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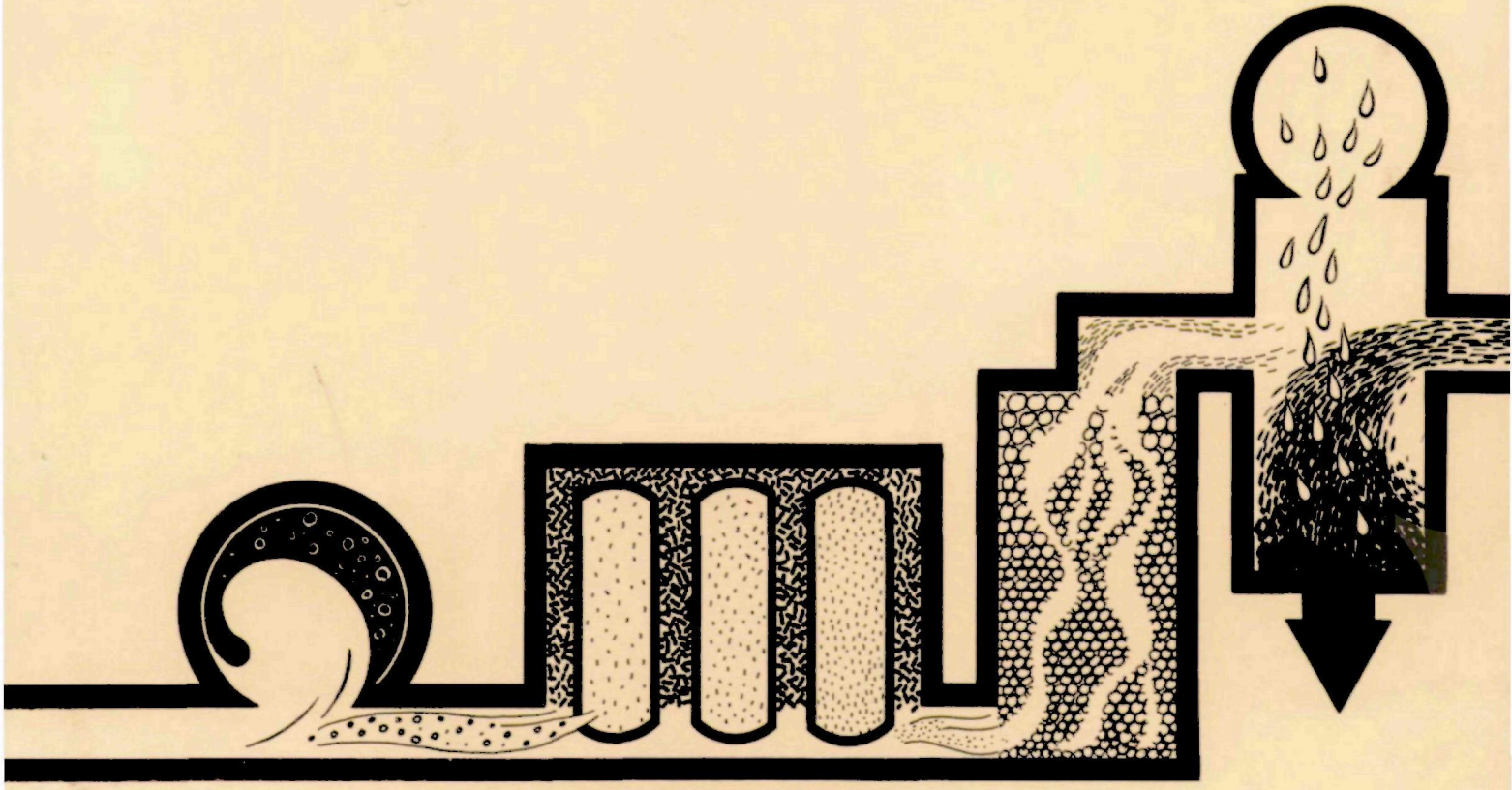
Soluble Phosphorus in the Activated Sludge Process

Part 1
Chemical-Biological Process Performance



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SOLUBLE PHOSPHORUS REMOVAL IN THE ACTIVATED SLUDGE PROCESS

PART I

CHEMICAL-BIOLOGICAL PROCESS PERFORMANCE

by

The Soap and Detergent Association

New York, N. Y. 10016

for the

Office of Research and Monitoring

ENVIRONMENTAL PROTECTION AGENCY

Project #17010 EIP

May 1971

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ABSTRACT

It was the objective of this research to develop and evaluate, at full plant scale, the combined chemical-biological process of phosphorus removal. The research was conducted in two major investigative phases using the final aeration and settling tanks of that portion of the Pennsylvania State University Wastewater Treatment Plant which treats wastewater from the PSU campus.

The Phase I investigations indicated an Al/P (filt. ortho) weight ratio of 2.25/1 was necessary to reduce the influent phosphorus of approximately 10 mg P/l to approximately 0.3 mg P/l in the filtered effluent. Alum proved to be a more effective precipitant than sodium aluminate in the moderately alkaline wastewater available for this study. The best results were obtained when the chemical was added at or near the effluent end of the aeration tank.

The total phosphorus concentration of the unfiltered effluent was dependent upon effluent suspended solids levels as well as on effluent soluble phosphorus concentrations.

Removal of organic matter was improved as a result of chemical addition in the chemical-biological process.

Alum addition into the effluent channel from the aeration tank resulted in an inhibition of nitrification apparently as a result of pH changes which occurred. No such effect was noted with the use of sodium aluminate.

The chemical-biological process produced approximately twice as much weight of sludge as did the parallel control. Alum addition did not reduce the sludge volume index (SVI) of the mixed liquor whereas sodium aluminate addition resulted in significant decreases.

Costs for chemical precipitation of phosphorus in the chemical-biological process to reduce the phosphorus from 10 mg P/l to 0.3 mg P/l are estimated to vary from 7.3 ¢/1000 gal in a 1 MGD plant to 4.1 ¢/1000 gal in a 100 MGD plant. Total treatment costs are estimated to vary from 39.6 ¢/1000 gal to 16.7 ¢/1000 gal for the 1 and 100 MGD plants respectively.

This report was submitted in fulfillment of Project Number 17010 EIP under the partial sponsorship of the Water Quality Office, Environmental Protection Agency, and by the Soap and Detergent Association, New York, New York.

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LIST OF SYMBOLS

GENERAL

BOD - biochemical oxygen demand

BOD_5 - five-day BOD

BOD_{5A} - BOD_5 applied

BOD_{5R} - BOD_5 removed

COD - chemical oxygen demand

IS - inorganic suspended solids

LF - activated sludge loading factor, wt BOD_{5A}/wt MLVS/t

MLSS - mixed liquor total suspended solids

MLVS - mixed liquor volatile suspended solids

R - correlation coefficient

Sr - wt BOD_{5R}/wt MLVS/t

SS - total suspended solids

SVI - sludge volume index

t - time

t_{SA} - solids age

VS - volatile suspended solids

VS_P - VS produced

MATHEMATICAL SYMBOLS AND ABBREVIATIONS

< - less than

= - equals

> - greater than

log - common logarithm to base 10

CONCLUSIONS

From the results of this study and other related work, it may be concluded that:

1. A very high degree of removal of soluble phosphorus can be obtained continuously in full plant scale operation using the chemical-biological process. The removal efficiency is dependent primarily upon the Al/P ratio. In the system studied, an Al/P (filt. ortho) ratio of 2.25/1 was necessary to achieve a filtered effluent total phosphorus concentration of approximately 0.3 mg P/l when aluminum sulfate (alum) was used as the precipitating chemical.

2. Alum was a more efficient precipitant than was sodium aluminate for the moderately alkaline wastewater available for this study. An Al/P (filt. ortho) ratio of 2.25/1 resulted in a filtered effluent total phosphorus concentration of approximately 0.5 mg P/l when sodium aluminate was used.

3. The best results were obtained when the chemical (alum or sodium aluminate) was added at the effluent end of the aeration tank. No deterioration in effluent quality was observed at very high Al/P (filt. ortho) ratios when alum was added at the effluent end.

4. It was not feasible to adjust chemical feed rates manually to compensate routinely and rapidly for changes in influent flow and phosphorus concentration. The effect of changing flows was much more significant than that of changing phosphorus concentrations in the system studied so that automatic pacing of chemical feeders with flow would have improved significantly the operating performance of the system

5. Removal of organic matter as measured by unfiltered effluent BOD_5 and COD was enhanced as a result of chemical addition.

6. Suspended solids losses from the chemical-biological system were very heavy when flows were high and surface settling rates in the final clarifier exceeded 800 gal/sq ft/day. At low flows, the effluent suspended solids were significantly lower in the chemical-biological system than in the parallel control.

7. Because of the demonstrated relationship between effluent suspended solids and effluent insoluble phosphorus concentration, it is essential that effluent filtration be provided where extremely high unfiltered

effluent total phosphorus removals are required. Effluent filtration may be advisable also in other situations as a factor of safety to protect against unexpected solids losses and resulting high phosphorus residuals.

8. Alum addition into the effluent channel from the aeration tank resulted in an inhibition of nitrification under the operating conditions experienced during the study. It is thought that this inhibition was a pH related phenomenon although this could not be shown conclusively from the observed data. No inhibition was observed with the use of sodium aluminate which does not depress the pH as alum does or when alum was added at the influent end of the aeration tank with higher MLSS.

9. The study demonstrated that approximately twice as many pounds of total solids were produced in the chemical-biological system as in the conventional activated sludge control when alum was used as the precipitant. The addition of alum did not decrease the SVI of the mixed liquor whereas addition of sodium aluminate significantly reduced the SVI. While these results reflect conditions observed in the system studied, they are not necessarily typical of results which would be obtained in other systems because of the lower than normal SVI observed in the activated sludge control.

10. Attempts to identify the "carry-through" which occurs when the precipitant is added at the head end of the aeration tank were not successful. It appears to be a finely divided "aluminum phosphate" precipitate which does not settle out in the clarifier. pH has an effect on the amount of "carry-through" as does the point of chemical addition but under the conditions of this study it was impossible to separate these two factors completely and to identify their respective roles.

11. The removal of phosphorus by alum addition resulted in lower fertility in the treated effluent compared to the untreated effluent as measured by the Provisional Algal Assay Procedure. These studies were very limited in scope and should not be considered generally applicable to field conditions.

12. Costs for phosphorus precipitation by the chemical-biological process for 97% filtered effluent total phosphorus removal (based on 10 mg P/l in the influent waste) vary from 7.3 ¢/1000 gal for a 1 MGD plant to 4.1 ¢/1000 gal for a 100 MGD plant. These costs do not reflect the costs of the primary and biological treatment

units or the cost of filtration and sludge handling and disposal. Inclusion of these costs raise the figures to 39.6 ¢/1000 gal (1 MGD) and 16.7 ¢/1000 gal (100 MGD) based on the assumptions made.

RECOMMENDATIONS FOR FURTHER RESEARCH

The observations and findings of this study suggest the following as areas where further research would be beneficial:

1. The relative role of biological and chemical removal of organic substrate should be identified so that process design and operation parameters can be optimized.

2. The effect of alum addition on nitrification should be identified conclusively so that process design and operation can be modified to achieve desired degrees of nitrification.

3. Additional investigations of the effect of both pH adjustment and polymer addition as means of improving effluent quality and optimizing chemical addition should be made.

4. Better definition of the role of phosphorus in controlling eutrophication should be determined so that realistic treatment requirements can be established.

INTRODUCTION

GENERAL STATEMENT OF THE PROBLEM

The problems created by "cultural eutrophication" of our surface waters now are recognized by the general public as well as by professionals working in water pollution control. The aesthetic and economic effects of the nuisance-level proliferation of aquatic plants no longer can be ignored or merely talked about.

Nutritional limitation has been suggested as a means of controlling eutrophication and phosphorus has been the nutrient most workers have focused attention on as being most feasible to control. Domestic and industrial wastewaters are, in many instances, the major sources of phosphorus input to our surface waters. Since these represent point discharges, they most easily are subject to control methods and hence most attention has been directed towards development of phosphorus removal methods for treatment of wastewaters.

Nesbitt (24, 25) in his reviews of phosphorus removal included the various work which has been done on the chemical precipitation of phosphorus. Hall and Englebrecht (11) have also presented a comprehensive review of currently employed phosphorus removal technology. Most workers seem to agree that some form of chemical precipitation of phosphorus is the best way to achieve the high degrees of removal being required. However, there is no general agreement as to which of the several available precipitating chemicals or which of the many process schemes is best. Nesbitt (24) concluded on the basis of the figures presented in his report that chemical precipitation combined with high rate activated sludge appeared to be the most economical of the chemical precipitation processes.

CHEMICAL-BIOLOGICAL PROCESS CONSIDERATIONS

Several investigators have studied phosphorus removal by precipitation with aluminim or iron salts within the aeration tanks of the activated sludge process. The original work suggesting this concept of phosphorus removal was done by Stumm (41) and was further developed and expanded by Tenney and Stumm (43). This basic work was then developed into a complete process design utilizing a high rate activated sludge system in a continuous flow bench scale study by Eberhardt and Nesbitt (9). The above studies used alum precipitation and showed the chemical-biological process to be capable of a high degree of phosphorus removal while at the same time achieving removals of organic carbon which are typical of high rate activated sludge systems. Barth and Ettinger (2) in a 100 gpd pilot plant study were also able to demonstrate excellent phosphorus removals using sodium aluminate as the precipitant. Brenner (4, 5) has reviewed the chemical-biological process and presents summary data from several studies of the process.

In order to demonstrate the applicability of the chemical-biological process for full plant scale use as well as to develop operating procedures and cost data for this process, it was proposed to study the process in a prototype plant scale at the Pennsylvania State University Wastewater Treatment Plant.

Objectives of the Present Investigation

The specific objectives of the study were:

1. To determine the relative merits of sodium aluminate and aluminum sulfate (alum) as sources of aluminum ion for the precipitation of phosphorus.

2. To determine the optimum precipitant dosage and point of application in the system.

3. To determine the efficiency of the precipitating agent in removing phosphorus and BOD over a one-year operating period and to compare these results with those obtained from a parallel control unit which was not to receive any chemical addition.

4. To develop recommended design and operating procedures and estimated costs for the process based on the system studied.

EXPERIMENTAL APPROACH

GENERAL PLAN OF RESEARCH

The research was conducted and is reported herein as two major investigative phases:

Chemical Selection and Process Optimization (Phase I)
Process Performance and Cost Analyses (Phase II)

The initial studies on chemical selection and process optimization were designed to evaluate the relative effectiveness of two aluminum compounds in precipitating phosphorus. Selection of the optimum chemical dosage and point of application for each of the two chemicals studied were also accomplished during this period.

