	60.0
NO_3-N	13.4	13.2	13.1	1.5	2.2
NO_2-N	0.16	0.18	0.20	-12.5	-25.0
COD	29	19	20	34.5	31.0
TSS	9	72	13	-700.0	-44.4

*The alumina doses averaged 5.6 and 7.1 g/gal (1.5 and 1.9 g/l) in Unit 1 and 2, respectively.

The average phosphorus removal in both units was 76.8 percent and was comparable to the values which had been obtained in the earier bench rapid mix-sedimentation studies, although the initial phosphorus concentration was lower (see Table VIII, p.63-64). The percent of Org-N removal also appeared to be substantial, however, it actually reflected only 0.2 to 0.3 mg N/1 reduction, which could have resulted from experimental error. When the concentration of total nitrogen* was considered (Figure 16), only minor changes were noted and the average value in the effluent from both units was only about 4 percent lower than the influent value. The removal of COD ranged from 31 to 34 percent, while TSS increased in the alumina-treated wastewater due to leakage of material; the extent of this leakage depended on the particle size employed and averaged in excess of 700 percent in Unit 1 and 44 percent in Unit 2. The alumina particles did not effectively settle in this experiment, even though the sedimentation tanks had been designed for a lower overflow rate than was experimentally determined.

The column test system was operated concurrently with the rapid mix-sedimentation units and was initially designed to consist of 4 columns; 2 of the columns were to be operated in series and the other 2 were to be added in stages when the lead column exhibited breakthrough of phosphorus and was removed from the system. Unfortunately, 1 of the columns was damaged by excessive pressure during the 1st day of Run S-1 and could not be repaired in time to be used again in this run. The operational and quality characteristics of Run S-1 are given in Tables X and XIII, respectively, and the quality of the secondary effluent which was fed to the columns is shown in Table XI. The columns were operated at an average hydraulic loading of 1.3 gpm/sq ft

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*The sum of NH_3-N, Org-N, NO_3-N, and NO_2-N.

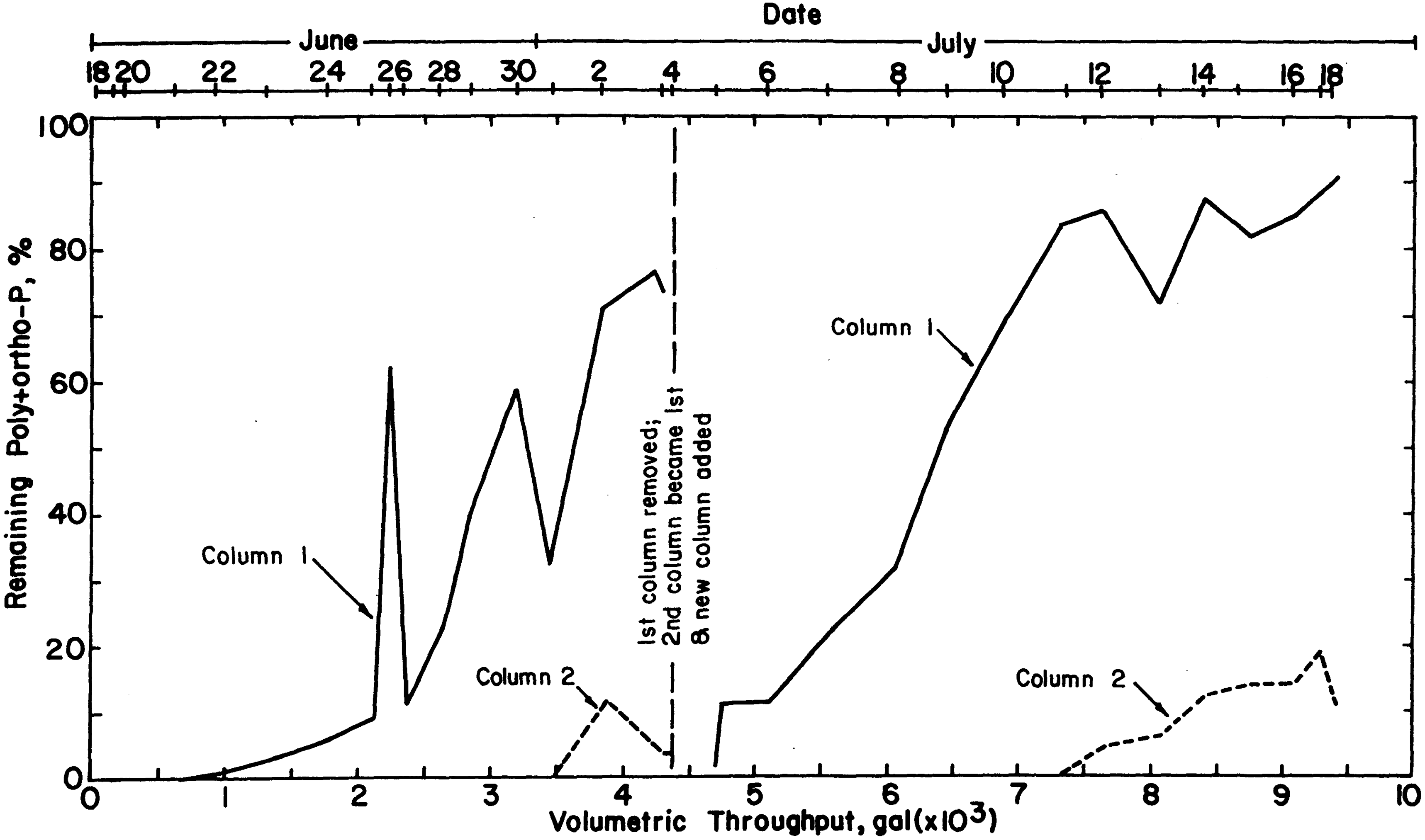
(53 l/min/sq m), and over the 31-day test period the 3 columns processed 9,385 gal (35,522 l) of effluent; considering that each column contained 25 lb (11.35 kg) of activated alumina, the corresponding alumina dose was 3.6 g/gal (1.0 g/l).

Phosphorus breakthrough curves for the 3 columns are plotted in Figure 17, and average values over the test period for each parameter tested and the corresponding removal efficiencies are given below.

	Avg Concentration, mg/l		
Parameter	Influent	Column 2 - F-1(28-48)	Removal, %
Poly+ortho-P	7.68	0.31	96.0
NH_3-N	1.49	0.87	41.6
Org-N	0.40	0.14	65.0
NO_3-N	13.4	13.8	-3.0
NO_2-N	0.18	0.18	0
COD	29	20	31.0
TSS	9	16*	-77.8*

*If the 1st-day effluent is not considered, the corresponding values would be 7 mg/l and +22.2 %.

The column system was able to produce a better quality effluent in terms of Poly+ortho-P (0.31 mg P/l compared to 1.78 mg P/l) and at an alumina dose which was 36 to 50 percent lower than used in the rapid mix-sedimentation system. If the run had been stopped on the 24th day of operation (July 11) when Column 2 (the 3rd column) began to breakthrough (Figure 17), the columns would have processed 7,339 gal (27,778 l) and the corresponding alumina dose would have been 4.6 g/gal (1.2 g/l), which was still significantly lower than the doses employed in the rapid mix-sedimentation system; at the same time the effluent Poly+ortho-P concentration would have averaged 0.07 mg P/l indicating a better than 99 percent removal. The removal of total nitrogen was less in the column system and over the total 31-day period it averaged less than 3 percent. The removal of COD was approximately



To convert gal to l multiply by 3.785

FIGURE 17. FIELD COLUMN TEST SYSTEM STUDIES - RUN S-1

the same and the concentration of TSS in the treated effluent was generally low, except in the beginning of the test run when the finer alumina particles were washed out of the column beds.

At the end of Run S-1 the used aluminas which had been removed from the sedimentation basins and the 3 columns were brought to the laboratory for regeneration. Part of these materials was employed in the regeneration study (see Figure 13, p.75), which is described later in this chapter, and the remaining aluminas were regenerated using the experimental conditions outlined in Table IX (p.76) for Run R-1. Sufficient F-1 (-325) and F-1 (-100) materials to enable operation of the rapid mix-sedimentation units for 2 wk and 2 of the columns were regenerated.

Run S-2 was started on September 28 and continued through October 10. Samples were again taken at 10:00 AM and 6:00 PM and the composites were analyzed for Poly+ortho-P, NH_3-N, Org-N, NO_3-N, NO_2-N, COD, TSS, turbidity, and pH. The procedures used in this run were essentially the same as those employed in Run S-1, and appropriate operational characteristics are listed in Table X (p.82-83).

F-1 (-325) and F-1 (-100) alumina doses* of 9.8 and 8.9 g/gal (2.6 and 2.4 g/l) were selected for Units 1 and 2, respectively. Although these doses were higher than those applied in Run S-1, they

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*These doses were based on the previously (p.90) selected values of 6.5 and 6.9 g/gal (1.7 and 1.8 g/l) for fresh F-1 (-325) and F-1 (-100) aluminas at an influent Poly+ortho-P concentration of 6.1 mg P/l. Since the Poly+ortho-P concentration was expected to average 7.8 mg P/l (Figure 15, p.81, September 25-26) and the weight increase of the 2 aluminas over the corresponding fresh materials was estimated as 18.73 and 1.27 percent, respectively (see Table IV, p.40; the regenerated aluminas were dried at 59° C for 7 days), the doses were adjusted to 9.8 and 8.9 g/gal (2.6 and 2.4 g/l).

reflected both a greater moisture content in the regenerated materials and an expected increase in the Poly+ortho-P concentration of the secondary plant effluent, and in fact provided the same dry alumina to phosphorus weight ratio as was employed in the 1st run. The actual alumina feed rates over the 13-day test period averaged 9.3 and 9.4 g/gal (2.5 and 2.5 g/l), corresponding to 7.9 and 9.3 g/gal (2.1 and 2.5 g/l) of fresh aluminas. A total volume of approximately 9,735 gal (36,847 l) of secondary plant effluent was treated by each unit at an average flow rate of 31.2 gph (118 l/hr), and since enough practical experience had been gained in the previous run, no operational difficulties were encountered during this test run.

Quality data pertaining to Run S-2 are presented in Table XI and XII (p.84-86) and Figure 18, and average values for each parameter tested are given below.

	Avg Concentration, mg/l*			Removal, %	
		Unit 1	Unit 2	Unit 1	Unit 2
Parameter	Influent	F-1(-325)	F-1(-100)	F-1(-325)	F-1(-100)
Poly+ortho-P	6.37	1.50	1.65	76.4	74.1
NH_3-N	0.66	0.64	0.66	3.0	0
Org-N	0.45	0.15	0.19	66.7	57.8
NO_3-N	11.1	11.4	11.2	-2.7	-0.9
NO_2-N	0.05	0.07	0.06	-40.0	-20.0
COD	24	18	20	25.0	16.7
TSS	11	105	23	-854.5	-109.1

*The alumina doses (fresh alumina basis) averaged 7.9 and 9.3 g/gal (2.1 and 2.5 g/l) in Units 1 & 2, respectively.

The average phosphorus removals of 76.4 and 74.1 percent for Units 1 and 2 were slightly lower than the 76.8 percent value obtained by both units in Run S-1. Also, because the actual average Poly+ortho-P concentration was only 6.4 mg P/l, rather than the anticipated 7.8 mg P/l, the regenerated alumina doses were correspondingly significantly

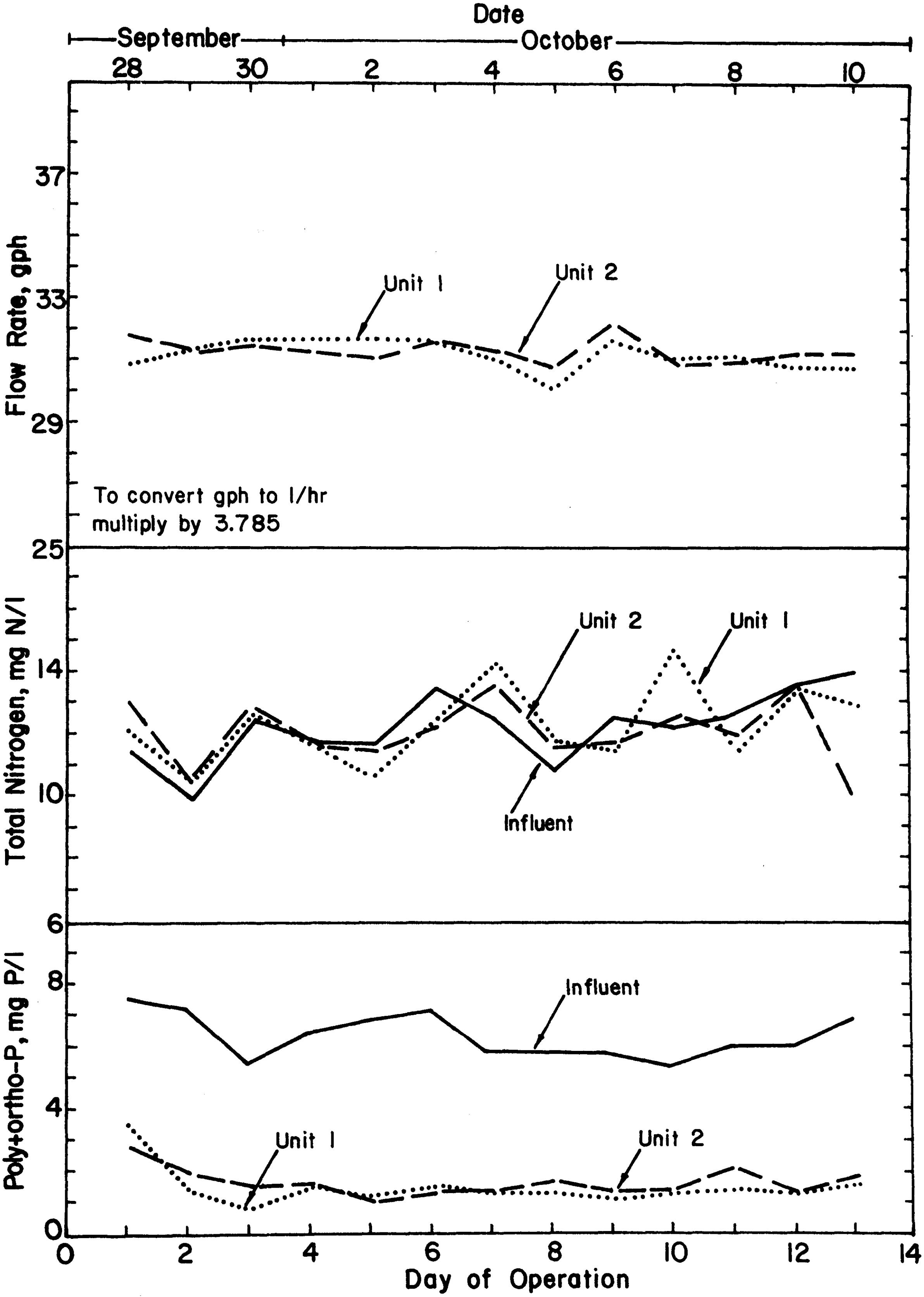
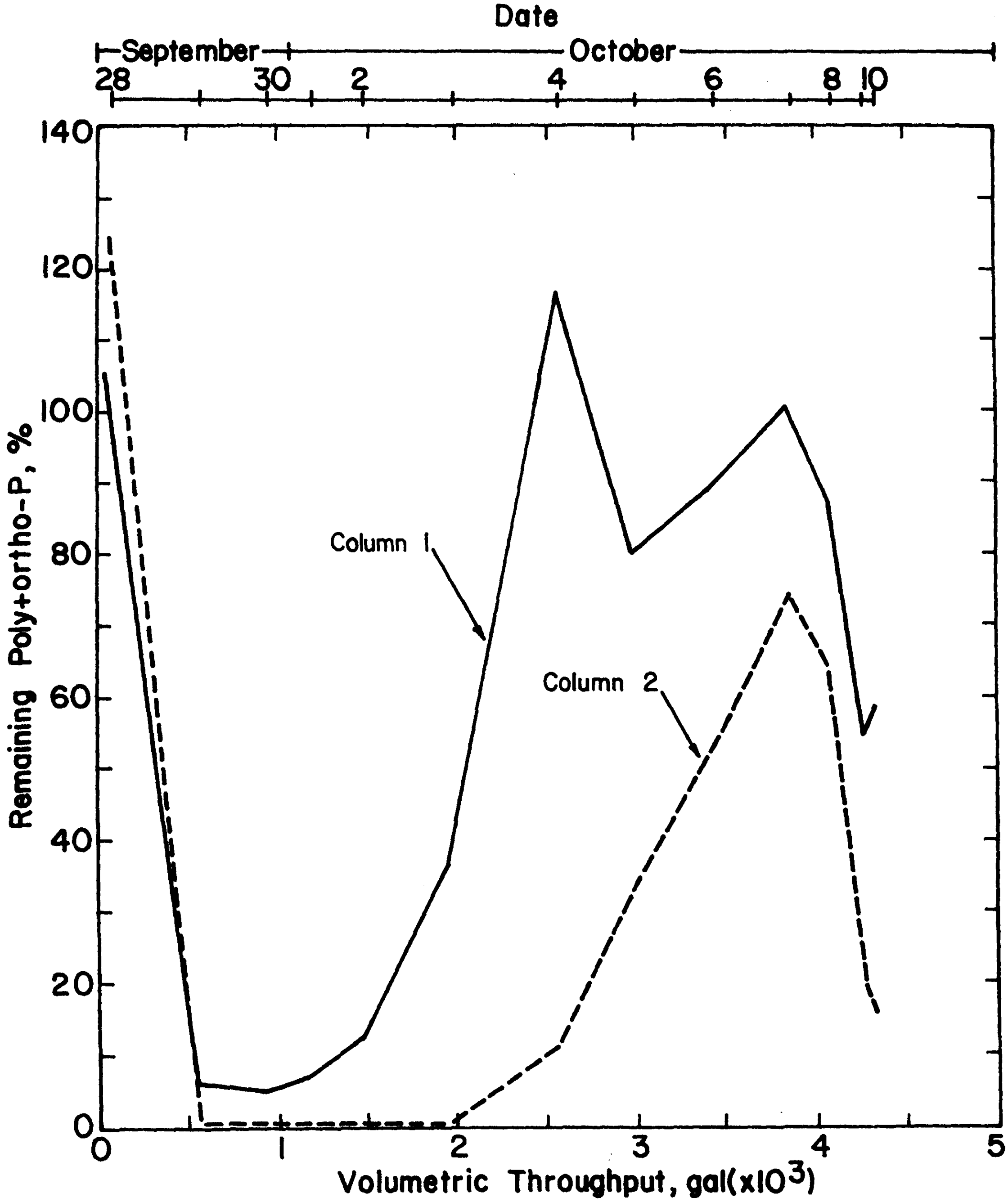


FIGURE 18. FIELD RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES - RUN S-2

higher; unfortunately, it was not feasible to adjust the alumina dosing rate during the run. Although it is not possible to determine from these data whether the regenerated aluminas had a reduced sorptive capacity, it is significant that the overdose which was actually applied did not result in a decreased phosphorus concentration in the effluent. It should also be pointed out that the Poly+ortho-P concentration of the effluent (Figure 18) remained essentially constant (in the neighborhood of 1.5 mg P/l) after the 3rd day, despite the fact that some of the influent phosphorus values were the lowest encountered in the field study. Again, little, if any, nitrogen was removed; in terms of total nitrogen the removal ranged from 0 in Unit 1 to 1.2 percent in Unit 2. The COD was reduced by 25 and 17 percent, and the TSS content increased by 854 and 110 percent, respectively, in Units 1 and 2. Twenty six percent of the total amount of TSS discharged from the units during the run was measured in samples collected during the 1st-day; if these samples were excluded from consideration, the TSS increases would have been similar to the values obtained in Run S-1.

The column test system in Run S-2 consisted of 2 columns containing regenerated alumina which were connected in series and were operated in the upflow mode. The study was conducted in a manner similar to Run S-1 and was continued until both columns were almost exhausted. The operational and quality characteristics are presented in Table X, XI and XIII, respectively, and breakthrough curves are plotted in Figure 19. Difficulty was encountered with clogging of the columns. During Run S-1 a lot of solid matter in the secondary effluent had been trapped on the beds and apparently was not removed during regeneration; in fact the bed material became more compact and partly agglomerated into lumps.



To convert gal to l multiply by 3.785

FIGURE 19. FIELD COLUMN TEST SYSTEM STUDIES - RUN S-2

When secondary effluent was charged to the columns during Run S-2 clogging and channelling were observed; as a result the run had to be interrupted on the 7th and 12th day of operation, the flange joints were opened, and the lumps were manually crushed. This problem was not noted during the laboratory studies using the bench column test system.

Average values for the experimental data are as follows:

Parameter	Avg Concentration, mg/l Influent	 Column 2 - F-1(28-48)	Removal, %
Poly+ortho-P	6.37	1.97	69.1
NH_3-N	0.66	0.67	-1.5
Org-N	0.45	0.07	84.4
NO_3-N	11.1	11.1	0
NO_2-N	0.05	0.11	-120
COD	24	20	20
TSS	11	89*	-709.1*

*If the 7th and 12th-day effluents are not considered, the corresponding values would be 7 mg/l and +36.4 %.

The 2 columns processed a total of 4,312 gal (16,321 l) of secondary effluent with an average Poly+ortho-P concentration of 1.97 mg P/l, which was higher than the values achieved by the rapid mix-sedimentation system. The average hydraulic loading was 1.5 gpm/sq ft (61 l/min/sq m) and the alumina dose was 5.3 g/gal (1.4 g/l), which was significantly lower than the doses employed in the rapid mix-sedimentation system [7.9 and 9.3 g/gal (2.1 and 2.5 g/l) of F-1 (-325) and F-1 (-100) on a fresh material basis]. The initial leakage of phosphorus (Figure 19) was attributed to incomplete water washing during the regeneration process. If the run had been stopped before a significant breakthrough of phosphorus had occurred, the 2 columns would have treated 1,959 gal (7,415 l) yielding an average phosphorus concentration of 0.04 mg P/l (a removal of 99.4 percent); the corresponding alumina dose, however, would had been 11.6 g/gal

(3.1 g/l). The reduction in total nitrogen and COD were respectively 2.5 and 20.0 percent, and the concentration of TSS in the treated wastewater was generally low, except when the columns were disturbed to overcome the clogging problem.

2. Laboratory Studies

A small portion of the used aluminas from Run S-2 was regenerated in the laboratory to provide material for Run S-3, which employed the bench test system. The F-1 (-325) and F-1 (-100) aluminas were regenerated using the 6-unit variable speed stirrer, and the F-1 (28-48) material was regenerated in 3 bench columns; the experimental conditions which were employed are outlined in Table IX (Run R-2). The use of the bench test system was considered appropriate because it had been found to adequately simulate the field test system; in addition, regeneration of all the materials that would have been needed for a field run would have required 6 to 8 wk, and consequently operational problems resulting from the onset of winter would have been present. The feed waste used in these studies was effluent from the Rolla treatment plant which was brought to the laboratory and stored in 1 or 2, 30-gal (114-l) epoxy-coated steel drums. The waste was stirred for 10 min prior to use.

The rapid mix-sedimentation study was conducted on March 3. F-1 (-325) and F-1 (-100) doses of 7.7 and 7.8 g/gal (2.0 and 2.1 g/l), corresponding to 7.1 and 7.7 g/gal (1.9 and 2.0 g/l) of fresh aluminas,*

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*The regenerated aluminas were dried at 104° C for 3 days. Considering that pre-wetted F-1 (-325) and F-1 (-100) aluminas dried at 104° C for 3 days showed a 4.77 percent weight gain and a 3.73 percent weight loss (Table IV, p.40), while the corresponding fresh aluminas dried at 104° C for 40 hr showed weight losses of 3.02 and 2.38 percent, the weight increase of the regenerated aluminas over the corresponding fresh materials was estimated to be 7.79 and 1.35 percent.

were employed in Units 1 and 2, respectively, and the liquid flow rate was adjusted to 1.0 gph (3.8 l/hr). Samples were taken at the end of 8 and 10 hr (approximately 3.5 and 4.5 detention times) after the units had been filled, and were analyzed for Poly+ortho-P, NH_3-N, Org-N, NO_3-N, NO_2-N, COD, TSS, turbidity, and pH. The operational characteristics and influent and effluent quality data pertaining to Run S-3 are presented in Table XIV, and summary values are given below.

Parameter	Avg Concentration, mg/l* Influent	 Unit 1 F-1(-325)	 Unit 2 F-1(-100)	Removal, % Unit 1 F-1(-325)	 Unit 2 F-1(-100)
Poly+ortho-P	3.98	1.08	1.08	72.9	72.9
NH_3-N	0.82	0.68	0.82	17.1	0
Org-N	0.30	0.34	0.52	-13.3	-73.3
NO_3-N	4.4	4.9	4.4	-11.4	0
NO_2-N	0.19	0.22	0.20	-15.8	-5.3
COD	28	38	27	-35.7	3.6
TSS	0	130	104	-	-

*The alumina doses (fresh alumina basis) were 7.1 and 7.7 g/gal (1.9 and 2.0 g/l) for Units 1 and 2, respectively.

✓ Unfortunately the strength of the secondary effluent used in Run S-3 was especially low, and consequently the results obtained in this run may not be fully comparable to those developed in the previous 2 field tests (Runs S-1 and S-2). Although the percent of phosphorus removal was somewhat lower in this run, the residual concentration was rather low compared to the values found in the field. Contrary to the other runs, the concentration of total nitrogen increased, while the reduction of COD was variable, ranging from -36 to +4 percent.

The column test system consisted of 2 columns, packed with 100 g (wet) regenerated alumina, which were operated in parallel and in the upflow mode. The run was conducted from February 5 to 11 and during this period samples were taken at frequent intervals and analyzed for

TABLE XIV. BENCH RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES - RUN S-3

Operational Characteristics

Date	Unit 1 - F-1(-325)				Unit 2 - F-1(-100)			
	Flow Rate gph*	Detention Time		Alumina Dose g/gal**	Flow Rate gph	Detention Time		Alumina Dose g/gal
		Mix min	Sed hr			Mix min	Sed hr	
3/3	0.96	16	2.0	7.7	0.90	17	2.0	7.8

*To convert gph to l/hr multiply by 3.785.
**To convert g/gal to g/l multiply by 0.264.

Quality Characteristics

Sample			Poly+ ortho P	Nitrogen				COD	TSS	Turb	pH
No.	Time of Operation hr#	Type		NH_3	Org	NO_3	NO_2				
			mg P/l	mg N/l				mg/l		jtu	
1	6	Influent	4.20	0.85	0.27	4.80	0.19	25	0	3	7.9
		Unit 1	1.10	0.90	0	5.00	0.22	36	122	132	8.4
		Unit 2	1.06	1.00	0.40	4.50	0.21	30	82	55	8.3
2	8	Influent	3.75	0.78	0.34	4.00	0.19	30	0	3	8.1
		Unit 1	1.05	0.45	0.67	4.80	0.23	41	138	133	7.1
		Unit 2	1.09	0.63	0.63	4.30	0.20	24	126	68	8.3

#After unit had been filled.

Poly+ortho-P only. The operational characteristics and phosphorus data are presented in Table XV, and phosphorus breakthrough curves are plotted in Figure 20. A total volume of 16.5 gal (62.5 l) secondary effluent was passed through each column at an average hydraulic loading rate of 0.301 gpm/sq ft (12.25 l/min/sq m), and the corresponding alumina dose (fresh alumina basis) was 4.9 g/gal (1.3 g/l).*

Considerable initial leakage of phosphorus was observed in both columns (Figure 20), however, once this had occurred, the effluent Poly+ortho-P concentration dropped to a very low level (below 0.1 mg P/l) where it remained for approximately one-half of the run; thereafter, the phosphorus concentration began to gradually increase and had reached the 1.0 to 1.2 mg P/l level by the end of the run. The average phosphorus removal ranged from 76.4 to 81.1 percent, but again the influent concentration was low (4.24 mg P/l average).

3. Alumina Loss

The physical loss of alumina, especially in the rapid mix-sedimentation test system, in addition to increasing the concentration of TSS in the effluent, constituted a significant economic consideration in evaluating the process. A study was therefore undertaken to determine these losses and was conducted using the bench test system and experimental conditions identical to Run S-3 (Table IX, p.76),

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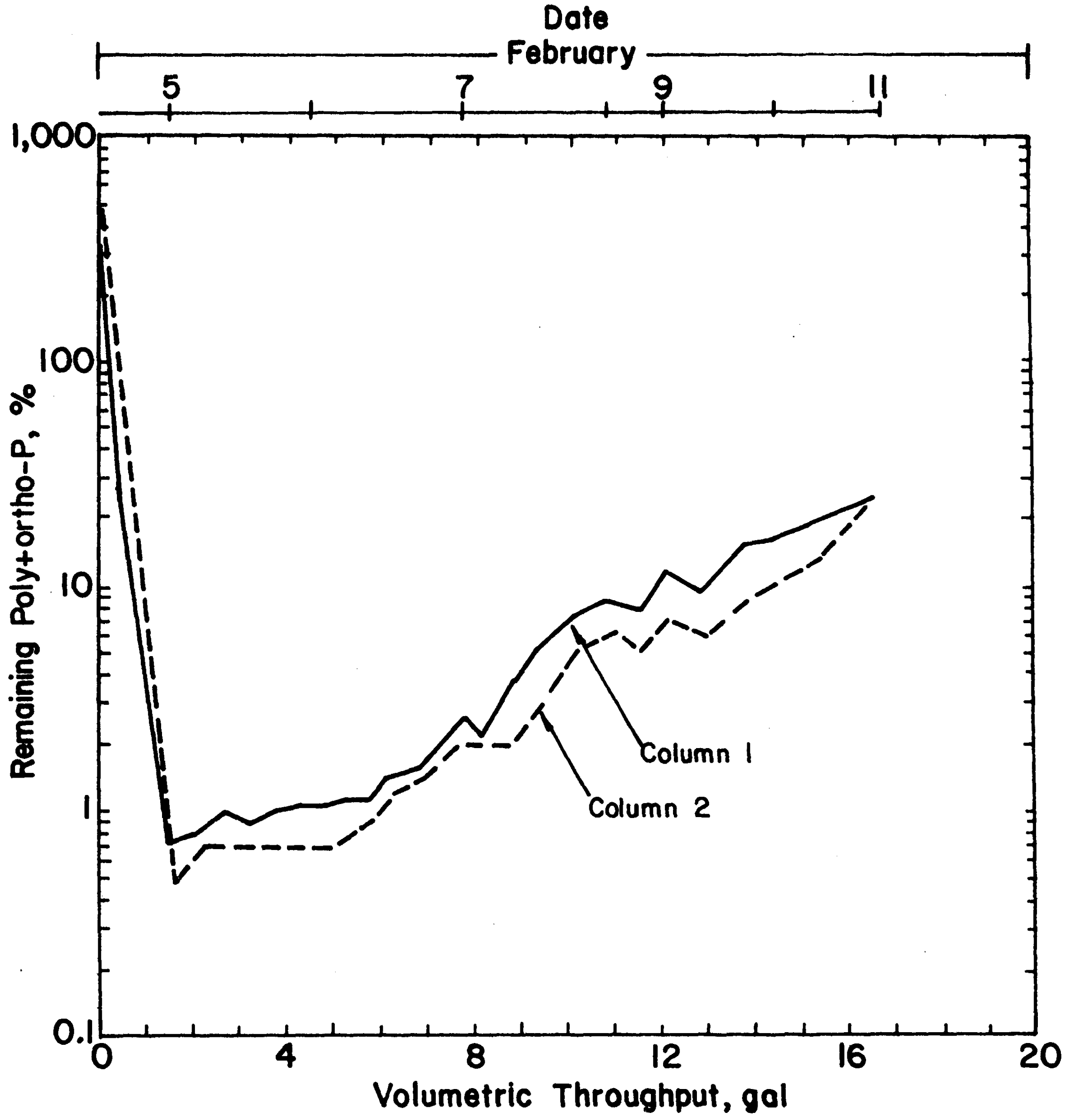
*Considering that 100 g wet alumina were equivalent to 81.6 g fresh alumina. Exhausted F-1 (28-48) alumina dried at 104° C for 47 hr showed a 23.58 percent weight loss, while fresh alumina dried at 104° C for 40 hr showed a 1.08 percent loss; consequently, the weight gain of the wet exhausted alumina was taken as the difference, or 22.5 percent (see Table IV, p.40).