The second phase of the project was designed to gather long term operating data on process performance. These data were then used as the basis for development of recommended operating procedures and cost data for the chemical-biological process of phosphorus removal.

PROCESS SCHEMES

The research was conducted using the final aeration and settling units of that part of the Pennsylvania State University Wastewater Treatment Plant which treats University wastewater and in the digestion units serving the entire plant. It is the purpose of this section to provide only a physical description of the treatment units. Pertinent operating conditions will be reported elsewhere.

A simplified flow sheet of the complete treatment plant is shown in Figure 1.

The final aeration tanks provide second stage biological treatment of the University wastewater following first stage high rate trickling filtration. Each of the two aeration tanks has a capacity of 15,600 cu ft which provides a theoretical detention time of 2.25 hours at the original design flow of 2.0 million gallons per day (MGD) plus 25% return sludge. Aeration is provided by rotary displacement variable drive blowers using valved orifice diffusers on swing drop pipes. Initial design air application rates were 0.56 cu ft/gal/day or 1,000 cu ft/day/lb BOD_5 (42).

The final settling tanks each have an area of 1,300 sq ft thus giving a surface settling rate of 770 gal/sq ft/day at a design flow of 2.0 MGD. In 1965, a sludge flotation thickener unit was added to thicken the waste activated sludge from the portion of the plant treating Borough of State College wastewater. The underflow from the thickener is discharged into the trickling filter effluent so that it receives

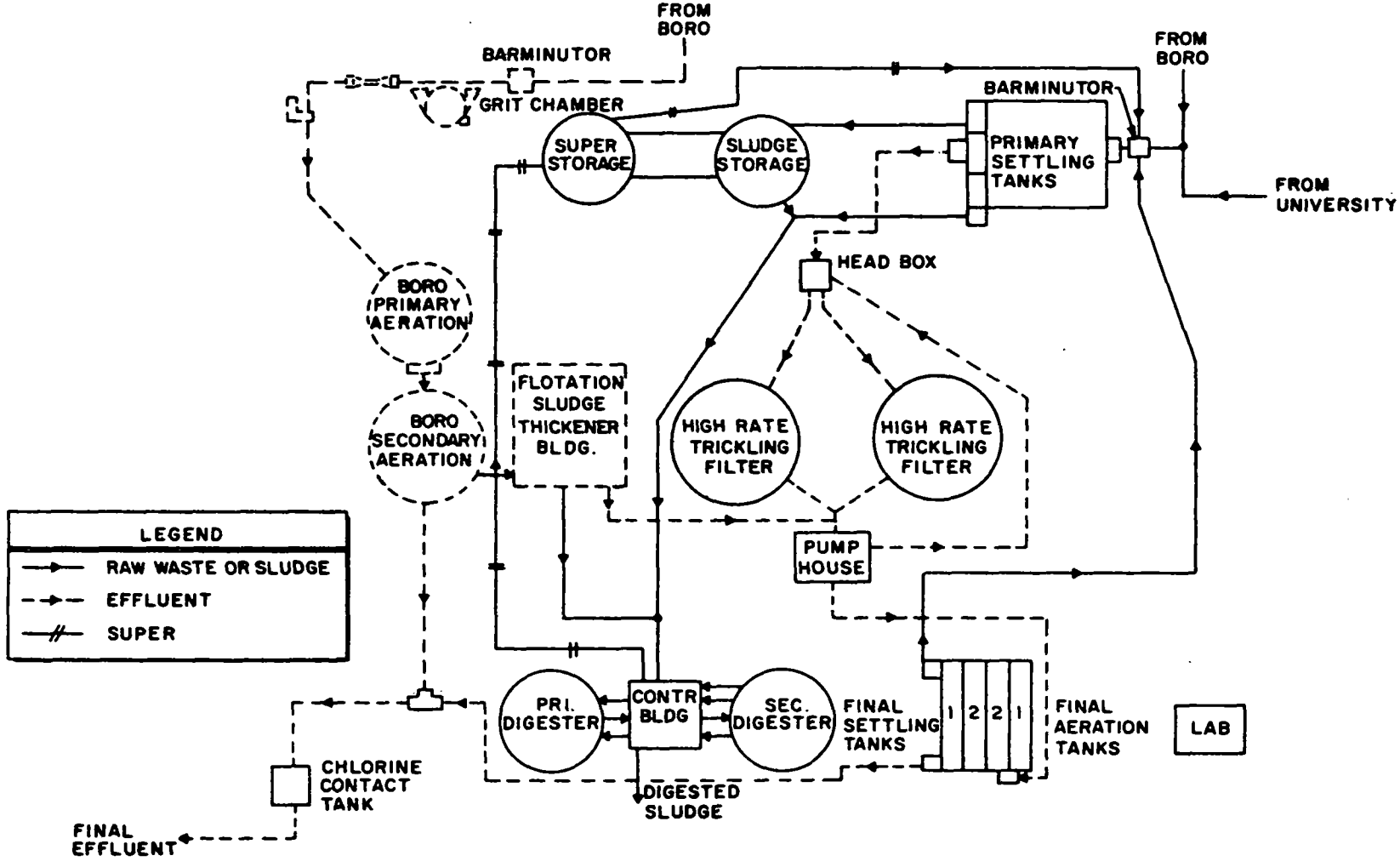


Figure 1. Schematic Flow Diagram University Wastewater Treatment Plant

treatment in the activated sludge units included in this study. This additional flow reduces the design detention time in the aeration tanks to 2.12 hours and increases the design surface settling rate to 825 gal/sq ft/day in the final settling tanks. The design air application rates are reduced to 0.53 cu ft/gal/day or 925 cu ft/day/lb BOD_5 (42).

Recirculation of return sludge to Aeration Tank No. 1 was accomplished using the existing sludge recirculation pumping station and a modified piping scheme to permit return to Tank No. 1 only. The existing telescopic drawoff valves in Final Settling Tank No. 2 were removed and 4 inch air lift pumps were installed in their place to permit recirculation of sludge to Aeration Tank No. 2. Sludge from each of the tanks was wasted by means of the existing waste sludge pumps. Return sludge recirculation flows and waste sludge flows for each tank were individually metered by magnetic flow meters.

Feeding of chemicals was accomplished by metering the chemical through a Wallace & Tiernan Model 747 diaphram pump with gravity flow through 1/2-inch insulated plastic lines to the point of chemical application. The chemicals were purchased in liquid form and were stored in a 5,000 gallon vinyl lined wooden tank. The amount of chemical fed each day was obtained from measured changes in the tank level. Pump calibration curves were prepared to permit accurate feed rate adjustment with the different chemicals used.

Typical properties of the commercial liquid chemicals used in the study are:

	Aluminum Sulfate	Sodium Aluminate
Total Soluble Al_2O_3	8.3%	26.7%
Na_2O_3	--	18.3%
Total Fe	0.2%	0.002%
Insoluble in water	0.3%	--
Viscosity, Centipoises		
60°F	27	2100
90°F	15	260
Weight lb/gal 60°F	11.2	13.1

ANALYTICAL TESTS AND PROCEDURES

Routine sampling of the influent to the aeration tanks (trickling filter effluent) and the final effluent from each settling tank was done on a 3-day per week schedule, usually Sunday, Tuesday and Thursday, so the samples could be analyzed on Monday, Wednesday and Friday. Samples were collected automatically over a 24-hour period by means of SERCO Model NW-3-8 samplers. Grab samples of the mixed liquor from each aeration tank were collected 5 days per week about 8:00 A.M.

Composite samples of waste sludge from each tank were collected twice weekly, usually on Monday and Wednesday.

A summary of the tests performed and analytical procedures used throughout this investigation follows:

Alkalinity -- Alkalinity determinations were made in accordance with Standard Methods (40) using a pH of 4.5 as the titration end point.

Aluminum -- Aluminum ion determinations were made using the "Rapid Modified Eriochrome Cyanine R Method for the Determination of Aluminum in Water" reported by Shull and Guthan (36). Samples were filtered and diluted prior to analysis.

Biochemical Oxygen Demand -- BOD was determined by the method given in Standard Methods (40). Nitrification was inhibited by means of allyl thiourea in all instances except where noted.

Calcium and Magnesium -- Ca and total hardness were measured by the EDTA titrimetric method of Standard Methods (40) using Betz calcium and hardness indicators. Mg was determined by difference from total hardness and calcium results.

Calcium in Sludges -- Total calcium in sludge samples was determined in accordance with the procedure reported by Menar and Jenkins (23) except that Betz Calcium Indicator was used in place of hydroxnapthol blue.

Chemical Oxygen Demand -- COD was measured by the procedure developed at the Sanitary Engineering Research Laboratory (SERL) of the University of California (32).

Color -- Color determinations were made using a Hellige Aqua Tester Model No. 611 with a 611-10 color disc.

Filtration -- Filtration for solids determinations and where used prior to other analytical tests was performed using 5.5 cm diameter Reeve Angel glass fiber filter pads and Millipore filter flasks and adapters.

Nitrogen -- Ammonia and total Kjeldal nitrogen were determined by the methods given in Standard Methods (40). Oxidized nitrogen was determined by the Standard Methods chromotropic acid method (40).

pH -- pH measurements were made using a Fisher Accumet pH meter Model 210.

Phosphorus -- The Stannous Chloride Method for Orthophosphate in Standard Methods (40) was used for all of the phosphorus determinations. All tests were conducted in an incubator controlled at 20°C and ten minutes were allowed for color development before readings were taken. Readings were taken at a wave length of 600 mμ using a Bausch and Lomb Spectronic 20 spectrophotometer with a 1-inch light path. The methods of sample preparation varied as indicated below:

> Total phosphorus determinations on mixed liquor and waste sludge samples followed a modified alkaline ash procedure used by Eberhardt and Nesbitt (9). Total phosphorus determinations on influent and effluent samples were made using a modification of the binary acid wet-ash procedure (46).
>
> Total and orthophosphate were determined on both filtered and unfiltered samples.

Sludge Volume Index -- SVI of the mixed liquor was determined in accordance with Standard Methods (40).

Suspended and Volatile Solids -- All suspended and volatile solids analyses were carried out using the procedure reported by Eberhardt and Nesbitt (9).

Sulfate -- Sulfate analyses were conducted using the Turbidimetric Method of Standard Methods (40). All samples were filtered and diluted prior to analysis.

Turbidity -- All turbidity measurements were made with a Hach Model 2100 Laboratory Turbidimeter.

PHASE I INVESTIGATIONS

PROGRAM OF STUDY

The primary purpose of Phase I of the project was to compare the relative merits of aluminum sulfate (alum) and sodium aluminate as precipitating agents for use in removing phosphorus from domestic wastewater. Selection of optimum points of chemical addition and dosages were also accomplished during this period of study.

Addition of chemical to both aeration tanks was undertaken in order to compare results obtained using various Al/P ratios and points of addition in less time than would have been necessary if one tank was maintained as a parallel control.

INFLUENT WASTE

The major portion of the raw waste influent to the part of the treatment plant used in the study was derived from the Pennsylvania State University campus. A portion of the flow originates from commercial and residential buildings along College Avenue in the Borough of State College. No significant industrial wastes are tributary to the plant but since the major portion of the wastes originate on campus they could be characterized as more typical of institutional wastes than residential domestic wastes. As can be seen from the flow diagrams Figure 1 and 2, the wastes receive barminution, primary settling and high rate trickling filtration prior to treatment in the activated sludge units used in this study. Underflow from the flotation thickener is directed to the activated sludge units under normal operation as indicated previously. Data on wastewater characteristics will be reported elsewhere.

Variations in student population during the different terms of the school year together with the relatively long vacation periods when students were nearly all absent from the campus created fluctuations in flow and phosphorus concentration that were atypical of most municipal installations. In addition, although the other portion of the plant, intended to treat Borough flow, has a design capacity of 2.0 MGD, flows in excess of 1.7 MGD cause severe operating problems. Therefore, all flows to this plant in excess of 1.7 MGD are diverted to the portion of the plant used in the study. These extreme variations in flows together with flows well in excess of design capacity (2.0 MGD) as a result of diversion from the other plant caused problems which will be discussed later.

PLANT OPERATIONAL PROCEDURES

General

Plant operational procedures followed those normally employed in conventional activated sludge plants. Addition of the precipitating

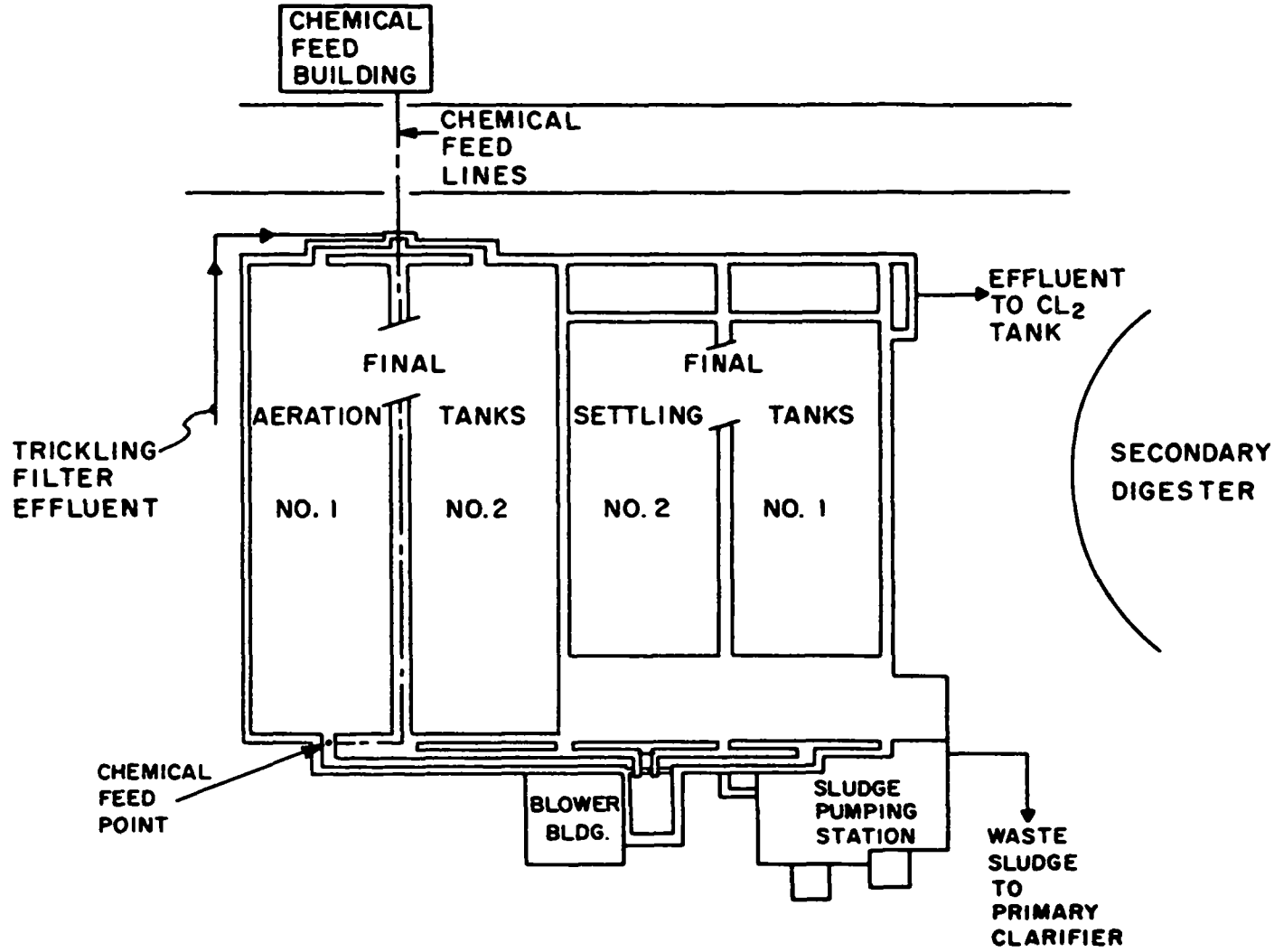


Figure 2. Phosphorus Removal Process Simplified Flow Sheet

chemical did not alter these procedures but did require some additional operational considerations and time.