TABLE XV. BENCH COLUMN TEST SYSTEM STUDIES - RUN S-3

Date	Sample		Influent	Column 1 - F-1(28-48)				Column 2 - F-1(28-48)			
	No.	Time of Oper- ation hr	Poly+ ortho P mg P/l	Thru- Put Volume gal*	Load Rate gpm/sq ft**	Deten- tion Time min	Effluent Poly+ ortho P mg P/l	Thru- Put Volume gal	Load Rate gpm/sq ft	Deten- tion Time min	Effluent Poly+ ortho P mg P/l
2/5	1	0.13	4.10	0.03	0.301	7.1	14.00	0.03	0.301	7.1	20.90
	2	1.8		0.4	0.306	7.0	1.12	0.4	0.301	7.1	-
	3	4.2		0.9			0.15	0.9			0.16
	4	7.2	4.26	1.5			0.03	1.6			0.02
2/6	5	9.7	4.15	2.1			0.03	2.2			0.03
	6	12.3		2.7			0.04	2.7			0.03
	7	14.6		3.2			0.04	3.2			0.03
	8	17.2	4.20	3.8	0.306	7.0	0.04	3.8	0.301	6.9	0.03
	9	19.7		4.4			0.05	4.4			0.03
2/7	10	21.7	4.20	4.8			0.05	4.9			0.03
	11	23.6		5.2	0.310	6.9	0.05	5.3	0.304	7.1	0.04
	12	25.5		5.7			0.05	5.7			0.04
	13	27.4		6.1			0.06	6.1			0.05
	14	30.5		6.8			0.07	6.8			0.06
	15	34.4	4.15	7.7	0.306	7.0	0.12	7.7	0.306	7.0	0.09
2/8	16	36.3	4.20	8.1			0.10	8.1			0.09
	17	38.8		8.7			0.16	8.7			0.09
	18	41.6		9.3			0.22	9.3			0.13
	19	45.2		10.1			0.31	10.1			0.20
	20	48.1	4.30	10.7	0.299	7.2	0.37	10.8	0.297	7.2	0.27
2/9	21	51.4	4.35	11.5			0.35	11.5			0.22
	22	53.9		12.0	0.297	7.2	0.38	12.0	0.297	7.2	0.30
2/10	23	57.6	4.30	12.8			0.42	12.9			0.27
	24	62.2		13.8			0.66	13.9			0.41
	25	64.5	4.35	14.3	0.289	7.5	0.75	14.4	0.293	7.4	0.48
2/11	26	74.5	4.35	16.5	0.295	7.3	1.18	16.5	0.291	7.4	1.03

*To convert gal to l multiply by 3.785.
**To convert gpm/sq ft to l/min/sq m multiply by 40.7.

<u>Note</u>: Columns were operated in parallel & only during daytime.



To convert gal to l multiply by 3.785

FIGURE 20. BENCH COLUMN TEST SYSTEM STUDIES - RUN S-3

except that tap water was used in place of secondary plant effluent.

A known amount (400 g) of regenerated F-1 (-325) and F-1 (-100) aluminas, which had been dried at 104° C for 1 hr, was fed to the rapid mix-sedimentation units over a period of 10 hr. At the end of the run, the aluminas were collected from the sedimentation and mixing tanks, dried at 104° C for 3 days, and weighed. Also, 100 g pre-dried, regenerated F-1 (28-48) alumina was packed into a bench column, which was then operated in the upflow mode for 10 hr; the alumina was removed from the column, dried in a similar manner, and weighed. The alumina losses during the sorption operation were as shown below.

	Loss, %	
Alumina	RMS	CTS
F-1(-325)	11.4	
F-1(-100)	7.3	
F-1(28-48)		1.2

B. REGENERATION STUDIES

The regeneration of exhausted alumina column beds had been studied by Yee (29,30), Ames and Dean (32,33), and Yue and Purushothaman (34,35) who had concluded that 8 to 9 cv of 2M sodium hydroxide were required for this purpose; it was also reported (34,35) that only 3.4 to 4.3 percent of the hydroxyl ions supplied were actually consumed. Because the chemical costs associated with the regeneration of the alumina were expected to be a significant consideration in evaluating the practicability of the process, a study was undertaken to establish an economical, yet effective, dose of sodium hydroxide to be used in this investigation.

1. Development of Regeneration Procedure

Used F-1 (-325) and F-1 (-100) aluminas from the field rapid mix-sedimentation system (Run S-1) were first dried in an oven at 104° C for 3 days. The aluminas were then regenerated with sodium hydroxide in 5 different tests using a 6-unit variable speed stirrer, and the efficiency of the regenerated materials in removing phosphorus was evaluated by means of both a batch procedure and the bench rapid mix-sedimentation system. Two or 1M sodium hydroxide was used to treat varying amounts of alumina, and the hydroxyl ion to alumina weight ratio ranged from 0.658 to 0.028 g OH^-/g alumina. The experimental conditions used are outlined in Table XVI. The alumina and sodium hydroxide mixture was stirred in a 1-l beaker at 100 rpm for 4.5 hr and allowed to settle for 2 hr; the alumina was then separated from the spent regenerant solution, washed with distilled water 2 or 3 times, and dried in an oven at 104° C for 53 or 74.5 hr.

The batch evaluation study consisted (Table XVI) of mixing 1.0 g fresh or regenerated alumina with 700 ml secondary effluent at 100 rpm for 25 min (the 6-unit stirrer was used), settling for 2 hr, siphoning off the supernatant, and determining the residual Poly+ortho-P concentration. The phosphorus data and corresponding sorptive capacity of the regenerated aluminas are presented in Table XVII. It should be noted that these tests were not all conducted at the same time, and this is reflected in the initial phosphorus concentration which ranged from 7.65 to 10.75 mg P/l. Very little difference in the sorptive capacity of Samples 1 through 6 was noted in Test 1, indicating that even at a 0.136 g OH^-/g alumina dose the hydroxyl ion was still in excess. In Tests 2 through 5, Sample 6 showed the highest sorptive

TABLE XVI. BATCH ACTIVATED ALUMINA REGENERATION - EXPERIMENTAL CONDITIONS

Test No.	Sample No.	Regeneration Conditions								Sorption Conditions			
		Alumina Treated*	NaOH Regenerant		Weight Ratio	Mix** Time	Wash Water		Dry# Time	Fresh or Regener. Alumina Used	Effluent Treated	Detention Time	
			Strength	Volume Used			Volume/Cycle	No. of Cycles				Mix*	Sed
		g	M	ml	gOH-/g alumina	hr	ml		hr	g	ml	min	hr
1	1	175.0	2	700	0.136	4.5	700	3	53.0	1.0##	700	25	2.0
	2	100.0			0.238								
	3	70.0			0.340								
	4	53.8			0.442								
	5	43.8			0.543								
	6	36.8			0.658								
2-5	1	300.0	1	500	0.028			2	74.5				
	2	250.0			0.034								
	3	200.0			0.042								
	4	150.0			0.057								
	5	100.0			0.085								
	6	50.0			0.170								

*F-1 (-325) & F-1 (-100) aluminas from field rapid mix-sedimentation system (Run S-1).

**At 100 rpm using a 6-unit variable speed stirrer.

#At 104° C in an oven.

##Since the regenerated aluminas were dried at 104° C, their moisture content was not significantly different than that of the fresh aluminas.

Note: Study was conducted in July 1973.

TABLE XVII. EVALUATION OF ACTIVATED ALUMINA REGENERATION - BATCH STUDIES*

Test No.	Type of Alumina	Initial Poly+ ortho P mg P/l	Fresh Alumina	Regenerated Alumina						Fresh Alumina	Regenerated Alumina					
				Sample No.							Sample No.					
				1	2	3	4	5	6		1	2	3	4	5	6
			Remaining Poly+ortho-P, mg P/l							Sorptive Capacity, mg P/g						
1	F-1(-325) F-1(-100)	7.65		2.80 3.30	2.80 3.35	2.75 3.25	2.85 3.70	2.58 3.30	2.60 3.21		3.40 3.05	3.40 3.01	3.43 3.08	3.36 2.77	3.55 3.05	3.54 3.11
2	F-1(-325)	8.60	3.75	4.15	4.55	4.00	4.00	4.35	3.60	3.40	3.12	2.84	3.22	3.22	2.98	3.50
3		10.60	4.98	6.60	5.50	5.50	6.35	5.20	5.28	3.93	2.80	3.57	3.57	3.00	3.78	3.72
4		10.75	4.65	5.35	5.40	5.45	5.70	5.20	5.10	4.27	3.78	3.75	3.71	3.54	3.89	3.96
5		10.75	4.65	5.50	5.40	5.50	5.25	4.80	5.40	4.27	3.68	3.75	3.68	3.85	4.17	3.75
Avg 2-5		10.18	4.51	5.40	5.21	5.11	5.33	4.89	4.85	3.97	3.35	3.48	3.55	3.40	3.71	3.73
2	F-1(-100)	8.73	3.83	3.78	3.34	3.16	3.60	3.84	3.48	3.43	3.47	3.77	3.90	3.59	3.42	3.68
3		8.85	3.85	4.95	4.50	4.88	4.60	3.20	4.43	3.50	2.73	3.05	2.78	3.00	4.00	3.09
4		8.75	3.83	5.60	4.73	4.50	5.83	4.65	4.13	3.44	2.21	2.81	2.98	2.04	2.78	3.23
5		10.75	4.15	5.55	5.50	5.40	5.63	5.35	4.80	4.62	3.64	3.68	3.75	3.57	3.78	4.17
Avg 2-5		9.27	3.92	4.97	4.52	4.49	4.92	4.26	4.21	3.75	3.01	3.33	3.35	3.05	3.52	3.54

*For experimental conditions see Table XVI.

Note: Study was conducted in July 1973.

capacity and was closely followed by Sample 5; the next highest capacity was measured for Sample 3. The 3 samples, with regenerant concentrations of 0.170, 0.085 and 0.042 g OH^-/g alumina, were therefore selected for further evaluation under continuous flow conditions.

An adequate amount of the 2 aluminas was regenerated as outlined in Table XVI. The bench rapid mix-sedimentation system was operated at approximately 1.0 gph (3.8 l/hr) for over 8 hr after the units had been filled, and at the end of the run the concentration of phosphorus in the effluent was determined. The operational characteristics and phosphorus data are given in Table XVIII. An evaluation of these data indicated that Sample 5 had the highest sorptive capacity for phosphorus, and this was true for both the F-1 (-325) and F-1 (-100) aluminas. Consequently, the regeneration conditions used in preparing Sample 5 were selected for the regeneration of the aluminas employed in the field studies (Table IX, p.76).

The regeneration of the exhausted F-1 (28-48) alumina from the field column system (Run S-1) was studied in 2 tests conducted in August and December 1973. In each case, 100 g (wet) portions of material extracted from Column 1 were packed into 3 bench columns where they were treated with varying amounts of sodium hydroxide, ranging from 0.375 to 0.024 g OH^-/g alumina (fresh alumina equivalent), and were washed with distilled water; the columns were then used to evaluate the sorptive capacity of the reclaimed alumina. The regenerant, wash and feed waters were passed through the columns in the upflow mode. The experimental conditions employed in both the regeneration and sorption phases are summarized in Table XIX. Also presented in this table is the total amount of Poly+ortho-P which had been eluted

TABLE XVIII. EVALUATION OF ACTIVATED ALUMINA REGENERATION - BENCH RAPID MIX-SEDIMENTATION TEST SYSTEM STUDIES*

Test No.	Sample No.	Type of Alumina		Regenerant Weight Ratio	Operational Characteristics					Poly+ortho-P			Sorptive Capacity
		Condition	Designation	gOH^-/g alumina	Flow Rate gph**	Detention Time Mix min	Detention Time Sed hr	Run Duration hr	Alumina Dose g/gal#	Influent mg P/l	Effluent mg P/l	Removal %	mg P/g
2-5		Fresh	F-1(-325)		0.93	16.8	2.1	8.3	7.5	7.95	0.75	96.6	3.63
	3	Regenerated		0.042				8.2	7.5##	7.50	3.13	58.3	2.20
	5			0.085				8.6	7.5##	8.00	2.88	64.0	2.58
	6			0.170				8.1	7.5##	7.80	2.95	62.2	2.45
		Fresh	F-1(-100)		0.97	16.5	2.0	8.3	7.3	7.95	2.95	62.9	2.60
	3	Regenerated		0.042				8.2	7.3##	7.50	4.80	36.0	1.40
	5			0.085				8.6	7.3##	8.00	2.95	63.1	2.63
	6			0.170				8.1	7.3##	7.80	3.05	60.9	2.47

*For regeneration conditions see Table XVI.

**To convert gph to l/hr multiply by 3.785.

#To convert g/gal to g/l multiply by 0.264.

##Since the regenerated aluminas were dried at 104° C, their moisture content was not significantly different than that of the fresh aluminas.

Note: Study was conducted in August 1973.

TABLE XIX. COLUMN ACTIVATED ALUMINA REGENERATION - EXPERIMENTAL CONDITIONS

Column		Alumina Treated & Used	Regeneration										Sorption	
			NaOH Regenerant		Weight Ratio	Regenerant Wash			Water Wash			Total Poly+ ortho-P Eluted#	Flow Rate	Det Time
No.	Volume ml	g	Strength M	Volume Used ml	gOH^-/g alumina*	Flow Rate ml/min	Time hr	Condition	Volume ml	Time hr	Condition	mg	ml/min	min
1	100	100$^+$ (wet)	2	900	0.375	6.0	11	circulation	3,432	9.7	flow thru	590.0	15.4	6.5
2			2	450	0.188	5.5			3,393			603.3	13.8	7.2
3			1	460	0.096	5.5			3,231			599.8	14.4	6.9
4			0.75	460	0.072	5.8	18.8		1,070	11.8	2 cyc circulation	569.9	14.0	7.1
5			0.50	460	0.048	5.6						539.3	14.0	7.1
6			0.25	460	0.024	6.2						436.1	15.1	6.6

*Based on an equivalent fresh alumina.
#In the regenerant and water washes.
+Equivalent to 81.6 g of fresh alumina.

Note: Study was conducted in August & December 1973.

from the columns and was present in the regenerant and wash water.

Phosphorus data are presented in Table XX and are plotted in Figure 21. Considerable initial leakage was observed in Columns 4 through 6 which had been washed with less than one-third the volume of wash water used with Columns 1 through 3. Following this initial condition, all columns produced effluents with comparable low residual phosphorus concentrations (Table XX); however, when these values were expressed as percentages of the initial phosphorus concentration (Figure 21), Columns 4 through 6 appeared to be less effective because of the low phosphorus content of the secondary effluent used (Table XX). Average values for the sorptive capacity of the regenerated alumina, computed on an equivalent fresh alumina weight basis,* were:

	Column No.					
	1	2	3	4	5	6
Sorptive capacity, mg P/g	4.22	3.89	4.00	2.11	2.12	2.04

The selection of the regeneration conditions for the field columns was based on the findings of the August study, and the December study served to confirm and extend the previous findings; this was indicated because it was necessary to complete the field studies before cold weather came to the area. Taking into the consideration both the elution requirements and the sorptive capacity of the regenerated material, the conditions represented by Column 3 were chosen for the regeneration of the field columns (Table IX). Column 4

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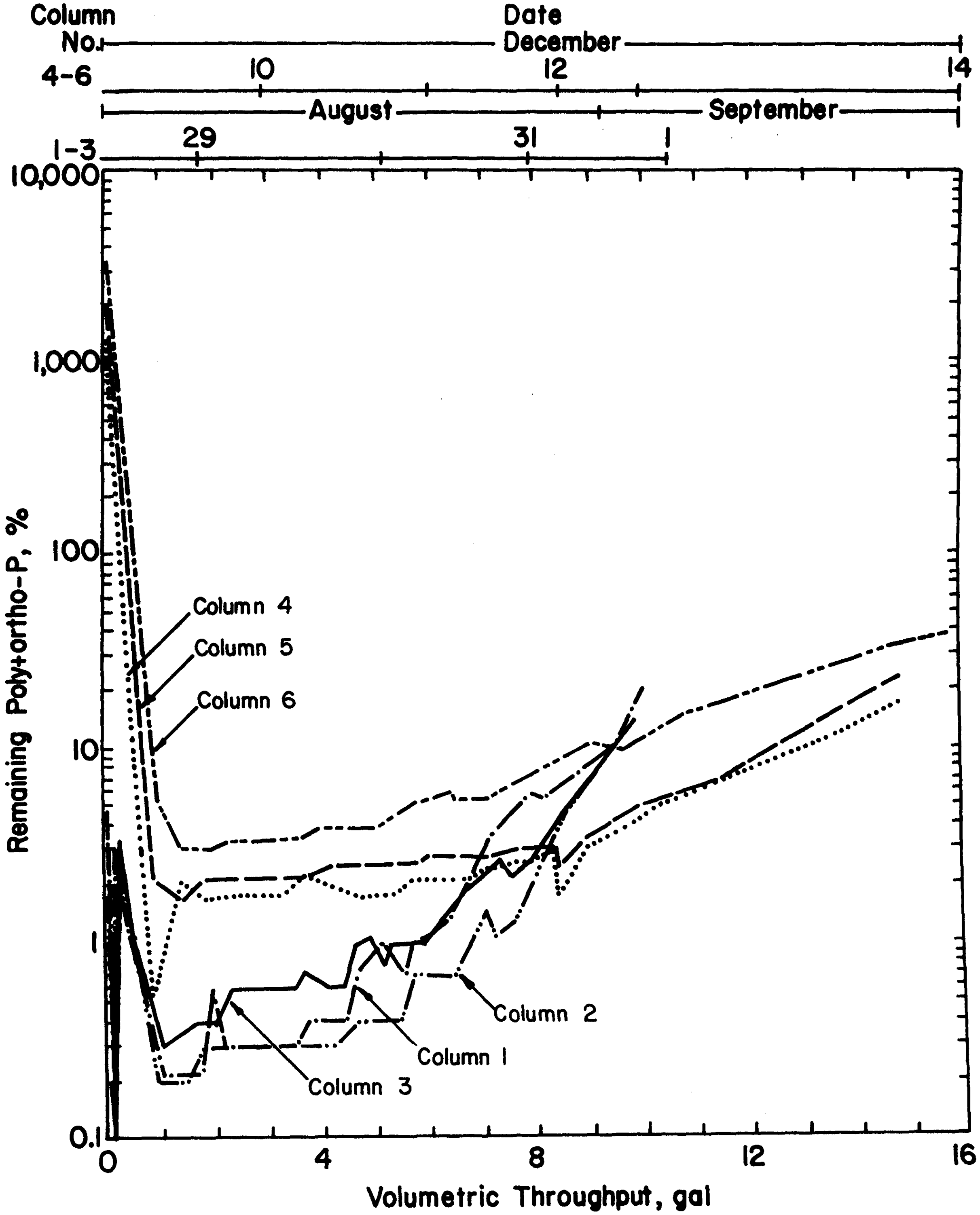
*Considering that 100 g wet alumina were equivalent to 81.6 g fresh alumina (see footnote on p.104).

TABLE XX. EVALUATION OF ACTIVATED ALUMINA REGENERATION - BENCH COLUMN TEST SYSTEM STUDIES

Date	Run Duration hr	Influent Poly+ortho-P mg P/l	Column No.			Date	Run Duration hr	Influent Poly+ortho-P mg P/l	Column No.		
			1	2	3				4	5	6
			Poly+ortho-P, mg P/l						Poly+ortho-P, mg P/l		
8/29	0.2	8.9	0.02	0.40	0.16	12/10	0.1	3.3	47.5	67.5	115.0
	0.5		0	0.03	0.01		2.2		-	1.36	-
	1.0	9.0	0.27	0.23	0.30		4.0		0.14	0.07	0.18
	2.0		0.10	0.14	0.13		6.2		0.07	0.06	0.10
	4.4		0.02	0.02	0.03		8.2	3.3	0.06	0.07	0.10
	7.1		0.02	0.02	0.04		9.5		0.06	0.07	0.11
8/30	8.1	9.0	0.05	0.03	0.04		11.5	3.3	0.06	0.07	0.12
	8.9		0.03	0.03	0.04		12.9		0.06	0.07	0.12
	10.1		0.03	0.03	0.05	12/11	13.0	3.3	0.06	0.07	0.11
	12.1		0.03	0.03	0.05		14.9		0.06	0.07	0.12
	13.2		0.03	0.03	0.05		16.6		0.07	0.07	0.13
	14.1	9.1	0.03	0.03	0.05		18.9		0.06	0.08	0.13
	15.3		0.04	0.03	0.05		20.9		0.06	0.08	0.13
	16.1		0.04	0.03	0.06		24.0	3.4	0.06	0.08	0.17
	18.2		0.04	0.03	0.05		25.6		0.07	0.08	0.19
	19.2		0.06	0.03	0.05		26.9		0.07	0.09	0.20
	20.2		0.08	0.04	0.09	12/12	27.0	3.4	0.07	0.09	0.19
	21.2	9.1	0.09	0.04	0.10		29.4		0.07	0.09	0.19
8/31	22.5		0.06	0.04	0.07		31.2		0.08	0.09	0.22
	23.2		0.09	0.04	0.09		34.9	3.4	0.09	0.10	0.30
	24.6		0.10	0.04	0.09		37.7		0.10	0.10	0.39
	26.0		0.14	0.06	0.09	12/13	37.8	3.4	0.06	0.08	0.30
	29.0		0.33	0.06	0.16		40.4		0.10	0.12	0.33
	32.3	9.1	0.54	0.14	0.25		44.5	3.4	0.14	0.17	0.48
9/1	33.1	9.1	0.50	0.10	0.20		51.2		0.17	0.20	0.70
	34.5		0.54	0.12	0.23	12/14	61.8	3.4	0.44	0.60	1.19
	39.1	9.0	1.08	0.40	0.60		66.7		0.58	0.77	1.36
	42.9	9.1	1.83	0.90	1.20						

Note: Columns were operated in parallel & only during daytime.



To convert gal to l multiply by 3.785

FIGURE 21. EVALUATION OF ACTIVATED ALUMINA REGENERATION – BENCH COLUMN TEST SYSTEM STUDIES

compared favorably to Column 3, except in sorptive capacity, and required 25 percent less sodium hydroxide. The smaller sorptive capacity, however, could be directly attributed to the lower strength of the influent wastewater, and consequently this column could have reflected the preferred regeneration conditions.

2. Alumina Loss

To determine the loss of alumina during regeneration, 100-g samples of pre-dried (104° C for 1 hr) F-1 (-325) and F-1 (-100) materials were stirred for 4.5 hr at 100 rpm with 500 ml 1M sodium hydroxide in a 1-l beaker; the mixture was allowed to settle for 2 hr, the supernatant was decanted, and the alumina was subjected to 2 cycles of washing. Each wash cycle consisted of stirring the alumina with 350 ml distilled water for 30 min, allowing the mixture to stand for 2 hr, and decanting the supernatant. After the water wash, the alumina was dried at 104° C for 3 days and weighed. To measure the loss of the F-1 (28-48) material, a 100-g column was treated with 460 ml 1M sodium hydroxide which was circulated for 11 hr; the column was drained and was washed 2 times with 500 ml distilled water which was circulated for 5 hr. The alumina was then withdrawn, dried at 104° C for 3 days, and weighed. The alumina losses during the regeneration operation were as follows:

	Loss, %	
Alumina	Batch	CTS
F-1(-325)	2.1	
F-1(-100)	1.9	
F-1(28-48)		0.6

C. SURFACE ALTERATION IN USED ALUMINAS

Because a significant loss was noted in the capacity of the regenerated aluminas during the sorption studies, a study was undertaken at the conclusion of the experimental runs in order to investigate the possibility of reduction in sorptive sites by coating of the alumina particles. Deposition of calcium carbonate had been reported by Ames and Dean (32,33), and was theoretically feasible under the experimental conditions employed in the present study. A sample of the secondary effluent from the Rolla treatment plant had the following characteristics:

Total alkalinity: 218 mg/l as $CaCO_3$
Calcium hardness: 142 mg/l as $CaCO_3$
pH: 7.6

Taking into consideration the 2nd ionization constant of carbonic acid, K_2 (55, p.59);

$$K_2 = \frac{[H^+]\,[CO_3^=]}{[HCO_3^-]} = 4.7\text{x}10^{-11}$$

the fact that at the pH of 7.6 essentially only bicarbonate alkalinity would have been present, and consequently (55, p.336);

$$[HCO_3^-] = \frac{\text{mg/l bicarbonate alkalinity x1.22}}{61{,}000} = \frac{218\text{x}1.22}{61{,}000} = 4.36\text{x}10^{-3} \text{ moles/l}$$

and the hydrogen ion concentration corresponding to the 7.6 pH value;

$$[H^+] = 10^{-7.6} = 10^{0.4}\text{x}10^{-8} = 2.5\text{x}10^{-8} \text{ moles/l}$$

the concentration of carbonate ions in the sample was computed to be:

$$[CO_3^=] = \frac{(K_2)\,[HCO_3^-]}{[H^+]} = \frac{(4.7\text{x}10^{-11})\text{x}(4.36\text{x}10^{-3})}{(2.5\text{x}10^{-8})} = 8.20\text{x}10^{-6} \text{ moles/l}$$

The concentration of calcium ions, computed from the carbonate hardness present, was

$$[Ca^{++}] = \frac{\text{mg/l carbonate hardness x0.4}}{40,000} = \frac{142\text{x}0.4}{40,000} = 1.42\text{x}10^{-3} \text{ moles/l}$$

and the product

$$[Ca^{++}]\ [CO_3^{=}] = (1.42\text{x}10^{-3})\text{x}(8.20\text{x}10^{-6}) = 11.64\text{x}10^{-9}$$

was greater than the solubility product of calcium carbonate, K_{sp}, reported (55, p.357) to be $5\text{x}10^{-9}$. Consequently, calcium carbonate could have precipitated from solution; in fact, since the pH of the alumina-treated wastewater effluent had an average value of 8 (a corresponding $[H^+]$ molar concentration of $1\text{x}10^{-8}$), the product could have actually been higher ($29.1\text{x}10^{-9}$).

The coating of the alumina particles was experimentally verified by subjecting fresh and exhausted or regenerated aluminas to X-ray diffraction for qualitative analysis and atomic absorption for quantitative determination.

The X-ray diffraction study was conducted using a diffractometer* equipped with a copper tube. Sample slides were prepared using the 3 fresh aluminas [F-1 (-325), F-1 (-100), and F-1 (28-48)], exhausted F-1 (28-48) alumina** which was extracted from Column 1 after Run S-1,

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*A Kristalloflex 4 diffractometer equipped with an AG Cu 30 tube was used; it was a product of Siemens and Halske, West Germany. This instrument was located in the Graduate Center for Materials Research, University of Missouri-Rolla.

**Since the F-1 (28-48) alumina was regenerated in columns which were subsequently employed in sorption studies, regenerated material was not available.

regenerated F-1 (-325) and F-1 (-100) aluminas which had been eluted during Run R-1, and analytical grade calcium carbonate which was used as a standard. The slides were scanned over an angle range from 20 to 45 deg, selected to incorporate the diffraction angles reported for calcium carbonate and most of the calcium phosphate compounds, including the insoluble hydroxyapatite (Table XXI). The results are summarized below.

		Diffraction Angle, 2θ, deg		
Material	Condition	Main Peak	1st Ref Peak	2nd Ref Peak
$CaCO_3$	Reagent grade	29.3	39.3	43.0
F-1(-325)	Fresh	28.3	--	--
F-1(-100)	Fresh	28.4	38.6	--
F-1(28-48)	Fresh	28.5	38.7	--
F-1(-325)	Regenerated	28.3	38.4	40.8
F-1(-100)	Regenerated	28.3	38.3	--
F-1(28-48)	Exhausted	28.4	38.7	--

The standard calcium carbonate sample showed 3 peaks, all in the correct positions. The alumina samples generally exhibited only 2 peaks; exceptions were the fresh F-1 (-325) alumina sample which had only 1 peak and the corresponding regenerated material which showed all 3 peaks. Although the peaks were slightly off the reported values, because the relative positioning between the angles was correct it was concluded that all alumina samples contained calcium carbonate; however, the presence of hydroxyapatite or any of the calcium phosphate compounds was not demonstrated.

The X-ray diffraction technique does not lend itself to quantitative measurement, especially with contaminants present in small amounts; consequently, the concentration of calcium was determined by

TABLE XXI. INTERPLANAR SPACINGS AND DIFFRACTION ANGLES OF CALCIUM COMPOUNDS

Chemical Compound		Interplanar Spacing, d,* Å			Diffraction Angle, 2θ,** deg		
		Peak					
Name	Formula	Main	1st Ref	2nd Ref	Main	1st Ref	2nd Ref
Calcium Carbonate	$CaCO_3$	3.04	2.29_2	2.10_2	29.3	39.3	43.0
Hydroxyapatite	$Ca_5(OH)(PO_4)_3$	2.81	2.78_6	2.72_6	31.8	32.2	32.9
Monocalcium Phosphate	$CaH_4(PO_4)_2$	3.48	3.25_8	7.40_6	25.5	27.4	11.9
Tricalcium Phosphate	$Ca_3(PO_4)_2$	2.88	2.61_7	3.26_6	31.0	34.3	27.7
	$Ca_3(PO_4)_2 \cdot nH_2O$	2.80	3.44_6	1.94_5	31.9	25.8	46.8
Calcium Metaphosphate	$Ca(PO_3)_2$	3.49	2.76_7	4.76_5	25.1	31.6	28.3
Calcium Pyrophosphate	$Ca_2P_2O_7$	2.93	3.10_8	3.06_8	30.5	28.8	29.1
	$Ca_2P_2O_7$	3.02	3.22_6	3.09_5	29.5	27.7	28.8
	$Ca_2P_2O_7$	3.30	3.21_9	1.99_7	27.0	27.7	45.5
Calcium Polyphosphate	$Ca_4P_6O_{19}$	3.09	2.96_{10}	4.77_8	28.9	30.2	18.5
Calcium Oxide & Calcium Orthophosphate	$Ca_4P_2O_9$	2.80	2.77_7	2.71_7	31.9	32.3	33.0

*The distance between each set of atomic planes of the crystal lattice; the subscript indicates percentage of the main peak (e.g., 2 = 20 %) (56).