Chemical Addition

Since addition of chemical was solely for removal of phosphorus, amounts of chemical to be added were calculated to achieve a desired aluminum to phosphorus (Al/P) ratio. Phosphorus in the influent waste can be measured in several different ways depending on the particular analytical procedure used, i.e., filtered or unfiltered, ortho or total, etc. It was decided for the purposes of this project to use the filtered orthophosphate in the trickling filter effluent (aerator influent) as the basis for chemical dosage calculations. This basis was selected since the particular test procedure is simple, fairly rapid and is particularly well suited for use in a typical wastewater treatment plant laboratory by plant personnel. All reported Al/P ratios are weight ratios since they were easier to use in day to day calculations thus minimizing errors.

Calculations for feed rate adjustment of chemical additions were based on the average orthophosphate concentration in the filtered trickling filter effluent, average wastewater flows and the desired Al/P ratio. Various Al/P ratios were selected for testing in order to determine the optimum ratio for each of the two chemicals tested and rates of chemical addition were then calculated to achieve the desired ratios. Actual Al/P ratios, for each day samples were collected, were later calculated from the data using actual flow, filtered trickling filter effluent orthophosphate concentration and the amount of aluminum fed.

Chemical feed rates were adjusted by treatment plant personnel three or four times daily (depending on flow patterns) in an attempt to optimize chemical addition. Rate changes were based only on average flow variations during the day. Variations in phosphorus concentrations during the day were also observed but the magnitude of change was not considered sufficient to incorporate into feed rate calculations during Phase I studies. Figure 3 shows typical variations in flow and phosphorus concentration for periods when the University was in session and a normal student population was on campus. Other workers (10) have observed that phosphorus concentration vary much more widely than those observed in this study. The relatively minor variations observed herein are most likely explained on the basis of the institutional nature of the raw waste and the habits of a student population which are atypical of a residential-commercial domestic waste flow pattern.

Because of daily variations in waste flow and influent phosphorus concentrations from values used for calculation of feed rates, it was impossible to achieve the desired Al/P ratio in all instances, in fact, the deviation from the desired ratio was much greater than had been anticipated. This will be considered again later when results of Phase II are discussed. As a result of this variation,

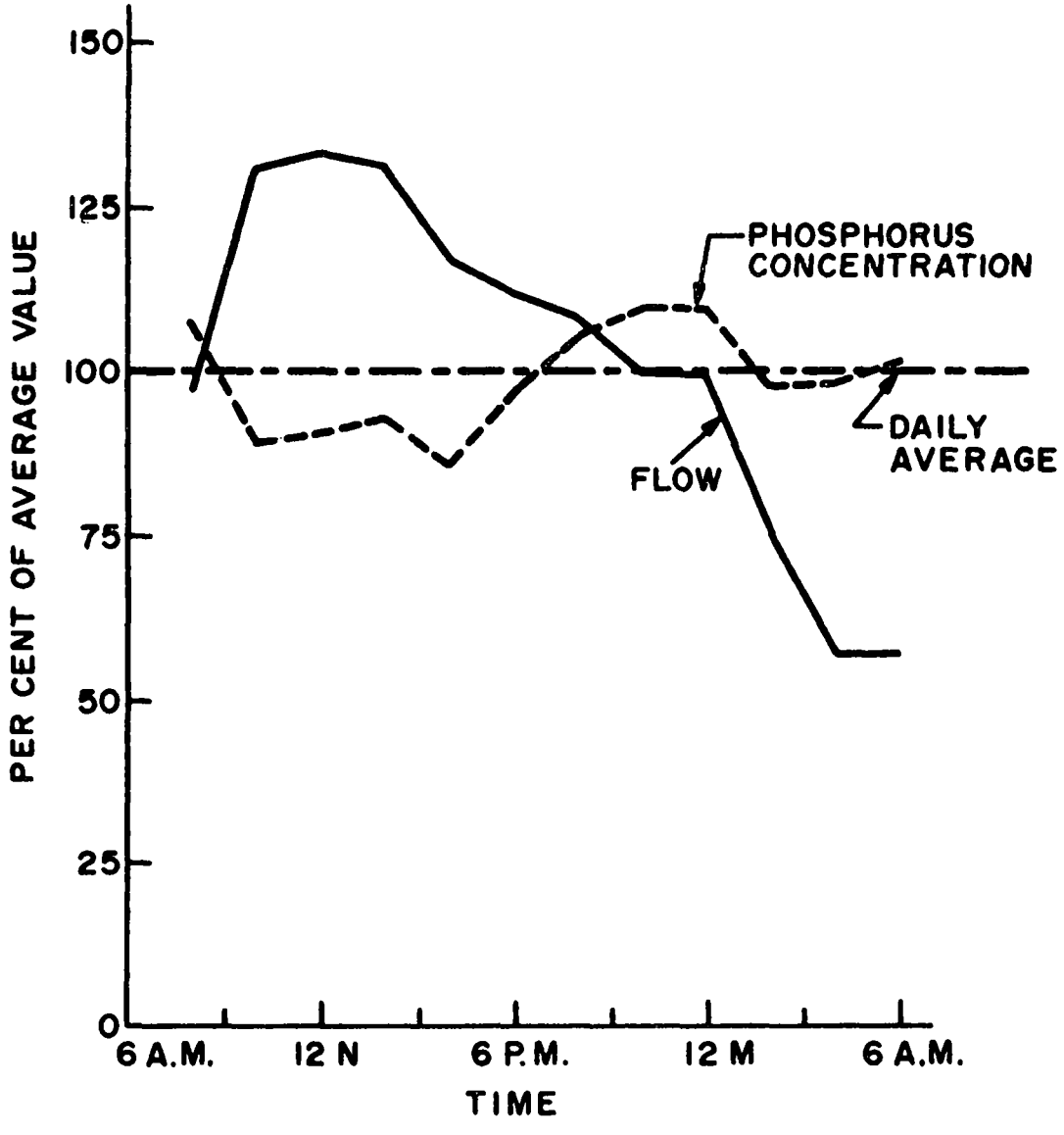


Figure 3. Typical Variation in Flow and Phosphorus Concentration

data presentation for Phase I studies is based on ranges of observed Al/P ratios rather than on time periods.

Sludge Wasting

A schedule for wasting excess sludge from the aeration tanks was established each day based on the mixed liquor suspended solids analysis for that day. Sludge was wasted over periods of time varying from 4 to 24 hours depending on the specific requirements necessary to maintain the desired solids in the aerators.

An attempt was made to carry approximately the same level of volatile solids (assumed to represent equal biomasses) in each aerator. It should be noted that the volatile fraction of mixed liquor suspended solids is much lower in the chemical-biological system than it is in a conventional activated sludge system. Therefore, it is necessary to carry a higher total mixed liquor suspended solids in the chemical-biological system than it is in conventional activated sludge if equal volatile solids concentrations are to be carried in each system. The volatile solids procedure which was used does not permit the direct determination of organic solids but includes, in addition, inorganic compounds which volatize at temperatures of up to 600°C. Although some of the compounds which are formed during the precipitation of phosphorus are aluminum-hydroxy-phosphates which undoubtably volatilize, no attempt was made to correct the apparent volatile solids data for purposes of plant control. Waste sludge volumes were measured with magnetic meters as indicated earlier. Waste sludge samples for phosphorus and solids analyses were also collected as indicated previously.

Mixed Liquor Solids Balance and Sludge Production Calculations

For purposes of performing a system solids balance, the following procedures were used: the weight of solids contained in the aeration tanks was calculated from the measured solids concentration and the design volume of the tanks. Effluent solids losses were computed from measured solids concentrations and effluent volumes (determined from raw wastewater flow data). No correction was made for the underflow from the flotation thickener or for solids in the clarifiers. Waste sludge volumes and solids concentrations were used to calculate the weight of sludge wasted.

Reported Solids Age

Solids age is defined consistently throughout this study as the quotient of the total system volatile solids under aeration divided by the volatile solids lost from the system and was calculated as follows:

$$\text{Solids Age } (t_{SA}) = \frac{\text{MLVS (mg/l) x Aeration tank volume (l)}}{\text{Eff VS (mg/l) x Eff volume (l) + (VS in Waste) } \pm \text{ MLVS (mg)}}$$

Sludge (mg)

Solids age data will be included with the other results presented later.

ALUMINUM SULFATE STUDIES

General Operation

Addition of liquid alum to one aeration tank (Tank No. 2) was begun on January 27, 1969 at a point two-thirds of the way along the tank from the influent end and directly above the diffusers so the roll of the tank would help to disperse the chemical. After an initial decrease in settling tank effluent suspended solids from the treated tank, observed for only a few hours after addition was started, these solids increased substantially over those observed in effluent from the untreated tank (Tank No. 1). In an attempt to remedy this solids loss, the point of chemical addition was moved to a point in the effluent channel carrying mixed liquor from the aeration tank to the clarifier. After this change, effluent suspended solids from the treated tank decreased and remained approximately the same as those from the untreated tank.

Alum addition to Tank No. 1 was started on February 21, 1969. Different Al/P ratios were established for each of the two tanks in order to obtain data which would permit evaluation of the optimum Al/P ratios for this system. The data obtained during the alum runs and during the brief period of no chemical addition are presented in Table 1. These data are average values obtained from all observations wherein the actual Al/P ratio observed fell into the ranges shown. Data from both Tanks No. 1 and No. 2 are averaged together since the period prior to chemical addition showed there was no significant difference in the results obtained from each individually.

Influent Waste (Trickling Filter Effluent)

Data presented in Table 1, Part A, show the characteristics of the influent waste to the aerators. As can be seen from the data, a considerable variation in wastewater quality was observed. The relatively low BOD was not unusual considering the removal that occurred during high rate trickling filtration prior to activated sludge treatment. Plant operating records show the BOD of the raw waste normally varies between 300 and 600 mg/l with an average of about 400 mg/l. The values observed for nitrogen and phosphorus are typical of domestic wastewater. The high percentage of orthophosphate (approximately 82%) is evidently a result of the biological treatment in the trickling filter. Eberhardt and Nesbitt (9) indicated that approximately 52% of the phosphate in the primary clarifier effluent from the University Treatment Plant was in the ortho form. Only a trace of aluminum was observed in the trickling filter effluent during the brief control period and the sulfate concentration was sufficiently low so as not to create a problem.

Table 1. Summary Data from Aluminum Sulfate Studies Phase I

A. Trickling Filter Effluent Characteristics

Parameter[a]	No Chemical Added	Chemical Added Run Code I	II	III	IV	V
Suspended Solids						
Total	88±37	145±26	124±26	134±30	134±21	138±14
Volatile	62±20	120±30	97±23	100±31	99±17	105±16
Unfiltered BOD_5	60±32	61±19	75±15	87±20	74±24	68±15
Unfiltered COD	194±52	257±78	216±49	244±77	227±47	249±135
Phosphorus - P						
Filtered						
Ortho	7.6±1.8	5.7±.9	6.3±1.1	6.4±0.6	6.9±0.8	7.7±0.9
Total	9.4±2.7	6.5±.6	7.9±1.5	7.6±1.7	7.7±1.5	8.4±1.0
Unfiltered						
Ortho	7.9±1.9	8.3±1.8	9.2±2.1	10.4±1.4	10.1±1.6	10.8±1.9
Total	10.1±1.9	9.9±2.2	10.4±2.5	12.4±2.7	13.4±2.0	13.2±1.2
Nitrogen - N						
Ammonia	16.1±5.6	20.2±5.0	21.5±3.7	19.5±3.1	19.5±3.2	19.6±3.4
Oxidized	4.4±3.8	0.7±0.3	0.6±0.2	0.5±0.2	0.5±0.2	0.6±0.3
T. Kjeld.	21.7 ±10.5	33.2 ±5.2	32.5 ±6.9	33.2 ±7.1	31.5 ±4.5	34.0 ±4.2
Aluminum - Aℓ	Tr.	0.10±.14	0.15±.07	0.15±.07	0.15±.07	0.20
Sulfate - SO_4	28±3	26±3	25±7	24±4	24±3	25±1
pH (units)	-	7.35±.30	7.40±.10	7.40±.10	7.40±.10	7.45±.20

Continued

[a]Values shown are averages for all data included in run plus or minus one standard deviation where more than one determination was made. All values are mg/ℓ except as noted.