**Defined by the relationship $m\lambda = 2d \sin \theta$, where m = the order of the diffraction and $\lambda = 1.54050$ Å; obtained from tables (57).

atomic absorption using a spectrophotometer* equipped with a calcium lamp** at a 4,226-Å wave length and 100-μ slit width in an air-acetylene flame. The alumina samples were first digested with concentrated nitric or hydrochloric acid. One-g pre-dried (104° C for 1 hr) sample was placed in a 250-ml beaker and mixed with 20 ml of the corresponding acid; the beaker was covered with a watch glass and heated on the hot plate for 4 hr with occasional stirring. The beaker and contents were allowed to cool, the watch glass was washed with redistilled water into the beaker, and the digested sample was diluted to approximately 50 ml; it was then filtered through filter paper,# the alumina and remaining acid on the paper were washed, and the filtrate was further diluted to a total volume of either 100 ml (fresh aluminas) or 1,000 ml (exhausted or regenerated aluminas). The diluted, digested samples were read on the spectrophotometer, and the concentration of calcium ions was determined from a standard curve prepared using a stock calcium chloride solution (1,000 mg/l as Ca^{++}). The following values were obtained.

		Calcium Concentration, mg Ca^{++}/g alumina	
Alumina	Condition	HNO_3 Digestion	HCl Digestion
F-1(-325)	Fresh	0	0.03
F-1(-100)	Fresh	0	0.16
F-1(28-48)	Fresh	0	0.10
F-1(-325)	Regenerated	0.07	1.42
F-1(-100)	Regenerated	0.03	1.60
F-1(28-48)	Exhausted	0.04	1.40

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*Type AA-5, Series 108, a product of Varian-Techtron Pty. Ltd., Melbourne, Australia; this instrument was located in the Graduate Center for Materials Research.

**No. CH842, Hollow Cathode Lamp, a product of Atomic Spectral Lamps, Melbourne, Australia.

#No. 4 Whatman filter paper, a product of W & R Balston Limited, England.

Considering that only the presence of calcium carbonate had been verified in the X-ray study, the net amount of material deposited on the alumina particles was as follows:

Alumina	Condition	Calcium Carbonate Coating mg/g alumina	%
F-1(-325)	Regenerated	3.48	0.35
F-1(-100)	Regenerated	3.60	0.36
F-1(28-48)	Exhausted	3.25	0.32

These values were based on the data obtained from digestion with hydrochloric acid which was much more effective than nitric acid in leaching calcium carbonate.

VII. DISCUSSION

Sorption on activated alumina, both in the rapid mix-sedimentation and column modes of operation, was found effective in removing phosphorus from secondary wastewater treatment plant effluent; however, it was not effective in reducing the concentration of nitrogen in the effluent.

Experimental findings obtained with fresh and regenerated aluminas over a 9-month period (June 1973 to March 1974) using the field (Runs S-1 and S-2) and bench-scale (Run S-3) test systems are summarized in Table XXII. Phosphorus removal averaged 76 percent in the rapid mix-sedimentation system and in excess of 88 percent in the column system. The latter system could also effect essentially complete removals of phosphorus, but at significantly reduced throughputs. The selectivity of the aluminas for total nitrogen was low, although between 10 and 35 percent of NH_3-N and 56 and 75 percent of Org-N were removed; however, little reduction was obtained in NO_3-N, which at 12.5 mg N/l represented more than 87 percent of the total nitrogen, while the concentration of NO_2-N increased, probably as a result of continued biological activity. It should be pointed out that because the Rolla Southwest Sewage Treatment Plant where the study was conducted was operating at approximately 20 percent of design capacity, its effluent was uncommonly highly nitrified; consequently, it is believed that under normal conditions the activated alumina sorption process would be capable of producing a greater overall removal of nitrogen. Approximately 30 percent of the COD was also removed, and this was attributed to a reduction in the TSS initially present in the effluent, despite the fact that the TSS concentration in the treated water was

TABLE XXII. REMOVAL OF NUTRIENTS BY SORPTION ON ACTIVATED ALUMINA - SUMMARY OF EXPERIMENTAL DATA

Parameter	Influent Concentration mg/l				Rapid Mix-Sedimentation Mode						Column Mode					
					Unit 1 - F-1(-325)			Unit 2 - F-1(-100)			Columns 1 & 2 - F-1(28-48)					
	To End of Run		At Breakthrough*		To End of Run									At Breakthrough		
					Effl Conc mg/l		Removal %	Effl Conc mg/l		Removal %	Effl Conc mg/l		Removal %	Effl Conc mg/l		Removal %
	Avg	Range	Avg	Range	Avg	Range		Avg	Range		Avg	Range		Avg	Range	
Poly+ ortho-P	7.22	5.02	5.53	3.40	1.68	3.50	76.7	1.73	3.26	76.0	0.80	20.89	88.9	0.40	20.90	92.8
NH_3-N	1.24	4.25	1.25	4.25	1.12	4.50	9.6	1.12	4.28	9.6	0.81	1.55	34.6	0.81	1.55	35.2
Org-N	0.40	1.32	0.44	1.32	0.13	1.35	68.2	0.18	0.86	56.0	0.12	0.75	70.7	0.11	0.75	75.0
NO_3-N	12.5	8.1	12.7	7.8	12.5	12.6	0	12.4	13.2	0.8	13.0	9.6	4.0	12.6	9.6	0.7
NO_2-N	0.13	0.49	0.14	0.49	0.15	0.27	-15.3	0.16	0.39	-23.0	0.16	0.94	-23.0	0.20	0.94	-42.8
COD	28	60	30	60	19	62	32.1	20	43	28.5	20	61	28.5	20	61	33.3
TSS	9	42	9	22	83	324	-822.2	18	124	-100.0	38#	846	-322.2	17	294	-88.8

*Considering only data obtained before the CTS effluent Poly+ortho-P concentration, except for initial leakage, had reached the 0.1-mg P/l level. If initial leakage is excluded from these data, the Poly+ortho-P values would be:

Influent concentration, mg P/l,	Avg	7.27
	Range	3.40
Effluent concentration, mg P/l,	Avg	0.01
	Range	0.06
Removal, %	Avg	99.9

#A large amount of TSS was released in the effluent on the 1st day in Run S-1, when alumina fines were washed-out of the columns, and on 2 occasions in Run S-2, when the columns were disturbed to overcome clogging difficulties; if these values are not considered, the avg effluent TSS would be 7 mg/l.

significantly higher, resulting from the discharge of alumina particles.

During the studies the character of the plant effluent varied widely, as indicated by the range observed for each parameter tested, and accordingly the quality of the alumina-treated water also fluctuated (Table XXII). The concentration of phosphorus ranged from 3.9 to 9.0 mg P/l, and even within a test run, broad variations were noted (6.1 to 9.0 mg P/l in Run S-1, 5.2 to 7.5 mg P/l in Run S-2); similar variations were found for nitrogen, especially NH_3-N and Org-N. Operation under the widely varying influent characteristics made the control of experimental conditions difficult, especially alumina dosing of the rapid mix-sedimentation units, and affected the uniformity of data complicating their analysis and evaluation; nonetheless, it was considered highly desirable because it closely approximated plant operation.

The performance of the field and bench-scale rapid mix-sedimentation and column test systems, which were especially designed and built for this study, was generally good and for a given influent waste quality the bench units could produce results essentially comparable to the field units. Some problems were encountered, however, with the test equipment during the studies, and 2 modifications would be desirable in order to overcome these difficulties: the addition of column backwash facilities and the use of heavy-duty mixers.

Solid matter in the secondary effluent was apparently trapped on the column beds during Run S-1 and was not removed during regeneration; in fact the beds became more compact and were partly agglomerated into lumps. This resulted in clogging and channelling during Run S-2, which prevented the effective use of the beds and caused a significant drop in sorptive capacity. This problem did not occur in Run S-3, however, the laboratory columns used were packed with material removed from the top of the 1st field column, which apparently contained less trapped solids; also, the lumps were most likely crushed during the transfer and repacking steps. A high-rate backwash at the end of the regeneration process would help overcome this problem and at the same time reduce the initial leakage of phosphorus observed during the 1st day after regeneration (Figure 19, p.99).

The type of stirrer employed to mix the coarser alumina [F-1 (-100)], a laboratory high-speed model rated for continuous duty, was unable to carry the load in field operation and had to be replaced with a slower cone-driven unit which was able to give continuous service but could not provide adequate agitation. The reduced mixing intensity did not seriously affect process efficiency, but periodic manual mixing was required in order to transfer the alumina to the sedimentation unit. Use of heavy-duty pilot plant stirrers should eliminate this problem.

The process developed for the regeneration of the exhausted aluminas depended solely on the use of sodium hydroxide as the regenerant at doses which, expressed in g OH^-/g alumina, ranged from 0.085 for the rapid mix-sedimentation system [F-1 (-325) and F-1 (-100) aluminas] to 0.096 for the column system [F-1 (28-48) alumina]. These doses were considerably less than the regenerant requirements reported in the literature, which ranged from 0.17 g OH^-/g alumina used by Ames and Dean (32,33) to 0.212 g OH^-/g alumina employed by Yue and Purushothaman (34,35). Treatment with the regenerant caustic solution (1M NaOH) was followed by a water wash in order to remove the caustic and any residual nutrients that might have remained. The volume of regenerant and wash water represented a small fraction (1.4 to 4.6 percent) of the volume of the secondary effluent treated;

System	Run S-1/R-1* Effluent Treated gal	Run S-1/R-1* Regenerant+ Wash Used gal	Run S-1/R-1* Regenerant+ Wash Used %	Run S-2/R-2* Effluent Treated gal	Run S-2/R-2* Regenerant+ Wash Used gal	Run S-2/R-2* Regenerant+ Wash Used %
Rapid Mix-Sedimentation						
Unit 1 - F-1(-325)	20,982	435.6	2.1	9,728	377.3	3.9
Unit 2 - F-1(-100)	21,125	566.1	2.7	9,740	444.1	4.6
Column						
Columns 1,2+3 - F-1(28-48)	9,385	133.5	1.4			
Columns 1+2 - F-1(28-48)				4,312	89.0	2.1

*Data from Tables IX and X, p.76 and 82-83.

although the elutants contained a significant percentage (estimated to be in excess of 90 percent*) of the phosphorus which had been removed during the sorption process, the initial leakage of phosphorus during Runs S-2 and S-3 would indicate that the water wash was still inadequate. No attempt was made during this study to investigate the recycle potential of the spent regenerant or to evaluate requirements for its disposal; however, Ames and Dean (32,33) have suggested the use of lime to precipitate phosphorus and thereby reclaim the residual hydroxide. The feasibility of regenerant recovery and the cost involved in handling this waste, which were beyond the scope of this investigation, warrant further attention because they would have a

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*This percentage was determined by considering that Column 1, Run S-1, by the time it was removed from operation had sorbed an average of 7.9 mg P/g alumina (see Tables X, XI and XIII, p.82-84 and 87-88), and that 599.8 mg P were eluted during regeneration from 81.6 g of this alumina (Table XIX, p.113); assuming that the sorbed phosphorus was uniformly distributed throughout the column, the recovery was 93.0 percent.

significant effect on the overall economic evaluation of the sorption process.

The sorptive capacity for phosphorus of the 3 aluminas (fresh and regenerated), measured in the 3 test runs, is reported in Table XXIII together with applicable average values for the influent and effluent Poly+ortho-P concentration, the alumina dose, and the contact time. Also presented in this table are adjusted sorptive capacity values, which were developed in an attempt to compensate for the operational malfunctions and varied conditions encountered during the studies, thereby reducing the data to an equivalent basis and enabling comparative evaluation. Special attention was given to the effects on the rapid mix-sedimentation units of reduced flow over a 12-day period in Run S-1, alumina overdosing in Run S-2, and exceptionally low influent phosphorus concentration in Run S-3, and to the effect on the column units of clogging and channelling in Run S-2. Consideration was also given to the single-column operation employed in Run S-3.

Sorptive capacities for the aluminas evaluated in the rapid mix-sedimentation mode during Run S-1 were adjusted by excluding the data obtained during the period of reduced flow. Since there was no way to actually determine the effect of channelling through the columns in Run S-2, adjusted values were computed using the capacities developed for the fresh alumina in Run S-1 and the average regenerated to fresh alumina sorptive capacity ratio established in Runs S-1 and S-2 for Units 1 and 2. Further to compensate for the single-column arrangement in Run S-3, the relationship between the overall capacity determined for 2 columns in series in Run S-1 and the corresponding capacity of the 1st column was employed.

TABLE XXIII. SORPTIVE CAPACITY OF ACTIVATED ALUMINAS FOR PHOSPHORUS

Run No.	Influent Conc mg P/l		Rapid Mix-Sedimentation Mode								Column Mode							
			Unit 1 - F-1(-325)				Unit 2 - F-1(-100)				Columns 1 & 2 - F-1(28-48)							
			To End of Run												At Breakthrough			
	To End of Run	At Break-through*	Effl Conc mg P/l	Alum Dose g/gal#	Cont Time min	Capacity mg P/g	Effl Conc mg P/l	Alum Dose g/gal	Cont Time min	Capacity mg P/g	Effl Conc mg P/l	Alum Dose g/gal	Cont Time min	Capacity mg P/g	Effl Conc mg P/l	Alum Dose g/gal	Cont Time min	Capacity mg P/g
S-1	7.68	7.50	1.78	5.6	27	4.0	1.78	7.1	27	3.2	0.31	3.6	45	7.8	0.07	4.6	50	6.1
Adj	7.79		1.82	5.0	27	4.5	1.94	6.5	27	3.4				-				-
S-2	6.37	6.66	1.50	7.9	24	2.3	1.65	9.3	24	1.9	1.97	5.3	33	3.1	1.45	8.8	32	2.2
Adj						3.0				2.2				5.1				4.0
S-3	3.94 4.24	4.18	1.08	7.1	16	1.6	1.08	7.7	17	1.4	0.90	4.9	7	2.6	1.25	10.5	7	1.1
Adj						1.8				1.5				3.6				2.6

*See Table XXII.

#Fresh alumina basis; to convert g/gal to g/l multiply by 0.264.

Note: The justification & procedures employed in adjusting sorptive capacity values were:

1. Run S-1. Data obtained during the period of reduced flow to RMS (6/23 to 7/4, Figure 16, p.89), resulting from operational malfunction, were excluded.
2. Run S-2. On the basis of f(rem-res) values of 0.51 & 0.45 (mg P/l)$^{-1}$ for Units 1 & 2, the required alumina doses would have been (Figure 23, p.137) 6.1 & 8.0 g/gal, respectively; consequently, the 7.9 & 9.3 g/gal actually applied reflected overdoses of 29.5 & 16.2 % & the sorptive capacities were correspondingly adjusted. Considering that the low capacities observed in the CTS reflected the effect of channelling, capacities were adjusted using Run S-1 CTS values & the Run S-2/Run S-1 avg ratio for Units 1 & 2 (0.66).
3. Run S-3. For an f(rem-res) value of 0.67 (mg P/l)$^{-1}$, the required doses for Units 1 & 2 would have been 6.3 & 7.3 g/gal; sorptive capacities were therefore increased by 12.7 & 5.5 % to adjust for overdosing. Since a single-column arrangement was used in this run, sorptive capacities were adjusted by considering the ratio for Run S-1 of the 7.8 & 6.1-mg P/g overall values & values of 5.7 & 2.6 mg P/g determined for Column 1 when its effluent approached the 0.9 & 0.1-mg P/l levels (Table XIII, p.87-88).

The development of a method which could be used to correct for alumina overdosing, resulting from either the application of a higher than required dose or the occurrence of a lower than anticipated influent phosphorus concentration, proved to be a difficult undertaking. It was recognized that under equilibrium conditions the required dose would be a function of both the amount of phosphorus removed and the residual phosphorus concentration. Experimental data obtained during the period of reduced flow (and therefore increased dosing) to the rapid mix-sedimentation system in Run S-1 (Tables X, XI, and XII), and information collected from the bench test system during the development work to establish design characteristics (Table VIII, p.63-64) were examined in an effort to determine an appropriate relationship. After a number of trials, it was observed that a logarithmic relationship appeared to exist between the alumina dose and the ratio of phosphorus removal to phosphorus residual; plotting of the corresponding values (Table XXIV) on semi-logarithmic graph paper (Figure 22) indicated a linear relationship which could be expressed by means of the following equation.

$$f(\text{rem-res}) = Ke^{D} \qquad \text{(Eq 1)}$$

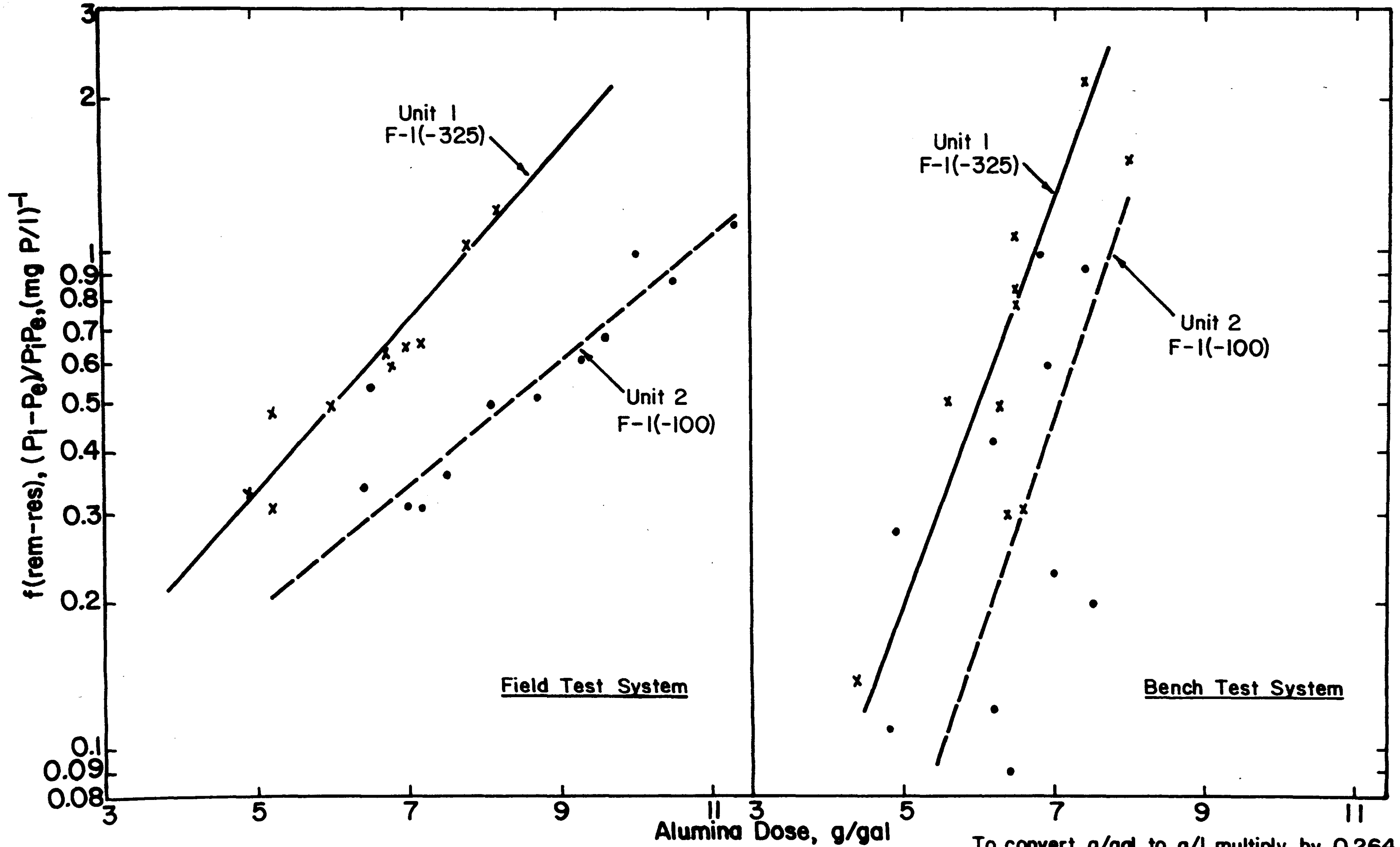
where: $f(\text{rem-res}) = (P_i - P_e)/P_iP_e, (\text{mg P/l})^{-1}$
P_i = influent phosphorus concentration, mg P/l
P_e = effluent phosphorus concentration, mg P/l
D = alumina dose, g/gal
K = constant

Although the relationship held well for the field system, it was not as well defined in the bench system where the data were considerably more scattered (Figure 22); this was attributed to the relatively broad range of experimental conditions which had been employed during the development study. It was concluded that the relationship offered an

TABLE XXIV. PHOSPHORUS REMOVAL-RESIDUAL AND ALUMINA DOSE RELATIONSHIP - RAPID MIX-SEDIMENTATION STUDIES

Date	Day of Oper-ation	Run No.	Influent Poly+ortho-P P_i mg P/l	Unit 1 - F-1(-325) Effluent Poly+ortho-P P_e mg P/l	Unit 1 - F-1(-325) Alumina Dose g/gal*	Unit 1 - F-1(-325) f(rem-res) $\frac{P_i - P_e}{P_iP_e}$ $(mg\ P/l)^{-1}$	Unit 2 - F-1(-100) Effluent Poly+ortho-P P_e mg P/l	Unit 2 - F-1(-100) Alumina Dose g/gal	Unit 2 - F-1(-100) f(rem-res) $\frac{P_i - P_e}{P_iP_e}$ $(mg\ P/l)^{-1}$
Field Test System#									
6/23/73	6	S-1	7.30	2.14	4.9	0.33	2.10	6.4	0.34
6/24/73	7		7.30	2.22	5.2	0.31	2.20	7.0	0.31
6/25/73	8		8.10	3.86	5.8	0.14	2.30	7.2	0.31
6/26/73	9		7.30	2.87	6.0	0.21	2.00	7.5	0.36
6/27/73	10		7.70	1.62	6.2	0.49	1.60	8.1	0.50
6/28/73	11		6.50	1.28	6.7	0.63	1.50	8.7	0.51
6/29/73	12		6.40	1.34	6.8	0.59	1.30	9.3	0.61
6/30/73	13		6.40	1.24	7.0	0.65	1.20	9.7	0.68
7/1/73	14		8.60	1.28	7.2	0.66	0.90	10.0	0.99
7/2/73	15		7.80	0.86	7.8	1.03	1.10	10.5	0.78
7/3/73	16		8.30	0.76	8.2	1.20	0.80	11.3	1.13
7/4/73	17		8.00	1.62	5.2	0.49	1.50	6.5	0.54
Bench Test System+									
8/23/72	N/A	1	8.80	3.90	4.4	0.14	4.50	4.8	0.11
9/4/72		2	7.10	0.60	8.0	1.52	2.90	7.5	0.20
9/29/72		3	8.30	1.10	6.5	0.79	4.20	6.2	0.12
11/28/72		4	3.80	0.90	6.5	0.85	0.80	6.8	0.98
12/16/72		5	6.10	1.50	6.3	0.50	1.30	6.9	0.60
12/19/72		6	6.40	1.50	5.6	0.51	2.30	4.9	0.28
1/10/73		7	6.10	0.80	6.5	1.09	1.70	6.2	0.42
1/17/73		8	7.40	2.30	6.4	0.30	4.40	6.4	0.09
1/20/73		9	4.10	1.80	6.6	0.31	2.10	7.0	0.23
1/27/73		10	3.10	0.40	7.4	2.18	0.80	7.4	0.93

*To convert g/gal to g/l multiply by 0.264.
#Data from Tables X, XI, & XII, p.82-86.
+Data from Table VIII, p.63-64.



To convert g/gal to g/l multiply by 0.264

FIGURE 22. PHOSPHORUS REMOVAL-RESIDUAL AND ALUMINA DOSE RELATIONSHIP - RAPID MIX-SEDIMENTATION STUDIES

appropriate means for adjusting sorptive capacities determined under overdose or underdose operation, and the method was used to correct the values established for the rapid mix-sedimentation system in Runs S-2 and S-3. It should be pointed out, however, that although Equation 1 holds considerable promise, its application to experimental conditions other than those employed in the present study has not been verified. Further evaluation of this concept would be highly desirable.

Although both the aluminas [F-1 (-325) and F-1 (-100)] evaluated in the rapid mix-sedimentation mode produced essentially the same quality effluent, the finer material was more effective and required a smaller dose. Column operation produced a higher quality effluent, being capable of achieving essentially complete removal of phosphorus, and resulted in improved sorptive capacity even though the alumina used [F-1 (28-48)] was the coarsest tested in the study. All aluminas lost sorptive capacity upon regeneration, especially after the 1st cycle, however, the reduction in capacity was comparable to levels established by other investigators (32,33) who had employed significantly higher regenerant doses. The following tabulation has been prepared to facilitate comparisons.

Cycle No.	Sorptive Capacity, % of fresh alumina			
	F-1(-325)	F-1(-100)	F-1(28-48)	Boehmite(28-48)*
1	100.0	100.0	100.0	100.0
2	66.7	64.7	65.4	65.3
3	40.0	44.1	46.2	51.0

*These values were calculated on the basis of data reported by Ames and Dean (32,33) who employed a 1-l column (Note: It was assumed that the column contained 1 kg alumina) to treat charcoal-filtered Richland, WA, secondary effluent having the following characteristics: phosphorus 10.3 mg P/l, calcium 25-40 mg/l, alkalinity 180-190 mg/l as $CaCO_3$, and pH 7.2-7.8; regeneration was accomplished using 1M NaOH (0.17 g OH^-/g alumina) followed by water wash.

The loss of sorptive capacity in the regenerated materials might have resulted in part from coating of the alumina particles with calcium carbonate. The existence of this material was established by X-ray diffraction, and quantitatively measured by atomic absorption using acid-hydrolyzed samples. The amount of calcium carbonate deposited was rather small, ranging from 0.32 to 0.35 percent (p.123), but the coating could have been extremely thin, covering a relatively large area. Modification of the regeneration process to incoporate the removal of this coating would help to restore the sorptive capacity of the reclaimed aluminas and should be investigated. It might be accomplished by means of an acid wash (using carbonic or hydrochloric acid) to dissolve the deposited material.

Chemical costs associated with the removal of nutrients by sorption on activated alumina are computed and tabulated in Table XXV. Costs were determined on the basis of either 77.5 or 90 (column mode only) percent reduction of phosphorus in secondary effluent containing 7.5 mg P/l. Pricing information was obtained from appropriate manufacturers (58,59), and all other design data were as determined during the course of this investigation, except for the sorptive capacities after 3 or 4 regenerations (Cycles No. 4 or 5) which were estimated from Figure 23. Computations were carried to the 5th cycle (4 regenerations), where the total chemical costs, expressed in $/1000 gal, appeared to be stabilizing.

The quantity of fresh alumina initially required, and the make-up alumina needed to replace material lost during sorption and regeneration and to provide additional sorptive capacity in order to restore efficiency, was computed by the equations shown on p.138.

TABLE XXV. REMOVAL OF NUTRIENTS BY SORPTION ON ACTIVATED ALUMINA - CHEMICAL COST

Conditions

Phosphorus Data Influent Concentration: 7.5 mg P/l

Effluent Concentration: 1.7 mg P/l Removal: 77.5 %
at breakthrough-column: 0.08 mg P/l 99.0 %

Regenerant Requirements (Table IX, p.76)

RMS: 0.085 g OH^-/g alumina
0.20 lb NaOH/lb alumina

CTS: 0.094 g OH^-/g alumina
0.22 lb NaOH/lb alumina

Chemical Cost Data (58,59)

Alumina F-1(-325): $0.19/lb
F-1(-100): $0.19/lb
F-1(28-48): $0.23/lb

Sodium Hydroxide: $0.1025/lb

Sortive Capacity, mg P/g (Table XXIII, p. 130 & Figure 23, p.137)

Cycle No.	Rapid Mix-Sedimentation Mode F-1(-325) 77.5 % Removal	Rapid Mix-Sedimentation Mode F-1(-100) 77.5 % Removal	Column Mode F-1(28-48) 77.5 % Removal	Column Mode F-1(28-48) 99.0 % Removal
1	4.5	3.4	7.8	6.1
2	3.0	2.2	5.1	4.0
3	1.8	1.5	3.6	2.6
4	1.1	0.9	2.6	1.6
5	0.7	0.6	1.8	0.9

Alumina Loss, %/cycle (p.107 & 117)

Alumina	Sorption	Regeneration	Total
F-1(-325)	11.4	2.1	13.5
F-1(-100)	7.3	1.9	9.2
F-1(28-48)	1.2	0.6	1.8

Alumina Requirement

Basis (p.138)

$$A_1 = 8.34\,\frac{P_i - P_e}{S_1} \quad \text{and} \quad A_n = A_1 - \frac{1}{S_1}\left(A_{n-1}YS_2 + A_{n-2}Y^2S_3 + \ldots + A_1Y^{n-1}S_n\right)$$

where: A_1 = initial alumina required, lb/1000 gal
A_n = make-up alumina required for nth cycle, lb/1000 gal
P_i = influent phosphorus concentration, mg P/l
P_e = effluent phosphorus concentration, mg P/l
S_1 = sorptive capacity of fresh alumina, mg P/g
S_n = sorptive capacity of alumina after n-1 regenerations, mg P/g
Y = 1 - L
L = fractional loss of alumina per sorption-regeneration cycle

Alumina Required, lb/1000 gal

Cycle No.	Rapid Mix-Sedimentation Mode F-1(-325) 77.5 % Removal	Rapid Mix-Sedimentation Mode F-1(-100) 77.5 % Removal	Column Mode F-1(28-48) 77.5 % Removal	Column Mode F-1(28-48) 99.0 % Removal
1	10.7	14.2	6.2	10.1
2	4.5	5.9	2.2	3.6
3	4.9	5.6	2.0	3.6
4	4.8	6.0	2.0	3.8
5	4.8	5.8	2.0	3.9

Regenerant Requirement

Basis (p.138)

$$R_n = CY^{n-2}\sum_{2}^{n}\frac{A_{n-1}}{Y^{n-2}}$$

where: R_n = NaOH regenerant required for nth cycle, lb/1000 gal
C = regenerant requirement, lb NaOH/lb alumina; 0.20 for RMS & 0.22 for CTS

NaOH Required, lb/1000 gal

Cycle No.	Rapid Mix-Sedimentation Mode F-1(-325) 77.5 % Removal	Rapid Mix-Sedimentation Mode F-1(-100) 77.5 % Removal	Column Mode F-1(28-48) 77.5 % Removal	Column Mode F-1(28-48) 99.0 % Removal
1	0	0	0	0
2	2.1	2.8	1.4	2.2
3	2.8	3.8	1.8	3.0
4	3.4	4.5	2.2	3.7
5	3.9	5.3	2.6	4.5

Chemical Cost

Cycle No.	Rapid Mix-Sedimentation Mode						Column Mode					
	F-1(-325)			F-1(-100)			F-1(28-48)					
	77.5 % Removal									99.0 % Removal		
	Cost, $/1000 gal*											
	Alumina	NaOH	Total	Alumina	NaOH	Total	Alumina	NaOH	Total	Alumina	NaOH	Total
1	2.03	0	2.03	2.70	0	2.70	1.43	0	1.43	2.32	0	2.32
2	1.45	0.11	1.56	1.91	0.15	2.06	0.97	0.07	1.04	1.58	0.11	1.69
3	1.27	0.17	1.44	1.63	0.23	1.86	0.81	0.11	0.92	1.30	0.18	1.48
4	1.18	0.22	1.40	1.51	0.29	1.80	0.72	0.14	0.86	1.21	0.23	1.44
5	1.13	0.25	1.38	1.42	0.34	1.76	0.67	0.17	0.84	1.15	0.28	1.43

*To convert $/1000 gal to $/1000 l multiply by 0.264.