Table 1 (Continued)

B. General Performance and Effluent Quality

Parameter[a]	No Chemical Added	Chemical Added Run Code I	II	III	IV	V
Suspended Solids						
Total	31±16	16±4.5	30±14	19±11	23±11	25±12
Volatile	20±9	15±2.6	22±16	11±5	14±8	14±7
Unfiltered BOD_5						
mg/ℓ	18±8	6±3	8±4	6±2	6±2	7±2
% Removal	66.6±9.8	88.8±6.4	88.7±4.8	92.7±2.3	89.3±5.9	88.9±3.6
Unfiltered COD						
mg/ℓ	94±45	43±17	33±17	31±15	36±16	54±21
% Removal	57.5±15	83.0±7.8	83.1±9.9	86.3±9.0	83.1±8.1	74.4±18.1
Nitrogen - N						
Ammonia	7.8±4.6	19.3±4.7	20.3±3.5	17.5±3.0	18.5±3.0	19.5±3.1
Oxidized	12.9±7.8	1.6±1.6	1.0±0.3	1.5±1.1	1.5±0.7	1.7±0.9
T. Kjeld.	14.6±5.8	23.1±6.4	26.3±6.1	21.0±3.8	22.5±4.8	25.4±6.3
Aluminum - Aℓ	Tr.	Tr.	0.15±.10	0.23±.12	Tr.	0.20
Sulfate - SO_4	28±3	167±24	139±18	131±32	77±12	73±15
pH	--	6.70±20	6.85±.10	7.10±.15	7.20±.10	7.30±0.10
Chemical Dose $A\ell_2(SO_4)_3 \cdot 14\ H_2O$	--	311±37	259±61	160±35	128±20	108±20

Continued

Table 1 (Continued)

C. Final Effluent - Phosphorus Removal Performance

Parameter[a]	No Chemical Added	Chemical Added Run Code I	II	III	IV	V
Phosphorus - P						
Filtered						
Ortho	8.0±2.0	0.05±.04	0.16±.16	0.28±.21	0.80±.34	1.57±.46
% Removal		99.1±0.9	97.4±2.7	94.6±3.3	88.8±4.8	77.2±9.6
Total	9.2±2.3	0.09±.05	0.18±.20	0.27±.23	1.02±.36	1.97±.74
% Removal		98.4±0.9	97.0±3.2	96.4±3.0	86.5±5.8	78.2±7.7
Unfiltered						
Ortho	8.2±1.9	0.40±.17	1.07±.40	1.17±.71	1.92±.92	3.9±3.0
% Removal		95.2±2.3	88.0±5.6	85.9±7.1	79.9±11.2	70.9±9.9
Total	9.7±1.9	0.54±.25	1.34±.62	1.48±.76	2.4±1.2	4.7±4.2
% Removal		94.1±2.7	86.5±7.2	87.2±6.7	82.6±9.4	78.2±7.6
$A\ell/P_{filt.\ ortho}$ Ratio		4.73/1 ±0.84	3.01/1 ±0.23	2.04/1 ±0.19	1.55/1 ±0.10	1.17/1 ±0.11

Key:

No chemical added - period from December 2, 1968 to January 27, 1969, no chemical addition

I - Alum addition with $A\ell/P_{filt.\ ortho}$ Ratio $\geq$ 3.50/1

II - Alum addition with 2.50/1 $\leq$ $A\ell/P$ $\leq$ 3.49/1

III - Alum addition with 1.75/1 $\leq$ $A\ell/P$ $\leq$ 2.49/1

IV - Alum addition with 1.35/1 $\leq$ $A\ell/P$ $\leq$ 1.74/1

V - Alum addition with 0.95/1 $\leq$ $A\ell/P$ $\leq$ 1.34/1

General Effluent Quality

Data presented in Table 1, Part B, show that addition of alum definitely enhanced removal of BOD and COD over that observed during the limited period of no chemical addition as indicated by the increase in BOD removals from approximately 67% to 89 - 93% and of COD removals from approximately 58% to 74 - 86% depending on the Al/P ratio employed. Allyl thiourea was used in all BOD determinations to inhibit nitrification, hence, results shown reflect only carbonaceous demand.

The loading factors (LF) during the period in which alum addition was used were as follows:

LF (lb BOD_{5A}/lb MLVS/day)

	Average ± 1 std. dev.	Range
Tank No. 1	0.517 ± 0.192	0.104 to 0.975
Tank No. 2	0.474 ± 0.194	0.119 to 0.932

From these results it can be seen the loadings on the activated sludge units were generally in the normal range for so called conventional activated sludge operation.

The BOD removal characteristics (Sr) for the same period were as follows:

Sr (lb BOD_{5R}/lb MLVS/day)

	Average ± 1 std. dev.	Range
Tank No. 1	0.462 ± 0.196	0.086 to 0.923
Tank No. 2	0.428 ± 0.200	0.087 to 0.983

The difference in the loading factors and removal rates between the two tanks were not significant at the 5% level.

Figure 4 shows the relationship between BOD loading and BOD removal for each tank during the alum studies. Regression analysis of the data yielded the following equations for the lines of best fit:

Tank No. 1 $\quad$ lb BOD_{5R} = 0.94 lb BOD_{5A} - 0.02 lb MLVS $\quad$ (1)

Tank No. 2 $\quad$ lb BOD_{5R} = 0.99 lb BOD_{5A} - 0.04 lb MLVS $\quad$ (2)

The correlation coefficients were found to be highly significant statistically.

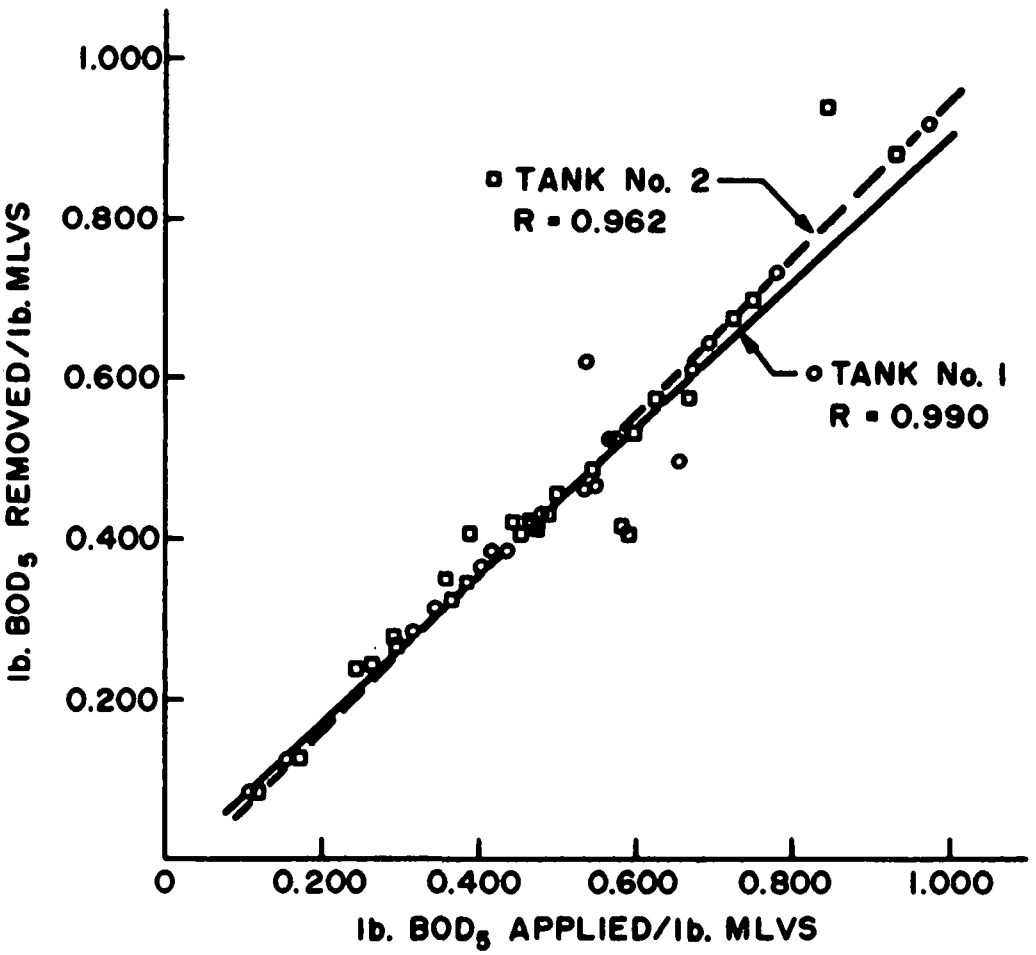


Figure 4. BOD Removal as a Function of BOD Loading Phase I Aluminum Sulfate Studies

Because hydraulic overloading of the final clarifiers during peak flow periods during the day results in washout of solids from the clarifiers, the effect of alum addition on suspended solids removal was impossible to assess during Phase I. Indications were that improved removal of suspended solids could be realized if hydraulic overloading could be eliminated. Data presented later with the results of Phase II support this observation.

The nitrogen data presented in Table 1, Part B, indicate that some inhibition of nitrification occurred as a result of alum addition. The results during the control period showed rather highly nitrified effluents as could be expected from a two stage plant such as this. However, since a major portion of the control period occurred during a time when most of the students were away from the University and consequently, the treatment plant was underloaded, it is impossible to tell from these data how much of the observed change was due to chemical addition and how much to change in organic loadings. Data obtained during this period were too limited to permit comparison of organic loading rates.

Aluminum values in the effluent remained quite low, never exceeding 0.2 mg/l as an average value. Some "carry-through" of aluminum was indicated by the increase in aluminum in the trickling filter effluent after chemical addition was begun. Waste sludge from the aerators was returned to the primary clarifiers and hence aluminum may have carried through to the trickling filters.

Increased sulfate concentrations in the effluent were observed with alum addition as was expected. The observed changes generally follow the changes in alum dosage as indicated in Table 1, Part B. In no instance did the effluent sulfate concentration reach the recommended permissible limit for receiving waters intended for use as public water supplies of 250 mg SO_4/l but it did exceed the desirable criteria of < 50 mg/l (48).

The pH in the system varied from 6.7 at Al/P (filt. ortho) ratios over 3.50/1 to 7.3 at the lowest Al/P ratios. Later discussion of pH values observed should be noted as it affects the results reported above.

Phosphorus Removal

Filtered phosphorus removals were excellent at high Al/P ratios as shown in Table 1, Part C. Filtered effluent phosphorus concentrations increase sharply at ratios less than 2/1. Figure 5 shows the effect of varying Al/P ratios on the filtered effluent total phosphorus concentration. These results indicate an Al/P (filt. ortho) ratio (based on filtered orthophosphate) of approximately 2.25/1 is necessary in the particular system studied to achieve filtered effluent total phosphorus concentrations of approximately 0.3 mg P/l. Comparable values for ratios based on unfiltered total phosphorus [Al/P (unfilt. total)] and filtered total phosphorus [Al/P (filt. total)] are approximately 1.8/1 and 2.0/1 respectively.

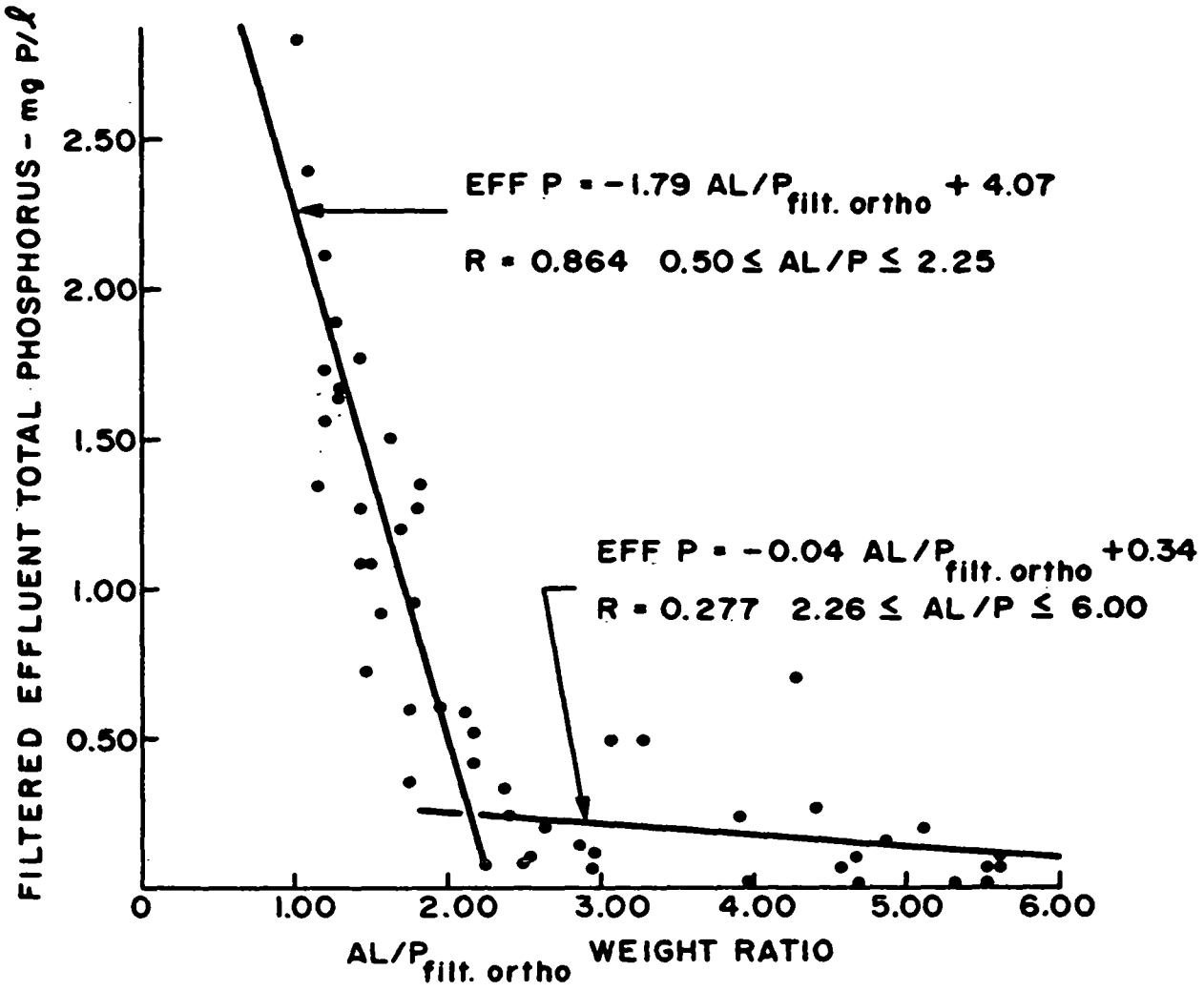


Figure 5. Effluent Phosphorus Concentration as a Function of $Al/P_{filt.\ ortho}$ Weight Ratio
Phase I Aluminum Sulfate Studies

Unfiltered effluent phosphorus removals were significantly lower at all Al/P ratios indicating that considerable amounts of phosphorus were escaping in the effluent suspended solids. Most of this was undoubtably precipitated phosphorus which was either entrapped in the chemical-biological floc or chemical floc which was too small to settle under the hydraulic conditions experienced.

On May 12, 1969 the points of alum addition were changed to the influent end of each aeration tank. The effluent data collected during this period indicated some decrease in BOD and COD removals (81% and 63% removal respectively) when compared with the results obtained when the chemical was added at the effluent end (Table 1). There was an even more pronounced decrease in removal of unfiltered phosphorus (50-60% removal). Filtered phosphorus removals were also somewhat lower (82-88% removal). Insufficient data were available from this portion of the study to permit comparison of results by the method used to develop Table 1 and, therefore, were not included in Table 1. Visual observation of effluents during this period showed them to be cloudy or "milky" and certainly not as clear as when the alum was added to the effluent end of the tanks. This same observation has been made by other workers who have added the precipitant to the influent end of the aerator (2, 52).