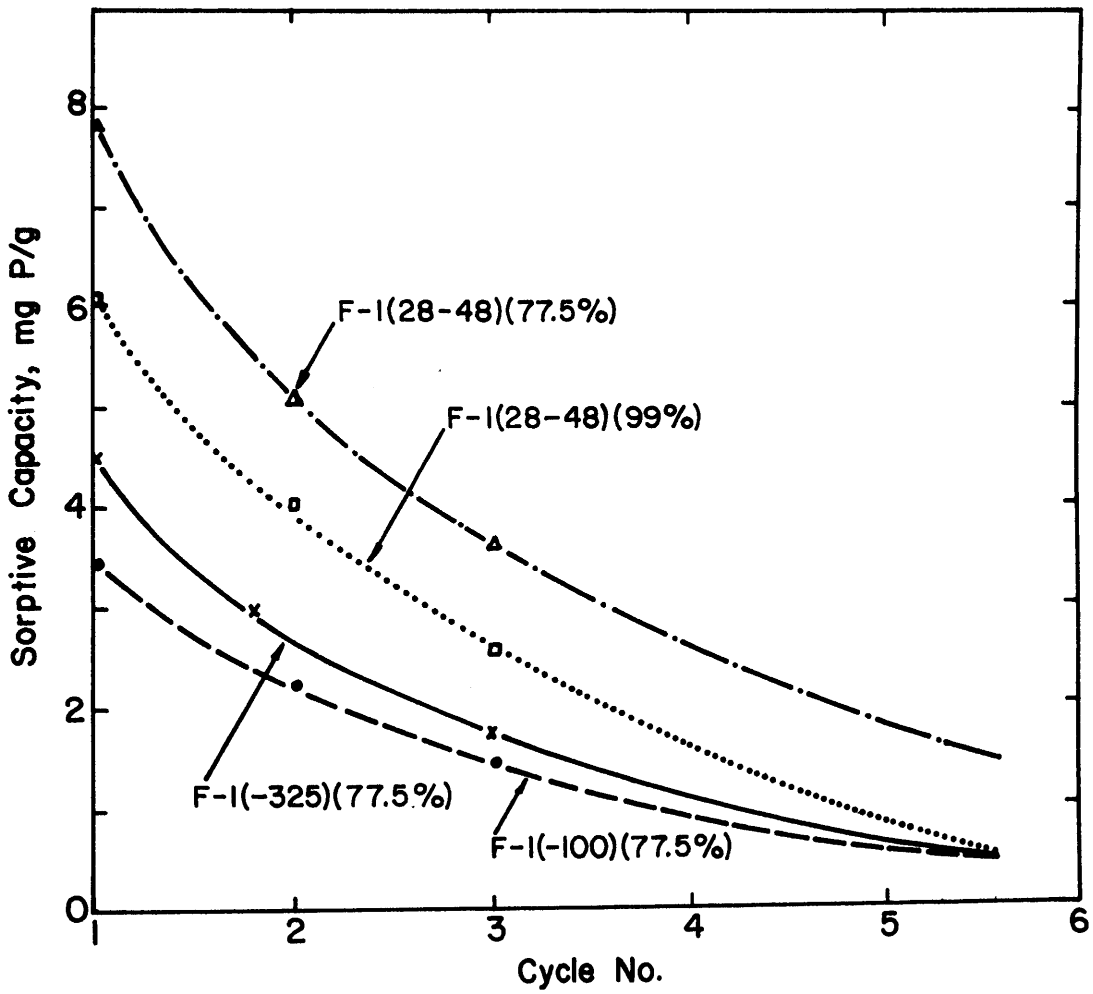


FIGURE 23. SORPTIVE CAPACITY OF REGENERATED ALUMINA — PROJECTION OF VALUES

$$A_1 = \frac{Pi - Pe}{S_1} \times \frac{3.785 \times 1000}{454} = 8.34\,\frac{Pi - Pe}{S_1} \qquad \text{(Eq 2)}$$

$$A_2 = A_1 - A_1Y\,\frac{S2}{S_1} = A_1 - \frac{1}{S_1}\,(A_1YS_2)$$

$$A_3 = A_1 - A_1Y^2\,\frac{S3}{S_1} - A_2Y\,\frac{S2}{S_1} = A_1 - \frac{1}{S_1}\,(A_2YS_2 + A_1Y^2S_3)$$

$$A_n = A_1 - \frac{1}{S_1}\,(A_{n-1}YS_2 + A_{n-2}Y^2S_3 + \ldots + A_2Y^{n-2}S_{n-1} + A_1Y^{n-1}S_n) \qquad \text{(Eq 3)}$$

where: A_1 = initial alumina required, lb/1000 gal
$A_2, A_3, \ldots, A_n$ = Make-up alumina required for 2nd, 3rd, ..., nth cycle, lb/1000 gal
P_i = influent phosphorus concentration, mg P/l
P_e = effluent phosphorus concentration, mg P/l
S_1 = sorptive capacity of fresh alumina, mg P/g
$S_2, S_3, \ldots, S_n$ = sorptive capacity of alumina after 1,2, ..., n-1 regenerations, mg P/g
$Y = 1 - L$
L = fractional loss of alumina per sorption-regeneration cycle

The amount of sodium hydroxide regenerant required for each cycle could be determined using the following equations.

$$R_2 = CA_1$$

$$R_3 = CA_1Y + CA_2 = CY\,(A_1 + \frac{A2}{Y})$$

$$R_4 = CA_1Y^2 + CA_2Y + CA_3 = CY^2\,(A_1 + \frac{A2}{Y} + \frac{A3}{Y^2})$$

$$R_n = CA_1Y^{n-2} + CA_2Y^{n-3} + \ldots + CA_{n-2}Y + CA_{n-1} \text{ or}$$

$$R_n = CY^{n-2}\,(A_1 + \frac{A2}{Y} + \ldots + \frac{A_{n-2}}{Y^{n-3}} + \frac{A_{n-1}}{Y^{n-2}}) \text{ or}$$

$$R_n = CY^{n-2}\sum_{2}^{n}\frac{A_{n-1}}{Y^{n-2}} \qquad \text{(Eq 4)}$$

where: $R_2, R_3, R_4, \ldots, R_n$ = NaOH regenerant required for 2nd, 3rd, 4th, ..., nth cycle, lb/1000 gal
C = regenerant requirement, lb NaOH/lb alumina

On the basis of the regenerant requirements determined in the studies, which were 0.085 and 0.094 g OH^-/g alumina for the rapid mix-sedimentation and column systems, the value of C was taken as 0.20 and 0.22 lb NaOH/lb alumina for the F-1 (-325) and F-1 (-100) and for the F-1 (28-48) aluminas, respectively.

The chemical costs determined for this process were considerably higher than values reported in the literature (13) for chemical precipitation. Considering an 80 percent reduction of the total phosphorus in primary treatment using alum and ferric chloride at a 1.5:1 Al:P or Fe:P molar ratio, and a 10-mg P/l raw wastewater concentration, the chemical costs, including polymer requirements, were estimated in 1971 to be $0.036 and $0.042/1000 gal (3785 l) for ferric chloride and alum. Under similar conditions, the cost for lime treatment was reported to be $0.014/1000 gal (3785 l). These values, adjusted to present cost levels,* would have been $0.015, $0.038, and $0.044/1000 gal (3785 l) respectively for lime, ferric chloride, and alum. All these values do not reflect capital and operating costs which would depend on the size of the plant and its location. One fundamental advantage of the sorption process is its ability to effect essentially 100 percent removal of phosphorus; however, this would only be possible in the column mode. Wastewater effluent standards limiting the residual phosphorus concentration to 0.1 mg P/l, or specifying removals ranging up to 95 percent have been reported (13) and chemical precipitation would not be capable of meeting these limits.

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*For "heavy and agricultural chemicals" the cost index was 121.52 on October 11, 1971, and 127.44 on September 16, 1974 (60); consequently, a 1.049 factor was applied in order to update these values.

VIII. CONCLUSIONS

The findings of this investigation permit the following conclusions to be drawn.

1. The bench and field-scale rapid mix-sedimentation and column test systems, which were especially designed and built for this investigation, were an appropriate means for studying the removal of nutrients by sorption on activated alumina; although field operation was highly indicated because it closely approximated plant conditions, widely varying influent waste characteristics made this system difficult to control and affected the uniformity of the data produced, complicating their analysis and evaluation.
2. The F-1 (-325)* and F-1 (-100) aluminas in the rapid mix-sedimentation mode, and the F-1 (28-48) alumina in the column mode substantially reduced the phosphorus content, but did not significantly affect the total nitrogen concentration of a highly nitrified secondary wastewater treatment plant effluent.
3. The exhausted aluminas could be regenerated for reuse by treatment with sodium hydroxide followed by a water wash, however, the regenerated materials were not as effective as the corresponding fresh aluminas.
4. The removal of phosphorus averaged 76 percent in the rapid mix-sedimentation system, and in excess of 88 percent in the column system, from an average influent concentration of 7.2 mg P/l; the column system could also effect essentially complete removals of phosphorus, but at significantly reduced volumetric throughputs.

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*The aluminas were products of the Aluminum Company of America, Pittsburgh, PA; the number in parenthesis indicates mesh size.

5. The removals of NH_3-N and Org-N ranged from 10 to 30 and from 56 to 75 percent, respectively, and the corresponding influent concentrations were 1.24 and 0.40 mg N/l; less than 4 percent reduction was obtained in NO_3-N, which at 12.5 mg N/l represented more than 87 percent of total nitrogen, while NO_2-N increased by 0.02 to 0.07 mg N/l.
6. The effluent from the rapid mix-sedimentation system had approximately 30 percent less COD, however, discharge of alumina particles increased its TSS concentration by an average of 100 [F-1 (-100)] to 822 [F-1 (-325)] percent; the column effluent had 35 percent less COD, and except for initial wash-out of alumina fines, the TSS concentration was not significantly affected.
7. The average sorptive capacity of fresh F-1 (-325), F-1 (-100), and F-1 (28-48) aluminas, based on phosphorus data, was 4.5, 3.4, and 7.8 (6.1 at column breakthrough) mg P/g, respectively; sorptive capacity was affected by the alumina dose applied, the amount of phosphorus removed, and the residual phosphorus concentration.
8. The regeneration of exhausted aluminas with 1M sodium hydroxide required doses ranging from 0.085 (rapid mix-sedimentation system) to 0.096 (column system) g OH^-/g alumina; the volume of regenerant and wash water constituted 1.4 to 4.6 percent of the volume of the secondary effluent treated.
9. The reclaimed aluminas lost approximately 34 percent of their sorptive capacity following the 1st regeneration and an additional 22 percent following the 2nd regeneration; this loss could have resulted in part from coating of the alumina particles by calcium carbonate.

10. The physical loss of material in a sorption-regeneration cycle was 13.5, 9.2, and 1.8 percent, respectively for the F-1 (-325), F-1 (-100), and F-1 (28-48) aluminas.

11. The chemical cost (alumina and sodium hydroxide) of a 77.5 percent reduction of phosphorus in secondary effluent containing 7.5 mg P/1 using F-1 (-325), F-1 (-100), and F-1 (28-48) aluminas was estimated at $1.38, $1.76, and $0.84/1000 gal (3785 1), respectively; the cost increased to $1.43/1000 gal (3785 1) if 90 percent removal were to be achieved using the F-1 (28-48) material (column mode only).

12. The cost of phosphorus removal by sorption on activated alumina was significantly higher than the corresponding cost of treatment by chemical precipitation; however, the sorption process was capable of effecting essentially 100 percent removal of phosphorus and should be considered when the required degree of treatment cannot be obtained by the precipitation method.

IX. RECOMMENDATIONS FOR FUTURE WORK

On the basis of the experience gained in this study, the following areas of research would appear to merit consideration.

1. The feasibility of regenerant recovery and related cost, and the ultimate disposal of the wastes generated by the sorption process should be investigated; these would have a significant effect on the practicality and overall economic evaluation of the method.
2. The modification of the regeneration process to incoporate removal of the calcium carbonate coating warrants further study; it would help to restore the sorptive capacity of the reclaimed aluminas, thereby reducing chemical cost, and might be accomplished by means of an acid wash (using carbonic or hydrochloric acid) to dissolve the deposited material.
3. The logarithmic relationship which appeared to exist between the alumina dose and the ratio of phosphorus removal to phosphorus residual needs further experimental verification and analytical justification to assure its applicability to a broad range of operational conditions.
4. The fate of nitrogen in the activated alumina sorption process should be further investigated using secondary effluent from a treatment plant operating near design conditions.
5. The design of the alumina column system should be revised to include high-rate backwashing, necessary in order to reduce the clogging and channelling problems.
6. The capital and operational costs should be determined in addition to the chemical cost in order to establish the full economic potential of the sorption process.

BIBLIOGRAPHY

1. Sawyer, C.N., "ABC's of Cultural Eutrophication and Its Control. Part I-Cultural Changes." Water and Sewage Works, 118, 278 (1971).

2. Kuentzel, L.E., "Bacteria, Carbon Dioxide, and Algal Blooms." Journal Water Pollution Control Federation, 41, 1737 (1969).

3. Lange, W., "Effect of Carbohydrates on the Symbiotic Growth of Planktonic Blue-Green Algae with Bacteria." Nature, 215, 2177 (1967).

4. Mackenthun, K.M., Keup, L.E., and Stewart, R.K., "Nutrients and Algae in Lake Sebasticook, Maine." Journal Water Pollution Control Federation, 40, R72 (1968).

5. King, D.L., "The Role of Carbon in Eutrophication." Journal Water Pollution Control Federation, 42, 2035 (1970).

6. Ghassemi, M. and Christman, R.F., "Properties of the Yellow Organic Acids of Natural Waters." Limnology and Oceanography, 13, 583 (1968).

7. Massey, A. and Robinson, J., "A Review of the Factors Limiting the Growth of Nuisance Algae." Water and Sewage Works, 118, 352 (1971).

8. King, D.L., "Carbon Limitation in Sewage Lagoons." Nutrients and Eutrophication Special Symposia, American Society of Limnology and Oceanography, 1, 98 (1972).

9. Goldman, J.C., Oswald, W.J., and Jenkins, D., "The Kinetics of Inorganic Carbon Limited Algal Growth." Journal Water Pollution Control Federation, 46, 554 (1974).

10. Sawyer, C.N., "Biological Engineering in Sewage Treatment." Sewage Works Journal, 16, 925 (1944).

11. Albertson, O.E. and Sherweed, R.J., "Phosphate Extraction Process." Journal Water Pollution Control Federation, 41, 1467 (1969).

12. Sawyer, C.N. and Ferullo, A.F., "Nitrogen Fixation in Natural Waters Under Controlled Laboratory Conditions." Algae and Metropolitan Wastes, U.S. Public Health Service, Publication No. SEC TR W61-3, 100 (1961).

13. "Process Design Manual for Phosphorus Removal." U.S. Environmental Protection Agency Technology Transfer (October 1971).

14. Sawyer, C.N., "The need for Nutrient Control." Journal Water Pollution Control Federation, 40, 363 (1968).

15. Mercer, B.W., Ames, L.L., Touhill, C.J., Van Slyke, W.J., and Dean, R.B., "Ammonia Removal From Secondary Effluents by Selective Ion Exchange." Journal Water Pollution Control Federation, 42, R95 (1970).

16 Barth, E.F., "Control of Nitrogen in Wastewater Treatment." Environmental Protection Agency, Technology Transfer Seminar, Dallas, TX (July 1971).

17. Menar, A.B. and Jenkins, D., "The Fate of Phosphorus in Waste Treatment Processes: The Enhanced Removal of Phosphate by Activated Sludge." Proceedings 24th Industrial Waste Conference, Purdue University Extension Series 135, 655 (1969).

18. Vacker, D., Connel, C.H., and Wells, W.N., "Phosphate Removal Through Municipal Wastewater Treatment at San Antonio, Texas." Journal Water Pollution Control Federation, 39, 750 (1967).

19. Scalf, M.R., Pfeffer, F.M., Lively, L.D., Witherow, J.L., and Priesing, C.P., "Phosphate Removal at Baltimore, Maryland." Journal Sanitary Engineering Division, American Society of Civil Engineers, 95, SA5, 817 (1969).

20. Witherow, J.L., "Phosphorus Removal by Activated Sludge." Proceedings 24th Industrial Waste Conference, Purdue University Extension Series 135, 1169 (1969).

21. Barth, E.F., Jackso, B.N., Lewis, R.F., and Brenner, R.C., "Phosphorus Removal from Wastewater by Direct Dosing of Aluminate to a Trickling Filter." Journal Water Pollution Control Federation, 40, 1932 (1968).

22. Nesbitt, J.B., "Phosphorus Removal - The State of the Art." Journal Water Pollution Control Federation, 41, 701 (1969).

23. Zenz, D.R. and Pivnicka, J.R., "Effective Phosphorus Removal by Addition of Alum to the Activated Sludge Process." Proceedings 24th Industrial Waste Conference, Purdue University Extension Series 135, 273 (1969).

24. Schmid, L.A. and McKinney, R.E., "Phosphate Removal by a Lime-Biological Treatment Scheme." Journal Water Pollution Control Federation, 41, 1259 (1969).

25. Grigoropoulos, S.G., Vedder, R.C., and Max, D.W., "Fate of Aluminum-Precipitated Phosphorus in Activated Sludge and Anaerobic Digestion." Journal Water Pollution Control Federation, 43, 2366 (1971).

26. Minton, G.R. and Carlson, D.A., "Combined Biological-Chemical Phosphorus Removal." Journal Water Pollution Control Federation, 44, 1736 (1972).

27. Unz, R.F., "Microbiological Characterization of Activated Sludge in a Waste Water Treatment Plant Chemically Modified for Phosphorus Removal." U.S. National Technology Information Service, PB Report No. 210157 (1971); Chemical Abstracts, 78, 7517t (1973).

28. Anderson, D.T. and Hammer, M.J., "Effects of Alum Addition on Activated Sludge Biota." Water and Sewage Works, 120, 63 (1973).

29. Yee, W.C., "The Selective Removal of Mixed Phosphates from Water Streams by Activated Alumina." Oak Ridge National Laboratory, Report ORNL-TM-1135 (1965).

30. Yee, W.C., "Selective Removal of Mixed Phosphates by Activated Alumina." Journal American Water Works Association, 58, 239 (1966).

31. Neufeld, R.D. and Thodos, G., "Removal of Orthophosphates from Aqueous Solutions with Activated Alumina." Environmental Science and Technology, 3, 661 (1969).

32. Ames, L.L., "Alumina Columns for Selective Removal of Phosphorus from Wastewater." Robert A. Taft Water Research Center, Report No. TWRC-8 (March 1969).

33. Ames, L.L. and Dean, R.B., "Phosphorus Removal from Effluents in Alumina Columns." Journal Water Pollution Control Federation, 42, R161 (1970).

34. Yue, C.M., "Removal of Phosphates by Sorption on Activated Alumina." M.S. Thesis, University of Missouri-Rolla, (1970).

35. Purushothaman, K. and Yue, C.M., "Removal of Phosphorus from Waste Water to Control Eutrophication." Trace Substances in Environmental Health-V, University of Missouri, Columbia, 95 (1972).

36. Mulbarger, M.C., "Nitrification and Denitrification in Activated Sludge Systems." Journal Water Pollution Control Federation, 43, 2059 (1971).

37. Baumann, R.E., "Nitrogen Control in the Midwest." Presented at a Technology Transfer Seminar, U.S. Environmental Protection Agency, Region VII, Kansas City (1971).

38. Haug, R.T. and McCarty, P.L., "Nitrification with Submerged Filters." Journal Water Pollution Control Federation, 44, 2086 (1972).

39. Reeves, T.G., "Nitrogen Removal; A Literature Review." Journal Water Pollution Control Federation, 44, 1894 (1972).

40. Culp, G. and Slechta, A., "Nitrogen Removal from Sewage." Final Progress Report, U.S. Public Health Service Demonstration Plant Grant 86-01 (February 1966).

41. Culp, R., "Water Reclamation at South Tahoe." Water and Wastes Engineering, 6, No. 4, 36 (1969).

42. O'Farrell, T.P., Frauson, F.P., Cassel, A.F., and Bishop, D.F., "Nitrogen Removal by Ammonia Stripping." Journal Water Pollution Control Federation, 44, 1527 (1972).

43. Eliassen, R., Wyckoff, B.M., and Tonkin, C.D., "Ion Exchange for Reclamation of Reusable Supplies." Journal American Water Works Association 57, 113 (1965).

44. Eliassen, R. and Tchobanoglous, G., "Removal of Nitrogen and Phosphorus." Proceedings 23rd Industrial Waste Conference, Purdue University Extension Series 132, 35 (1968).

45. Midkiff, W.S. and Weber, W.J.,Jr., "Operating Characteristics of Strong-Base Anion Exchange Reactors." Proceedings 25th Industrial Waste Conference, Purdue University Extension Series 137, 593 (1970).

46. Evans, S., "Nitrate Removal by Ion Exchange." Journal Water Pollution Control Federation, 45, 632 (1973).

47. Winkler, B.F. and Thodos, G., "Kinetics of Orthophosphate Removal from Aqueous Solutions by Activated Alumina." Journal Water Pollution Control Federation, 43, 474 (1971).

48. Gangoli, N. and Thodos, G., "Phosphate Adsorption Studies." Journal Water Pollution Control Federation, 45, 842 (1973).

49. Pacific Northwest Laboratory, Battelle Memorial Institute, "Ammonia Removal from Agricultural Effluents by Selected Ion Exchange." Robert A. Taft Water Research Center, Report No. TWRC-5 (1969).

50. McLaren, J.R. and Farquhar, G.J., "Factors Affecting Ammonia Removal by Clinoptilolite." Journal of the Environmental Engineering Division, American Society of Civil Engineers, 99, EE4, 429 (1973).

51. "Standard Methods for the Examination of Water and Wastewater." 13th Edition, American Public Health Association, New York (1971).

52. "Activated and Catalytic Aluminas." ALCOA Product Data Chemicals, Section GB2A, Aluminum Company of America, Pittsburgh (1967).

53. Johnson, B.A., Aluminum Company of America, St. Louis, Personal Communication (1974).

54. Metcalf & Eddy, Inc., "Wastewater Engineering: Collection, Treatment, Disposal." McGraw-Hill Book Company, New York (1972).

55. Sawyer, C.N. and McCarty, P.L., "Chemistry for Sanitary Engineers." 2nd Edition, McGraw-Hill Book Company (1967).

56. "Inorganic Index to the Powder Diffraction File." Joint Committee on Powder Diffraction Standards, Philadelphia (1970).

57. "Tables of Interplanar Spacings for Angle 2θ." Code 8-2049, X-Ray Department, General Electric (Undated).

58. "Activated and Catalytic Aluminas and Alumina Gel." ALCOA Chemical Products Price Data, Section GB1A, Aluminum Company of America, Pittsburgh (1974).

59. Williams, J., Chemtech Corporation, St. Louis, Personal Communication (1974).

60. "Chemical Marketing Reporter." Schell Publishing Company, Inc., N.Y., <u>200</u>, No. 15, 20 (1971) and <u>206</u>, No. 12, 11 (1974).

VITA

Checkman Michael Yue was born on October 29, 1933, in Hong Kong, British Colony. He received his primary and secondary education in Hong Kong. He then enrolled at the Cheng Kung University, Taiwan, Republic of China, where he received a Bachelor of Science degree in Civil Engineering in June 1959.

Following graduation, he was employed as an engineering assistant by Yu Seto Authorized Architect, Hong Kong, July 1959 to June 1960; as an assistant engineer by the Pressure Piling Co., (Hong Kong) Ltd., September 1960 to February 1963; and as an assistant engineer by the Hong Kong Water Authority, Public Works Department, March 1963 to August 1968.

He was enrolled as a graduate student in civil engineering at the University of Missouri-Rolla in September 1968, and served as a Graduate Research Assistant in Civil Engineering, July 1969 to June 1970. He received a Master of Science degree in Civil Engineering in December 1970 and was awarded a Predoctoral Research Fellowship by the Office of Water Programs, U.S. Environmental Protection Agency, for doctoral study and research in nutrient removal, September 1970 to August 1972. He served as a Graduate Teaching Assistant in Civil Engineering, August 1972 to June 1974, and as a Graduate Research Assistant in Environmental Health, Summer 1974. He was the recipient of an Albert W. Happy Scholarship, Fall 1974.

He is a registered professional engineer in Missouri, a member of the Society of the Sigma Xi and the Chi Epsilon Fraternity, and a student member of the American Water Works Association, Water Pollution Control Federation, and Missouri Water Pollution Control Association.

He was married to Miss Cecilia Chow on February 21, 1966.

APPENDIX A

SEDIMENTATION COLUMN DATA

The settling characteristics of the activated aluminas in secondary wastewater effluent were determined using a 3-in. (7.6-cm) diam, 4.4-ft (1.34-m) high plastic settling column which was equipped with 4 sampling ports at 12-in. (30.5-cm) intervals from the top. Ten-l volumes of secondary effluent containing varying doses of alumina were first mixed for 22 min and were then introduced into the column. At predetermined time intervals, samples were withdrawn from the ports and analyzed for turbidity and TSS, and the results are given in Table A-1. An analysis of these data to determine the settling velocity and required detention time for the 3 aluminas is presented in Chapter V.

TABLE A-1. SEDIMENTATION COLUMN STUDIES WITH ACTIVATED ALUMINA

F-1(-325)

Alumina Dose g/l	Settling Time min	Secondary Effluent		Column Depth, ft							
				1		2		3		4	
		Turb. jtu	TSS mg/l	Turb. jtu	TSS mg/l	Turb. jtu	TSS mg/l	Turb. jtu	TSS mg/l	Turb. jtu	TSS mg/l
1.95	0		10		1808						
	10				770		710		716		692
	30				310		346		332		378
	60				158		256		210		220
	120				52		110		134		142
1.30	0	18	28	170	1010						
	10			200	734	200	734	200	724	200	568
	30			200	368	200	394	200	400	200	406
	60			160	97	180	232	180	242	180	258
	120			80	78	140	142	150	184	160	164
	240			70	64	80	80	80	82	95	108
	0	18	28	140	1378						
	10			220	600	220	484	220	532	220	498
	30			180	232	190	282	190	250	190	292
	60			130	130	140	158	140	160	150	174
	120			60	54	85	88	95	116	120	116
	240			50	40	60	52	75	68	90	94
	0	17	24	150	1162						
	5			160	986	160	1012	160	1066	160	1072
	10			190	682	190	728	180	790	180	770
	20			200	438	200	438	200	530	200	526
	30			200	302	200	358	200	392	200	400
	60			160	158	180	222	180	260	190	272
	120			70	48	140	132	150	166	160	196
	0	24	50	140	1144						
	5			160	1048	140	1170	140	1178	140	1174
	10			190	710	190	952	190	766	190	762
	25			200	382	200	420	200	456	200	476
	50			180	216	190	288	200	298	200	314
	100			120	84	160	174	120	192	120	204
	130			70	48	160	142	160	174	160	178
0.65	0	13	10	200	602						
	10			200	468	200	504	200	532	200	544
	30			180	234	190	288	180	302	190	330
	60			140	126	160	166	160	200	160	208
	120			80	46	120	88	130	112	140	152

TABLE A-1(cont.). SEDIMENTATION COLUMN STUDIES WITH ACTIVATED ALUMINA

F-1(-100)

Alumina Dose g/l	Settling Time min	Secondary Effluent		Column Depth, ft							
				1		2		3		4	
		Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l
1.95	0	13	38	120	580						
	10			75	170	85	228	85	254	85	236
	30			55	106	55	120	60	130	60	144
	60			45	80	48	86	50	84	50	96
	120			40	62	39	64	40	68	40	76
1.30	0	18	40	110	500						
	10			55	116	60	134	60	130	65	148
	30			35	62	40	72	45	76	45	96
	60			26	18	35	54	35	58	36	64
	120			21	2	20	4	27	14	25	44
	240			16	18	18	24	23	30	23	30
	0	18	40	100	306						
	10			45	58	50	66	55	92	60	110
	30			30	24	33	36	37	44	39	44
	60			22	6	25	18	28	14	31	26
	120			16	0	17	2	22	6	23	16
	240			18	6	18	2	17	0	17	4
	0	17	26	110	1154						
	5			70	202	85	168	90	324	95	336
	10			55	112	65	146	75	186	80	214
	20			45	60	52	94	55	96	60	104
	30			31	34	40	60	50	76	50	94
	60			26	28	38	54	40	58	45	72
	120			18	32	27	28	33	38	33	36
	0	12	10	120	630						
	5			75	190	80	230	95	304	100	378
	10			50	92	65	144	70	164	75	200
	25			40	66	45	70	50	80	55	106
	50			28	28	38	50	55	56	55	66
	100			18	18	28	34	30	44	32	40
	130			16	10	27	20	32	44	32	40
0.65	0	9	12	50	258						
	10			36	66	45	100	45	120	50	140
	30			27	38	28	50	31	54	35	62
	60			24	36	23	26	26	36	27	38
	120			20	22	20	24	21	26	20	22

TABLE A-1(cont.). SEDIMENTATION COLUMN STUDIES WITH ACTIVATED ALUMINA F-1(28-48)

Alumina Dose g/l	Settling Time min	Secondary Effluent		Column Depth, ft							
				1		2		3		4	
		Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l	Turb jtu	TSS mg/l
1.95	0	11	8	15	12						
	10			14	18	14	16	14	20	14	16
	30			13	16	13	12	13	12	13	12
	60			13	6	13	14	13	10	13	10
	120			13	10	12	6	12	8	12	6
	0	11	14	14	23						
	10			14	18	13	18	14	24	14	24
	30			12	18	13	12	13	24	13	18
	60			12	14	12	16	12	16	12	16
	120			9	8	10	12	11	18	11	18
1.30	0	13	12	17	58						
	5			16	24	16	10	16	12	17	24
	10			14	20	15	10	15	14	15	14
	20			15	14	15	10	15	12	15	14
	30			14	12	14	12	14	12	15	10
	55			14	6	13	12	13	8	13	10
	120			12	4	12	2	13	8	13	14
	0	13	32	18	34						
	5			18	16	19	18	19	16	18	10
	10			17	26	18	34	18	28	18	30
	25			15	6	17	16	17	28	17	24
	50			13	16	15	22	17	24	16	30
	100			13	16	14	22	14	24	15	24
	130			12	14	13	22	14	28	14	24
	0	18	16	22	24						
	5			20	24	20	20	19	20	19	24
	10			18	18	18	18	18	16	18	10
	20			17	10	18	16	18	14	18	10
	30			17	18	18	16	18	12	18	8
	60			17	8	17	16	17	8	17	8
	120			15	10	14	8	14	4	14	6
	0	18	16	23	18						
	5			22	10	22	26	22	26	22	20
	10			20	12	21	20	21	14	21	20
	25			20	4	20	12	20	6	18	12
	50			16	0	18	6	18	12	18	12
	100			12	0	13	2	16	8	17	10
	130			11	0	14	6	16	10	16	8
0.65	0	11	12	13	6						
	10			12	12	12	14	12	16	12	16
	30			12	16	12	12	12	16	12	12
	60			11	12	12	8	12	8	12	6
	120			12	4	12	14	11	6	11	8
	0	10	14	13	22						
	10			13	14	13	14	14	16	14	20
	30			10	14	11	14	12	16	12	16
	60			9	12	10	10	11	16	11	16
	120			9	8	10	4	10	14	11	14

APPENDIX B

ABBREVIATIONS

The following abbreviations have been used in this dissertation.

Acid-hydrolyzable phosphorus	Poly+ortho-P
Alkyl benzene sulfonate	ABS
Ammonia nitrogen	NH_3-N
Chemical oxygen demand	COD
Column or bed volume	cv
Nitrate nitrogen	NO_3-N
Nitrite nitrogen	NO_2-N
Organic nitrogen	Org-N
Suspended solids	SS
Total dissolved solids	TDS
Total kjeldahl nitrogen	Total kjeldahl-N
Total phosphorus	Total-P
Total suspended solids	TSS