The Phase I alum studies were terminated on May 25, 1969.

SODIUM ALUMINATE STUDIES

General Operation

Addition of sodium aluminate to both aeration tanks was started on May 28, 1969 following thorough cleaning of the chemical storage tank and recalibration of the chemical feed pumps. Initially, addition of aluminate was made into the effluent channels from the aeration tanks at the same points used for alum addition. After a few days operation it became visibly apparent that the effluent was more cloudy than had been observed when alum was added at the same point. Since the amount of aluminate which must be fed per day to achieve a given Al/P ratio is only about one-third that required when feeding alum, it was decided to move the points of chemical addition to the influent end of the tanks to see if increased mixing time would improve effluent quality. Several more days of operation under these conditions did not result in a notable improvement in the effluent, in fact, it deteriorated even further. The points of addition were then moved to a point two feet from the effluent end of the aeration tanks directly over the diffusers. Improvement in the visual appearance of the effluent was noted within two days so it was decided to continue to operate with chemical addition at this point.

Results obtained from the sodium aluminate runs are presented in Table 2. Data from the initial period prior to selection of the final point of chemical addition were excluded since they were atypical of what can be expected from normal operation with chemical addition at the proper point.

Table 2. Summary Data from Sodium Aluminate Studies Phase I

A. Trickling Filter Effluent Characteristics

Parameter[a]	Run Code IA	IIA	IIIA	IVA	VA
Suspended Solids					
Total	81±15	95±18	94±19	84±15	81±16
Volatile	58±9	69±13	69±11	59±12	58±12
Unfiltered BOD_5	65±17	61±21	50±26	54±10	51±8
Unfiltered COD	190±100	207±99	160±26	180±86	213±101
Phosphorus - P					
Filtered					
Ortho	4.9±0.7	5.3±0.5	5.4±1.2	5.5±1.5	5.3±1.4
Total	5.0±1.0	5.5±0.6	6.9±0.8	6.8±0.9	6.5±0.9
Unfiltered					
Ortho	6.1±1.5	6.5±1.1	6.2±1.9	6.6±1.8	6.1±1.1
Total	6.4±1.6	6.8±1.0	8.6±2.3	10.5±1.7	9.9±1.7
Nitrogen - N					
Ammonia	3.6±2.1	3.7±2.6	2.0±2.1	4.9±2.9	3.8±2.9
Oxidized	5.0±4.7	5.5±4.6	2.7±1.3	4.7±2.8	5.0±3.9
T. Kjeld.	11.3±6.7	12.8±5.8	12.6±6.1	14.5±2.7	15.0±3.1
Aluminum - Aℓ[b]	0.0	--	--	--	--
Alkalinity - $CaCO_3$[b]	156±37	--	--	--	--
pH	7.20±.10	7.20±.05	7.15±.15	7.25±.05	7.25±.05

Continued

[a]Values shown are averages for all data included in run plus or minus one standard deviation where more than one determination was made. All values are mg/ℓ except as noted.

[b]Results shown are for all data and are not separated on the basis of Aℓ/P ratios since too few data were available.

Table 2 (Continued)

B. General Performance and Effluent Quality

Parameter[a]	Run Code IA	IIA	IIIA	IVA	VA
Suspended Solids					
Total	17±10	23±10	25±7	18±9	20±3
Volatile	11±5	11±6	14±3	11±5	12±3
Unfiltered BOD_5					
mg/ℓ	7±2	8±4	7±4	10±2	11±2
% Removal	86.0±1.5	84.1±7	81.2±6.1	82.6±3.1	80.7±1.0
Unfiltered COD					
mg/ℓ	25±24	46±13	36±22	28±19	45±22
% Removal	84.5±14	76.9±10.2	78.7±10.4	79.4±6	78.1±10.6
Nitrogen					
Ammonia	0.5±0.6	0.2±0.3	0.2±0.5	0.3±0.4	0.2±0.3
Oxidized	9.3±6.3	12.5±4.1	13.7±6.5	13.3±9.9	13.1±4.1
T. Kjeld.	2.9±2.6	6.0±5.2	4.5±4.7	1.6±2.4	1.9±2.2
Aluminum - Aℓ[b]	0.4±0.1	--	--	--	--
Alkalinity - $CaCO_3$[b]	103±9	--	--	--	--
pH	7.65±.25	7.50±.20	7.25±0.15	7.45±.05	7.45±.20
Chemical Dose $Na_2Al_2O_4$	77±23	46±9	44±7	30±5	22±3

Continued

Table 2 (Continued)

C. Final Effluent - Phosphorus Removal Performance

Parameter[a]	Run Code IA	IIA	IIIA	IVA	VA
Phosphorus - P					
Filtered					
Ortho	0.12±.10	0.31±.16	0.51±.38	0.85±.50	1.37±.43
% Removal	97.4±1.5	93.9±4.2	92.6±4.8	87.5±8.0	82.5±7.1
Total	0.12±.07	0.34±.17	0.57±.25	0.89±.47	1.37±.45
% Removal	97.5±1.1	93.4±4.3	91.9±3.0	86.8±8.0	82.5±8.0
Unfiltered					
Ortho	0.32±.31	0.77±.32	1.14±0.56	1.40±.53	1.99±1.20
% Removal	96.8±2.3	88.1±6.7	81.1±7.3	78.6±8.4	65.1±25.9
Total	0.43±.40	1.17±.31	1.53±0.61	2.1±.4	3.1±2.0
% Removal	93.6±5.9	80.2±10.6	81.7±7.9	79.1±5.7	68.6±19.3
$A\ell/P_{filt.\ ortho}$ Ratio	6.23/1 ±2.37	2.80/1 ±0.46	2.04/1 ±0.23	1.47/1 ±0.13	1.19/1 ±0.05

Run Code Key:

IA - Sodium aluminate addition with $A\ell/P_{filt.\ ortho}$ Ratio $\geq$ 3.50/1

IIA - Sodium aluminate addition with 2.50/1 $\leq$ $A\ell/P$ $\geq$ 3.49/1

IIIA - Sodium aluminate addition with 1.75/1 $\leq$ $A\ell/P$ $\geq$ 2.49/1

IVA - Sodium aluminate addition with 1.35/1 $\leq$ $A\ell/P$ $\geq$ 1.75/1

VA - Sodium aluminate addition with 0.95/1 $\leq$ $A\ell/P$ $\geq$ 1.34/1

Influent Waste (Trickling Filter Effluent)

Comparison of the characteristics of the aerator influent with those observed during the alum studies (Tables 2A and 1A) show some differences. It should be noted that the sodium aluminate runs were conducted during the Summer term at the University when the student population on campus is only about 40% as large as it is during the Fall, Winter and Spring terms. This population reduction most likely accounts for the lower values observed for all of the parameters measured. The most noticable differences were those observed in the relative amounts of nitrogen in the ammonia, oxidized and total Kjeldal forms. The lower flows and higher temperatures apparently resulted in appreciable oxidation of ammonia in the trickling filter. It should be pointed out that considerable variability in results was observed and relatively few data were obtained in each of the Al/P ratio ranges shown.

General Effluent Quality

Data presented in Table 2, Part B, show that although BOD and COD removals obtained during aluminate addition were higher than those experienced during the period prior to alum addition, they were not as high as those observed during alum addition. The loading factors during the period in which sodium aluminate addition was used were as follows:

LF (lb BOD_{5A}/lb MLVS/day)

	Average ± 1 std. dev.	Range
Tank No. 1	0.400 ± 0.161	0.230 to 0.708
Tank No. 2	0.408 ± 0.133	0.229 to 0.653

While these loadings are somewhat lower than those experienced during the alum runs they were still in the normal range for conventional activated sludge. The BOD removal characteristics for this same period were as follows:

Sr (lb BOD_{5R}/lb MLVS/day)

	Average ± 1 std. dev.	Range
Tank No. 1	0.333 ± 0.146	0.172 to 0.632
Tank No. 2	0.358 ± 0.107	0.195 to 0.544

Figure 6 shows the relationship between BOD loading and BOD removal for each tank during the sodium aluminate runs. Regression analysis of the data yielded the following equations for the lines of best fit:

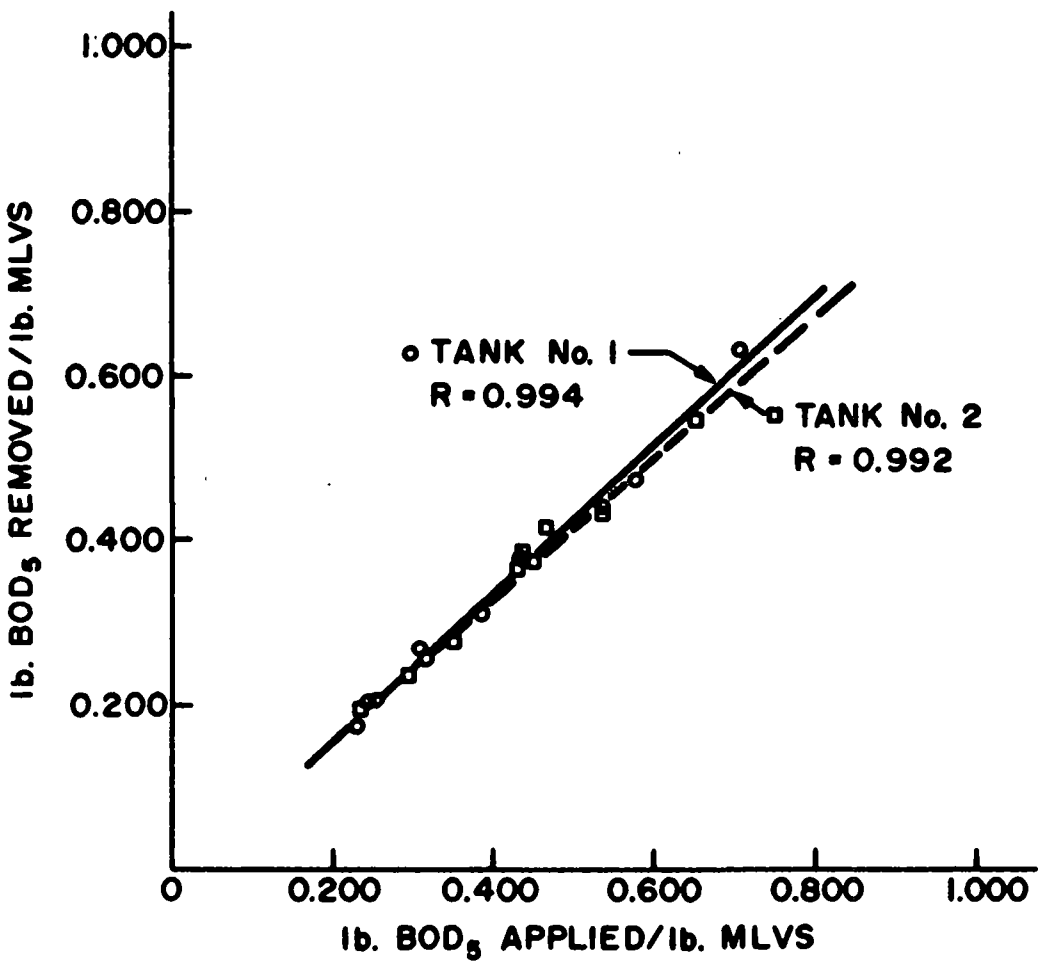


Figure 6. BOD Removal as a Function of BOD Loading Phase I Sodium Aluminate Studies

Tank No. 1 $\quad$ lb BOD_{5R} = 0.90 lb BOD_{5A} - 0.03 lb MLVS $\quad$ (3)

Tank No. 2 $\quad$ lb BOD_{5R} = 0.85 lb BOD_{5A} - 0.01 lb MLVS $\quad$ (4)

The correlation coefficients were found to be highly significant statistically.

The differences between the constants for the BOD loading and removal regression equations observed for the alum and sodium aluminate studies were significant at the 1% level. It is impossible to tell from the data whether the observed lower BOD removal rate and overall percentage removal for the sodium aluminate runs were due to the lower applied loading during the period or to the chemical used.

Although effluent suspended solids in the composite samples were generally lower than they were during alum addition, this reduction was probably due more to the occurrence of lower flows during this period than it was to the different chemical. Average flow through each tank was approximately 0.98 MGD during the alum runs whereas it was only about 0.66 MGD during the sodium aluminate runs.

Occasional visual inspection of settling tank effluents at various times during the day during the alum runs had shown that when peak flows occurred, periodic washout of solids resulted and at other times very few solids were being lost. Similar inspections during the aluminate runs when flows throughout the day were lower indicated a fairly uniform loss of solids during the day so it is impossible from the data to determine the relative effects of the two different chemicals on effluent suspended solids.

The nitrogen data presented in Table 2, Part B, show that significant nitrification occurred during chemical addition and hence no apparent inhibition from chemical addition was evident. However, these data do not permit a direct comparison with those obtained during the alum runs since other conditions were not the same and no control data for the aluminate runs are available. Temperatures and pH values were both higher during the aluminate runs than during the original control period and alum runs resulting in conditions which tend to optimize nitrification. Additionally, the aluminate runs were conducted during the Summer term at the University and because of a lower student population, the BOD loading on the aeration tanks was somewhat lower which also tends to favor nitrification. The data from this period are more nearly comparable to those obtained during the original period of no chemical addition in this respect.

Aluminum values were generally higher than those observed during the alum runs. Because of analytical problems with the aluminum test, it is the writer's opinion that residual soluble aluminum values for both the alum and aluminate runs were actually lower than those reported herein. Investigations which were conducted as part of the digester studies indicated some of the precipitated aluminum phosphate passes through the filter and is dissolved during the aluminum test and hence

is erroneously reported as "soluble" aluminum (26). This could explain the higher aluminum values observed during the aluminate runs since there was other evidence of greater "carry-through" of precipiated aluminum phosphate as indicated by the phosphorus results. The higher pH may also partially account for the higher Al^{+++} values observed since the precipitation reaction is not as efficient at the higher pH.

Sulfate data were not collected during this part of the study since sufficient background data on effluent sulfate concentrations were obtained during the original period of no chemical addition and no sulfate was being added to the system during the aluminate runs.

The effluent pH values generally ranged from 7.45 to 7.65 depending on the Al/P ratio employed. There is no apparent explanation for the low mean value of 7.25 experienced during Run Code III A. Individual values ranged from 7.00 to 7.85 throughout the aluminate runs and means shown were calculated from daily data correlated with Al/P ratio on a given day.

Phosphorus Removal

As was experienced during the alum runs, filtered phosphorus removals were very good at high Al/P ratios but they were not as good as those obtained with alum. Unfiltered phosphorus removals compared even less favorably with the alum results. This reduction apparently was due to a "carry-through" of very small particles of precipitated "aluminum phosphate" which did not occur with alum addition except when the alum was added to the influent end of the aeration tank. This "carry-through" was apparent visibly in the effluent as a cloudiness and on no occasion was the effluent as clear during the aluminate runs as was observed during the alum runs. Changing the point of chemical addition did not completely eliminate this "carry-through" as it had with alum. Figure 7 shows the effect of a varying Al/P ratios on the filtered effluent total phosphorus concentration for aluminate additions. At an Al/P (filt. ortho) ratio of 2.25/1, filtered effluent total phosphorus would be about 0.5 mg P/l which is about 70% higher than would be expected using alum at the same Al/P ratio. The sodium aluminate studies were terminated on August 12, 1969 thus completing Phase I of the study.

ACTIVATED SLUDGE STUDIES

Mixed Liquor

Table 3 presents summary data from the activated sludge analyses which were performed during Phase I. The volatile solids data presented have not been corrected for apparent volatile solids production due to formation of aluminum hydroxy-phosphate compounds which volatilize during the standard volatile suspended solids analysis procedure. The sludge volume index data for Tank No. 1 show there was no decrease in SVI as a result of alum addition which was contrary to what was expected.

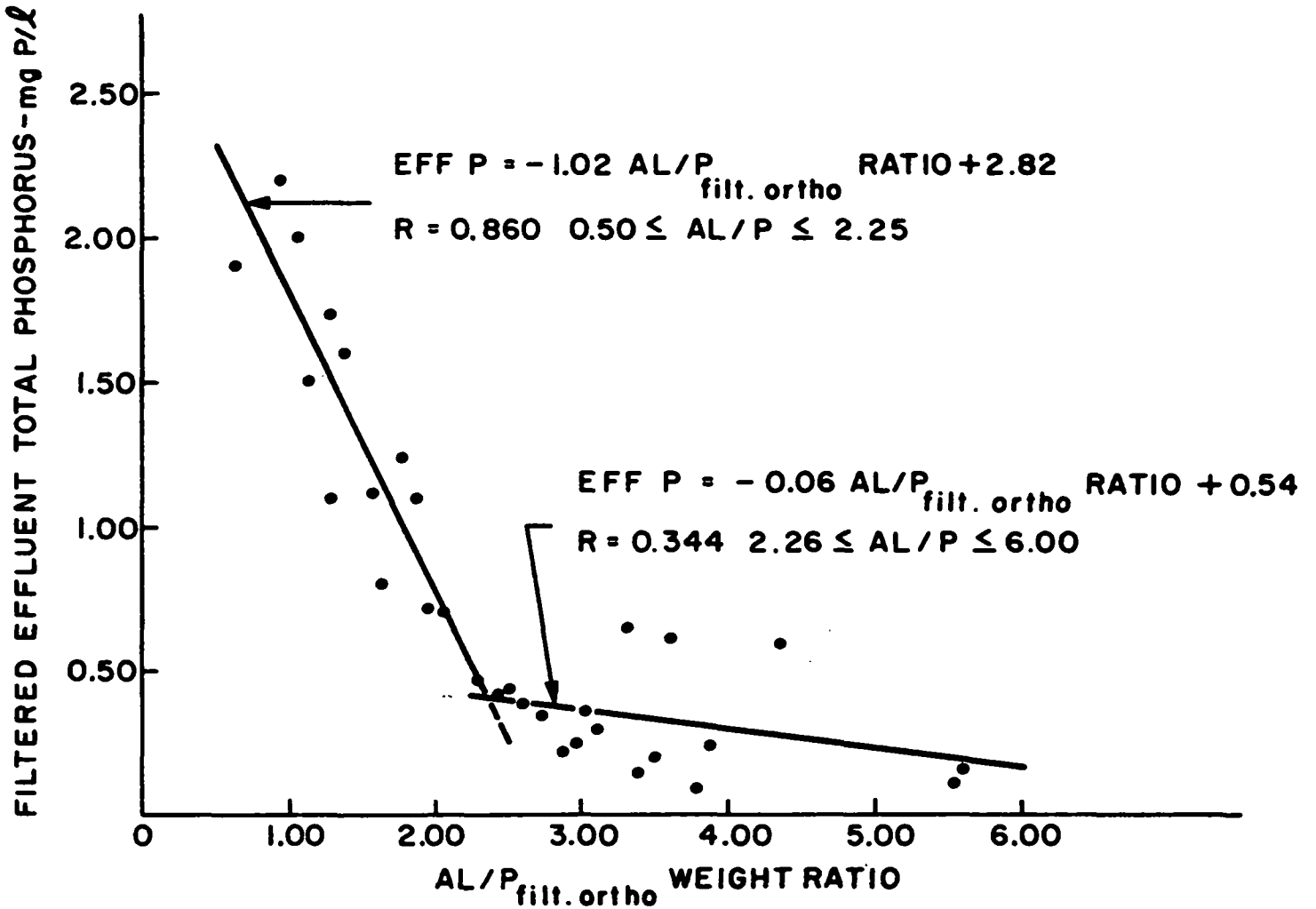


Figure 7. Effluent Phosphorus Concentration as a Function of $Al/P_{filt.\ ortho}$ Weight Ratio Phase I Sodium Aluminate Studies

Table 3. Summary of Activated and Waste Sludge Data Phase I

Run Code	Mixed Liquor mg/ℓ Total	Mixed Liquor mg/ℓ Volatile	SVI Mohlman	Waste Sludge gal/day	Waste Sludge lb/day Total	Waste Sludge lb/day Volatile	Solids Age Days	MLVS P %	pH	Temp °C
				A. Tank No. 1						
C[a]	1680±390	1260±280	68±13	12,300±5,540	504±120	321±84	1.33±.55	2.12±.74	7.10±.10	--
A	2400±570	1360±280	68±10	19,540±3,650	1443±573	775±326	1.29±.51	7.69±1.93	7.15±.25	17.8±2.4
SA	1980±420	1010±210	26±6	12,590±2,740	554±251	251±110	2.48±1.19	9.53±1.19	7.25±.25	23.5±.9
				B. Tank No. 2						
C[a]	1490±350	1190±230	83±9	-	-	-	-	-	-	-
A	2450±450	1390±250	60±11	10,380±2,350	1560±400	837±219	1.37±.54	6.76±1.78	7.15±.35	17.8±2.4
SA	2090±480	1050±210	23±8	6,380±2,270	639±298	302±137	2.58±1.20	9.92±3.30	7.30±.25	23.5±.9

Run Code:

C - Period of no chemical addition.

A - Alum addition to both tanks.

SA - Sodium aluminate addition to both tanks.

[a]Blanks -- indicate no data were collected during the period of no chemical addition.

Initial settling rates were not measured but visual observations indicated the chemical-biological sludge resulting from both alum and aluminate addition settled much more rapidly than is usual for biological sludge. The data from the period of no chemical addition for Tank No. 2 are too limited in number to permit any conclusions regarding the apparent reduction in SVI shown. The reduction in SVI as a result of sodium aluminate addition was very dramatic. SVI's during aluminate addition were approximately 30% as high as those observed during alum addition. It should be noted that throughout the Phase I operation, the SVI's for each of the tanks were lower than those normally expected in a conventional activated sludge plant treating domestic wastes. Barth and Ettinger (2) report sludge density indexes (SDI) for pilot plant operation using conventional activated sludge and sodium aluminate addition to the aerator of 0.5 and 1.3 respectively. Comparable values for SDI from Phase I results reported above are 1.5 (period of no chemical addition), 1.6 (alum addition) and 4.1 (sodium aluminate addition).

The solids age during the period of no chemical addition and the period of alum addition averaged 1.3 to 1.5 days which is much lower than that normally employed for conventional activated sludge operation. The solids age during the sodium aluminate runs was appreciably higher (approximately 2.5 days) but still well below that employed in conventional activated sludge operation. The higher solids age during the aluminate studies was a result of the lower flows and loadings experienced during this period.

Sludge Production

Sludge production is a very important consideration in wastewater treatment because of the problems of solids handling and ultimate disposal. Insufficient data were collected during the period of no chemical addition prior to the alum runs to permit a significant evaluation of the waste sludge production from the units under conventional operation. The data presented in Table 3 indicate that a significantly greater volume and weight of waste sludge was produced from the use of alum than from the use of sodium aluminate. However, if the data are correlated with flow (Table 4), these results indicate that, although waste sludge volumes are essentially the same regardless of which precipitant was used, the weight of total solids produced from the use of sodium aluminate is only about 59% of that produced from the use of alum and only about 40% as great for volatile solids. These values may be atypical since organic loadings and influent phosphorus concentrations were lower during the period of sodium aluminate addition than they were during the alum studies. This reduction would also reduce the amount of solids produced, hence direct comparison between the sludge production figures for the two precipitants is difficult.

Table 4. Comparative Waste Sludge Production Phase I

	Alum		Sodium Aluminate	
	Tank No. 1	Tank No. 2	Tank No. 1	Tank No. 2
gal/day/M	20,000	10,640	19,160	10,420
lb total solids/day/MG	1,470	1,600	837	965
lb volatile solids/day/MG	793	957	380	457

Mixed Liquor Phosphorus

The percentage of phosphorus in the activated sludge during the period of no chemical addition (2.12%) is typical of values which have been reported in the literature. Jenkins and Menar (14) reported a weighted mean value of 2.6% for the P content of activated sludge operating over a range of substrate loadings. The percentage phosphorus increased greatly as a result of chemical addition as shown by the data in Table 3. The observed higher percentage during the sodium aluminate runs seems reasonable since the amount of volatile solids produced was much less while the amount of phosphorus removed was nearly the same as with alum addition.

GENERAL DISCUSSION

Table 5 is a summary comparison of results achieved from the use of each of the two chemicals studied using data obtained with Al/P (filt. ortho) ratios in the range of 1.75/1 to 2.50/1. These data show the use of aluminum sulfate resulted in higher removals of BOD, COD and phosphorus than were realized with sodium aluminate. Because of this, alum was selected for use during Phase II of the project.

It should be noted that the pH values observed during both the alum and the sodium aluminate studies were well above the optimum reported in the literature for phosphorus removal using aluminum as the precipitant. Therefore, lower effluent filtered phosphorus concentrations would be achieved if the pH of the system were lowered in accordance with the findings of Eberhardt and Nesbitt (9). This should reduce the Al/P ratio required to attain a given effluent phosphorus concentration and depending on the economics of pH adjustment, may result in lower total chemical costs than those experienced without pH control. Full plant scale evaluation of pH control was not a part of this study so this question must be resolved at another time. However, some data on additional pH observations made during Phase II will be discussed later and will reflect on this.

It should not be concluded from the data shown that alum will be superior to sodium aluminate with all wastewaters. The chemistry of the sodium aluminate reaction favors low pH, low alkalinity systems which are not

Table 5. Comparison of Effluent Characteristics and Solids Production Using Alum and Sodium Aluminate Phase I[a]

Parameter	Chemical[b]	
	Alum	Sodium Aluminate
BOD_5 - % Removal	92.7±2.3	81.2±6.1
COD - % Removal	86.3±9.0	78.7±10.4
Phosphorus - % Removal		
Filtered		
Ortho	94.6±3.3	92.6±4.8
Total	96.4±3.0	91.9±3.0
Unfiltered		
Ortho	85.9±7.1	81.1±7.3
Total	87.2±6.7	81.7±7.9
Nitrogen - mgN/ℓ		
Ammonia	17.5±3.0	0.2±0.5
Oxidized	1.5±1.1	13.7±6.5
T. Kjeldal	21.0±3.8	4.5±4.7
pH	7.10±.15	7.25±.15
Aluminum - mgA/ℓ	0.23±.12	0.40±0.1
Sulfate - $mgSO_4/\ell$	131±32	-
$Al/P_{filt.\ ortho}$ Ratio		
Weight	2.04±.19	2.04/1±.23
Waste Sludge Production[c]		
gal/day/MG	20,000	19,160
lb total solids/day/MG	1,470	837
lb volatile solids/day/MG	793	380

[a]Data for comparison are taken from Table 1, Code III, Table 2, Code IIA, and Table 6.

[b]Chemical addition at effluent end of aeration tank only.

[c]Data from Tank 1 only.

typical of Penn State University wastewater. Limited alkalinity data which were collected during the latter part of the sodium aluminate studies showed an average alkalinity in the trickling filter effluent of 156 mg $CaCO_3$/l. Average pH values for the trickling filter effluent were 7.4 for the alum runs and 7.2 for the aluminate runs, both well above the desired pH for phosphorus precipitation with aluminum. Since it is the pH after chemical addition which is important, it should be noted that alum lowers the pH whereas sodium aluminate raises it. The higher effluent pH's observed with use of sodium aluminate are most likely the primary reason for the lower phosphorus removals experienced with this chemical in this study.

Brenner (4) also discusses the relative advantages of using sodium aluminate and alum when both chemicals were added at the head end of the aeration tank. His observations that poorer fine floc capture occurs as the pH approaches 6 is more likely due to conditions created by adding the chemical at the head end of the aeration tank than it is strictly to pH although pH is also important. Zenz and Pivnicka (52) also observed a carry-over of fine floc described by them as "milky white" and observed that the amount of floc increased with increasing alum dosages which would decrease the pH. Since they also added the precipitant at the head end of the tank, it is likely that this floc carry-over could have been reduced or prevented by changing the point of chemical addition to the effluent end of the tank. Recht and Ghassemi (29) have shown that the reaction between aluminum and orthophosphate is very rapid and may be instantaneous. Therefore, adequate reaction time for phosphate removal should exist when adding the chemical into the effluent line from the aeration tank.

The reasons for the "carry-through" of phosphorus which was experienced during the sodium aluminate studies and with alum when the chemical was added at points other than at the effluent end of the aeration tank and as noted by others are still not completely understood. It is believed to be a function of: 1) pH, 2) solids age, and 3) point of chemical addition. Since it does result in significantly higher effluent phosphorus concentrations than would otherwise be expected, additional study during Phase II was undertaken in an attempt to resolve some of the questions regarding this phenomenon. These observations will be reported elsewhere.

As indicated earlier, in the chemical feeding system employed in this study, liquid chemical was stored in a PVC lined wooden tank and diaphram chemical feed pumps were used to meter the chemical. Flow to the point of chemical addition was by gravity through 1/2-inch insulated plastic lines. No problems with chemical handling were experienced during the Phase I studies. Sodium aluminate is much more viscous than alum and could cause handling difficulties during cold weather in some instances. All of the aluminate runs were conducted during warm weather so it was impossible to assess cold weather operation. The period of study using alum began in January and no unusual problems were experienced during cold weather operation.

PHASE II INVESTIGATIONS

PROGRAM OF STUDY

Phase II of the project was conducted to obtain long term operating data on the use of alum to precipitate phosphorus from domestic wastewater as a result of the findings of Phase I studies. In addition, several aspects of the operation which were not investigated during Phase I were researched briefly during Phase II in an attempt to guide future research into detailed areas of study not included herein or yet generally understood.

The plan of operation and plant operational procedures for Phase II studies were as outlined earlier for Phase I, Aluminum Sulfate Studies, except as noted subsequently. In contrast to the procedure used during Phase I, variations in the phosphorus concentration as well as flow variations were incorporated into the chemical feed rate calculations during Phase II. It should be noted again that the effect of the phosphorus variation was very much less than that of flow variation but that these results are probably atypical.

Sampling schedules and analyses of samples were as reported for Phase I except that data on alkalinity, calcium, magnesium, and color were collected routinely whereas data on aluminum and sulfate were collected only at infrequent intervals.

General Operation

Phase II operation began on August 21, 1969 with the addition of liquid aluminum sulfate (alum) into the effluent channel from Aeration Tank No. 1 at the same point used for Phase I studies. Aeration Tank No. 2, operating in parallel with Tank No. 1, was maintained as the untreated control.

Operation over a one year period was accomplished in order to furnish data which would reflect operating capabilities of the chemical-biological process under varying operating conditions including those resulting from changing loads, student populations, weather, and process modification or adaptation as a result of chemical addition over extended periods.

The Pennsylvania Sanitary Water Board (now Pennsylvania Environmental Quality Board) has established water quality criteria for Spring Creek (the receiving stream for the University Plant) which sets a limit of 0.4 mg PO_4/l (0.13 mg P/l) total soluble phosphate (47). For the purposes of the Phase II studies it was desired to produce an effluent which contained not more than 0.3 mg P/l total phosphorus in a filtered sample. Allowing for dilution, this then should meet the water quality standards which have been established. Subsequent to the study, the Board now uses the 0.4 mg PO_4/l total soluble phosphate as an effluent standard for plants discharging to the receiving stream.

Daily flow variation during Phase II was extreme, varying from a low of 0.33 MG through each of the two tanks to a high of 1.37 MG. Design average flow is 1.04 MGD, based on a surface settling rate of 800 gallons per day per square foot for the final settlers. Most of the low flow days occurred during term breaks when students were absent from campus although Sunday flows were often less than design average even when students were on campus. The problem of flow variation was particularly severe during the Spring 1970 term at the University (March 30 - June 13, 1970). These extreme fluctuations in flow made evaluation of the effects of the chemical-biological process on the various parameters studied difficult and it was impossible to separate out completely the effects of varying flow in analyzing the results obtained. In an attempt to illustrate the effect of flow data presentation for Phase II operation has been broken down into three classifications: 1) data collected when daily flows did not exceed 1.040 MG, 2) data collected when daily flows exceeded 1.041 MG, and 3) all data collected during Phase II regular operation. The daily flow was greater than 1.040 MG 43.9% of the time during Phase II operation. Both median and mean values have been presented so as to reflect better the effect of varying flow and the resulting extreme values which occurred. Considerable variance was observed in the data for most of the parameters measured but it is believed the results which are presented herein do reflect the operating capabilities of the system. Due consideration should be given in the interpretation of results to the hydraulic overload that occurred on numerous occasions.

FLOWS AT OR BELOW DESIGN AVERAGE

Influent Waste (Trickling Filter Effluent)

Data presented in Table 6, Part A, show the characteristics of the influent waste to the aerators for those days on which flows did not exceed the design average flow of 1.04 MGD. The mean flow for this category was 0.74 MGD, well below design average. Peak rates of flow did exceed design at different periods of the day on many occasions but at these relatively low total flows they did not affect the results observed significantly. The results are generally similar to those observed during the aluminum sulfate studies of Phase I and are considered to be typical of what would be expected in a plant treating domestic wastes. Note that approximately 90% of the unfiltered influent phosphorus is in the ortho form and that virtually 100% of the filtered influent phosphorus was in the ortho form.

As expected, little oxidized nitrogen was found in the trickling filter effluent on most occasions. The difference between the median and mean values and the wide range of values observed suggest the flow and temperature variations which occurred had more influence on nitrification than on other processes involved.

Table 6. Summary Data from Phase II One Year Full Scale Study for Flows Not Exceeding 1.040 MG Total Daily Flow Per Tank.

A. Trickling Filter Effluent Characteristics

Parameter[a]	Median	Mean	Std. Dev.	Range	No. of Observ.
Suspended Solids					
Total	98	110	67	38 to 448	71
Volatile	74	85	57	21 to 396	70
Unfiltered BOD_5	72	71	34	15 to 211	57
Unfiltered COD	152	172	77	32 to 436	63
Phosphorus - P					
Filtered					
Ortho	6.5	6.7	2.0	2.6 to 14.2	70
Total	6.5	6.3	2.0	3.1 to 13.6	68
Unfiltered					
Ortho	9.1	8.9	2.8	2.9 to 21.2	70
Total	10.1	10.0	3.8	3.6 to 21.6	67
Nitrogen - N					
Ammonia	13.6	12.8	6.6	1.8 to 22.7	56
Oxidized	0.8	2.1	2.4	0.1 to 9.3	49
T. Kjeld.	21.0	21.0	10.1	5.8 to 47.5	55
Alkalinity - $CaCO_3$	180	168	40	85 to 230	61
Calcium - Ca	24	25	4	18 to 34	49
Magnesium - Mg	27	24	6	11 to 31	48
pH - Units	7.60	7.50	0.20	6.90 to 7.85	63
Color - Units	50	45	7	30 to 50	32
Flow - MGD	0.73	0.74	0.19	0.33 to 1.03	77

Continued

Table 6 (Continued)

B. General Performance and Effluent Quality

Parameter[a]	Tank 1[b] Median	Tank 1[b] Mean	Tank 1[b] Std. Dev.	Tank 2[c] Median	Tank 2[c] Mean	Tank 2[c] Std. Dev.
Suspended Solids						
Total	12	22	37	22	26	20
Volatile	8	14	19	19	20	15
Unfiltered BOD_5						
mg/ℓ	7	9	6	12	13	4
% Removal	90.6	88.6	5.8	82.1	81.4	5.9
Unfiltered COD						
mg/ℓ	44	55	47	58	68	50
% Removal	79.1	75.1	15.6	69.8	66.7	18.7
Nitrogen - N						
Ammonia	9.5	11.1	6.4	7.6	7.7	5.8
Oxidized	3.0	4.2	2.8	5.0	6.6	3.7
T. Kjeld.	10.6	13.2	7.8	7.8	9.7	7.5
Alkalinity - $CaCO_3$	76	80	42	120	120	35
Calcium - Ca	28	28	3	26	24	3
Magnesium - Mg	26	23	7	26	23	6
pH - Units	6.80	6.75	0.50	7.30	7.35	0.20
Color - Units	15	15	7	30	30	6

Continued

Table 6 (Continued)

C. Final Effluent - Phosphorus Removal Performances

Parameter[a]	Tank 1[b] Median	Tank 1[b] Mean	Tank 1[b] Std. Dev.	Tank 2[c] Median	Tank 2[c] Mean	Tank 2[c] Std. Dev.
Phosphorus - P						
Filtered						
Ortho	0.10	0.28	0.46	6.9	6.7	1.55
% Removal	98.8	97.5	3.0	33.5	31.2	16.1
Total	0.14	0.36	0.56	6.7	6.7	1.89
% Removal	98.1	96.9	4.5	35.8	33.3	14.5
Unfiltered						
Ortho	0.52	1.15	2.32	7.4	7.2	1.87
% Removal	94.3	92.1	6.8	26.5	26.1	17.1
Total	0.79	1.41	2.62	7.5	7.3	2.08
% Removal	92.8	91.1	6.9	21.2	22.9	12.7
$A\ell/P_{filt.\ ortho}$ Ratio	2.62/1	2.97/1	1.20	--	--	--

[a]All units are mg/ℓ except as noted.

[b]Alum addition to effluent end of tank.

[c]Control unit - no chemical addition.

General Effluent Quality

The data presented in Table 6, Part B, permit comparison of the performance of the chemical-biological system (Tank No. 1) with that of the control unit (Tank No. 2). These data also suggest that even though total daily flows were below design average, the flow rate fluctuation throughout the day is sufficient to cause widely varying effluent characteristics. While other factors can and do influence treatment plant efficiency, it was felt that flow variation was the most significant factor accounting for the major portion of the variability observed in plant performance during this study.

Comparison of the median values for suspended solids from each of the two tanks indicate that considerably improved capture of suspended solids can be expected from the chemical-biological system. However, when the mean values are compared, no such conclusion can be reached. It was noted earlier that the total solids which must be carried in the chemical-biological system are much higher than those carried in a conventional activated sludge system because of the large amount of nonbiological solids present in the form of precipitated phosphorus. This greater amount of solids which must be removed in the final settling tanks makes hydraulic loading even more critical in this system and probably accounts for the relatively small differences observed between median and mean values for Tank No. 2 compared to those observed for Tank No. 1.

The data also confirm the observation made during Phase I that alum addition enhances removal of BOD and COD. The effluent BOD's from the treated unit were only about 58% as high as those from the untreated unit if the median values are used for comparison. Comparison of mean values also shows a decided improvement in BOD removal for the chemical-biological system but the difference is not as great (69% as high). The same conclusions can be drawn from the COD data although the noted improvement achieved by the chemical-biological unit is not as great.

The nitrogen data in Table 6, Part B, also show a lower degree of nitrification for the chemical-biological system similar to that which was observed during the Phase I studies. The difference was not as great as observed during Phase I which suggests again the importance of flow and solids age as parameters affecting nitrification in activated sludge units.

Phosphorus Removal

The effluent phosphorus data presented in Table 6, Part C, also reflect the variability in results resulting from flow fluctuations even when all flows are within design average values. As noted earlier, low flows often occurred on Sundays even when a normal student population was on campus. On these occasions, no attempt was made to reduce the alum feed

rates from those normally used during the week. This resulted in an overdose of alum in these instances which did not adversely affect results but was uneconomical in terms of chemical usage.

Filtered effluent phosphorus removals were again excellent. The mean values reported for both ortho and total phosphorus include data obtained during periods when flows were changing and feed rate adjustments were being made. On several occasions during these periods, the effluent phosphorus increased to values in excess of 2 mg P/l before the adjustments were completed. Figure 8 shows the statistical distribution of effluent total phosphorus concentrations for Tank No. 1. The shape of the curve particularly at extreme values indicates the distribution of data is not normal throughout the range of observations and that results are affected by other factors such as very high or very low Al/P ratios resulting from unpredicted changes in flow or influent phosphorus concentration. In any event, the overall percentage removals of 98 to 99% for orthophosphate and 97 to 98% for total phosphorus show that with efficient solids separation either by sedimentation or filtration, the process is capable of a high degree of phosphorus removal at relatively high Al/P ratios, i.e., greater than 2/1. Later discussion will attempt to identify those operating problems and procedures which would optimize the economy and reliability of the process.

The data on unfiltered effluent phosphorus concentrations also show considerable variation for the reasons given above. Figure 9 presents the statistical distribution of these data for Tank No. 1. These data also are not normally distributed throughout the range of observation so that statistical inferences from the data must consider this. No attempt was made to normalize the data or to otherwise modify or utilize sophisticated statistical techniques in analyzing the data. The data on unfiltered effluent phosphorus demonstrate the importance of effluent suspended solids capture in achieving low residual effluent phosphorus values

FLOWS IN EXCESS OF DESIGN AVERAGE

Influent Waste (Trickling Filter Effluent)

Part A, Table 7, presents data on the characteristics of the aerator influent waste for those days on which flows exceeded the design average flow of 1.04 MGD. The mean daily flow for this category was 1.23 MG. Peak rates of flow during the day would often go as high as 1.6 MGD for short periods of time.

Data on the various parameters indicate heavier loadings on the plant along with the increasing flow but no other significant differences from earlier observations. These data show less variability than those observed at the lower flows. However, the range of flow observed was also much less in this category.

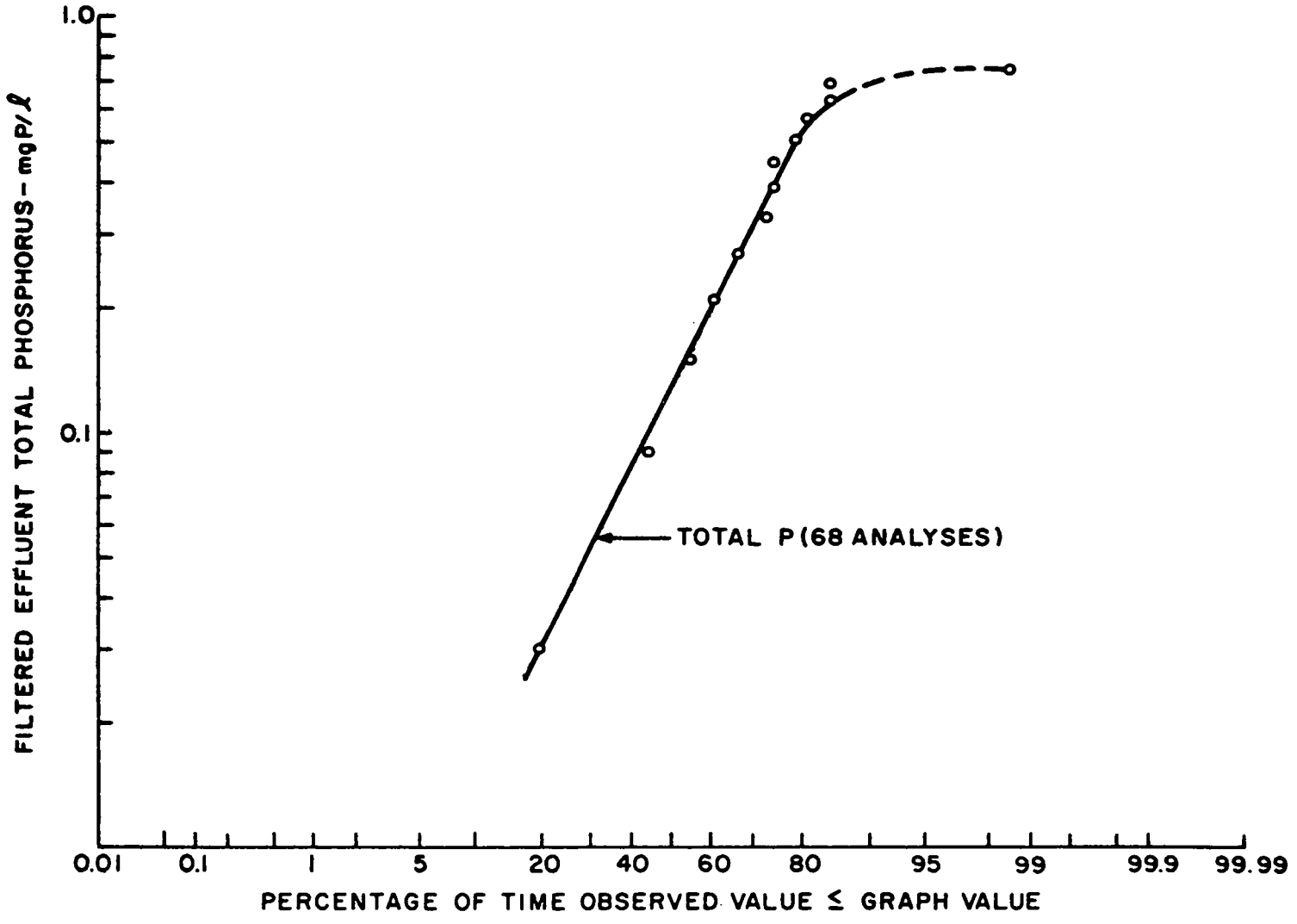


Figure 8. Statistical Distribution of Filtered Effluent Total Phosphorus Tank 1 Flow ≤ 1.041 MGD

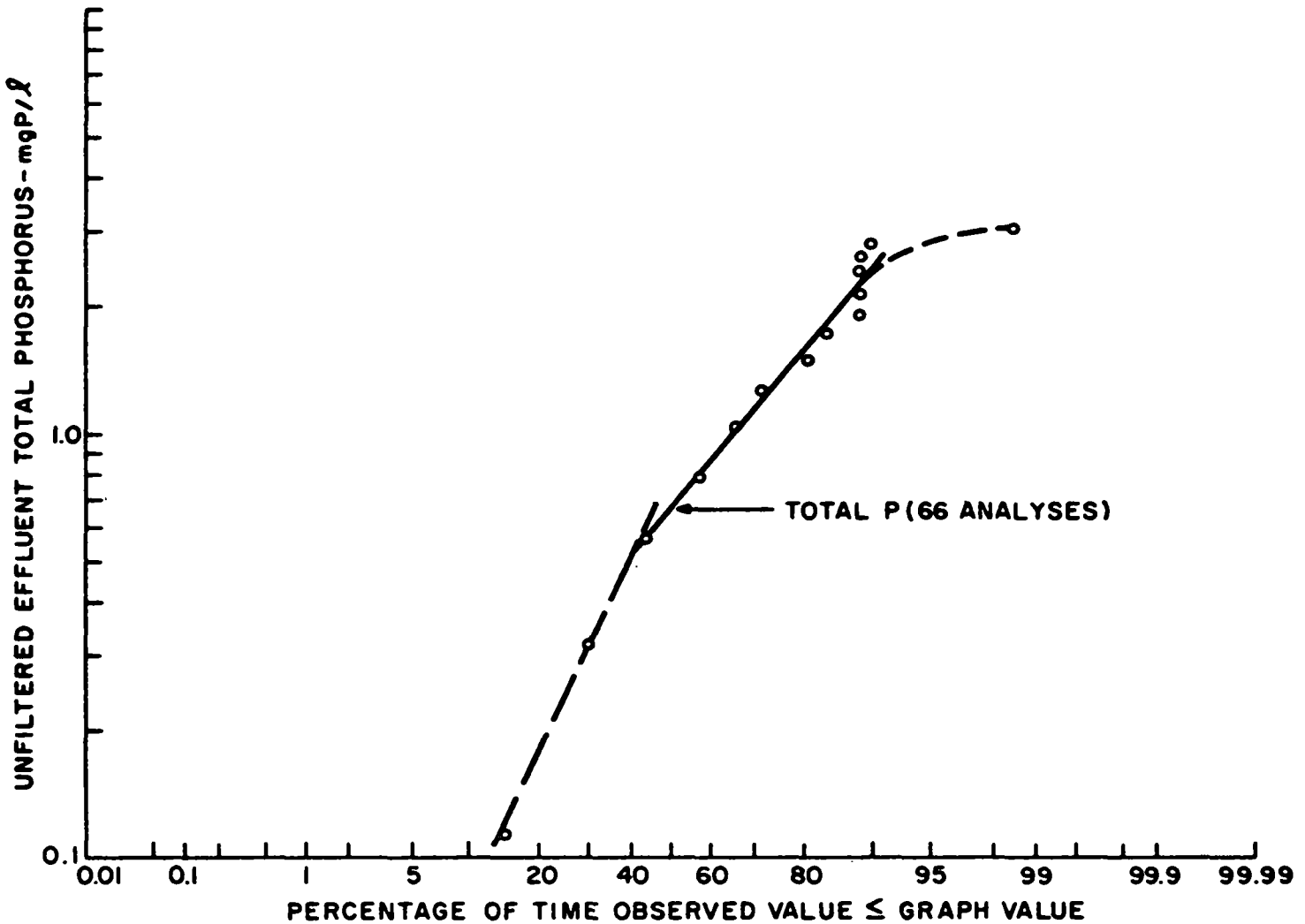


Figure 9. Statistical Distribution of Unfiltered Effluent Total Phosphorus Tank 1 Flow $\leq$ 1.040 MGD

Table 7. Summary Data from Phase II One Year Full Scale Study for Flows Exceeding 1.041 MG Total Daily Flow Per Tank

A. Trickling Filter Effluent Characteristics

Parameter[a]	Median	Mean	Std. Dev.	Range	No. of Observ.
Suspended Solids					
Total	112	117	35	63 to 275	61
Volatile	93	98	32	48 to 241	60
Unfiltered BOD_5	91	95	35	30 to 222	54
Unfiltered COD	216	223	55	122 to 342	53
Phosphorus - P					
Filtered					
Ortho	7.4	7.5	1.4	5.2 to 13.9	59
Total	6.9	6.9	1.3	4.3 to 9.5	49
Unfiltered					
Ortho	9.8	9.8	1.7	6.2 to 13.4	58
Total	10.8	10.5	2.3	5.6 to 15.7	53
Nitrogen - N					
Ammonia	18.6	18.7	2.0	11.9 to 23.9	55
Oxidized	0.6	0.7	0.4	0.0 to 2.0	49
T. Kjeld.	28.0	28.3	7.9	14.2 to 49.0	55
Alkalinity - $CaCO_3$	198	199	23	160 to 256	53
Calcium - Ca	24	25	3	20 to 32	39
Magnesium - Mg	22	23	5	14 to 35	38
pH - Units	7.70	7.65	0.15	7.20 to 8.05	59
Color - Units	50	50	5		41
Flow - MGD	1.23	1.22	0.07	1.05 to 1.37	64

Continued

Table 7 (Continued)

B. General Performance and Effluent Quality

Parameter[a]	Tank 1[b] Median	Tank 1[b] Mean	Tank 1[b] Std. Dev.	Tank 2[c] Median	Tank 2[c] Mean	Tank 2[c] Std. Dev.
Suspended Solids						
Total	39	105	127	30	30	13
Volatile	27	62	69	23	23	10
Unfiltered BOD_5						
mg/ℓ	14	22	29	16	15	4
% Removal	85.8	68.3	48.1	83.3	81.2	9.3
Unfiltered COD						
mg/ℓ	68	124	123	71	75	35
% Removal	76.2	58.6	42.0	68.0	64.9	16.3
Nitrogen - N						
Ammonia	17.4	17.1	2.6	13.1	12.7	3.6
Oxidized	1.5	1.8	1.0	3.5	4.5	2.1
T. Kjeld.	21.0	23.1	7.9	16.5	17.0	5.5
Alkalinity - $CaCO_3$	120	123	21	160	158	22
Calcium - Ca	30	29	3	26	26	3
Magnesium - Mg	19	22	6	25	24	6
pH - Units	7.10	7.15	0.25	7.50	7.45	0.15
Color - Units	20	25	10	30	30	5

Continued

Table 7 (Continued)

C. Final Effluent - Phosphorus Removal Performance

Parameter[a]	Tank 1[b] Median	Tank 1[b] Mean	Tank 1[b] Std. Dev.	Tank 2[c] Median	Tank 2[c] Mean	Tank 2[c] Std. Dev.
Phosphorus - P						
Filtered						
Ortho	0.54	0.80	0.93	7.0	7.2	0.8
% Removal	94.7	91.5	10.5	30.5	28.0	16.1
Total	0.65	0.80	0.82	6.2	6.5	1.2
% Removal	94.1	92.0	8.9	35.2	33.5	12.4
Unfiltered						
Ortho	2.9	7.0	8.9	7.9	8.2	1.7
% Removal	69.4	25.8	95.0	22.8	20.1	18.6
Total	2.9	7.7	11.5	8.1	8.2	2.1
% Removal	73.7	39.2	68.7	22.8	19.0	15.5
$A\ell/P_{filt.\ ortho}$ Ratio	2.28/1	2.18/1	0.61	--	--	--

[a]All units are mg/ℓ except as noted.

[b]Alum addition to effluent end of tank.

[c]Control unit - no chemical addition.

General Effluent Quality

The data reported in Table 7, Part B, dramatically illustrate the effect of flow on effluent quality. This effect is most apparent in the comparison of suspended solids data and in the differences between median and mean values for solids, BOD and COD. Figure 10 shows the variation in effluent suspended solids, flow and unfiltered effluent orthophosphate which can be considered typical of that which was observed almost daily particularly during the Spring Term 1970.

The median values for effluent suspended solids show that although the solids loss from Tank No. 1 was higher than that from Tank No. 2, it was not greatly different. However, the significant point is the contradiction of the results observed at the lower flows where comparison of medians showed significant improvement in removal of suspended solids as a result of chemical addition. Comparison of means reflects the extremely high loss of solids from Tank No. 1 with increasing flows whereas the loss of solids from Tank No. 2 did not increase significantly over that observed at the lower flows.

The BOD and COD data for this category show a slight improvement in BOD and COD removal for the treated system if median values are compared. The mean values again reflect the influence of high suspended solids which also increases the effluent BOD and COD and results in an apparent advantage for the untreated system. These data also show that flow has relatively less influence on the untreated system than on the treated system when they are compared with the data observed for flows below design average.

The higher flows and resulting lower solids age observed also effected a reduction in nitrification in both units as can be seen in the comparison of data in Table 7 with that reported in Table 6. The lower degree of nitrification observed for Tank No. 1 in the past also was noted in these data.

Phosphorus Removal

The effluent phosphorus data presented in Part C, Table 7, show very good removal of phosphorus on filtered effluent samples but the removals are significantly less than those observed at the lower flows. This is due largely to the lower Al/P ratios which resulted on those occasions when flows were considerably in excess of those used for computing chemical feed rates. It has been shown earlier in Phase I results that effluent phosphorus concentration rises quite rapidly as the Al/P (filt. ortho) ratio falls below 2/1. Figure 11 shows the statistical distribution of the phosphorus data for Tank No. 1 for this flow category.

The unfiltered effluent phosphorus removals were significantly higher than those observed from Tank No. 2 but could in no way be considered typical of chemical-biological process capabilities. The extremely

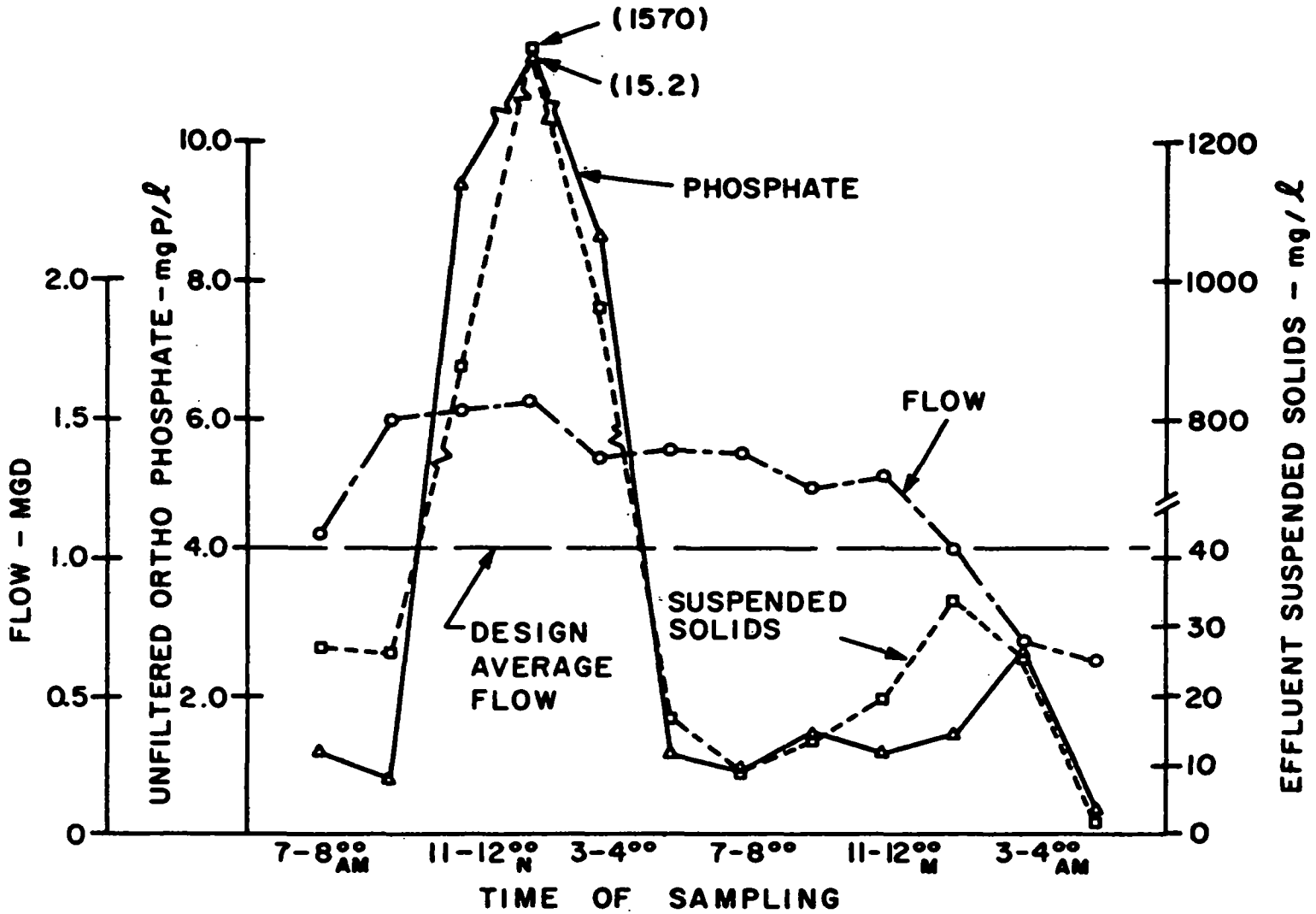


Figure 10. Daily Variation in Effluent Quality Tank 1 Flow $\geq$ 1.041 MGD

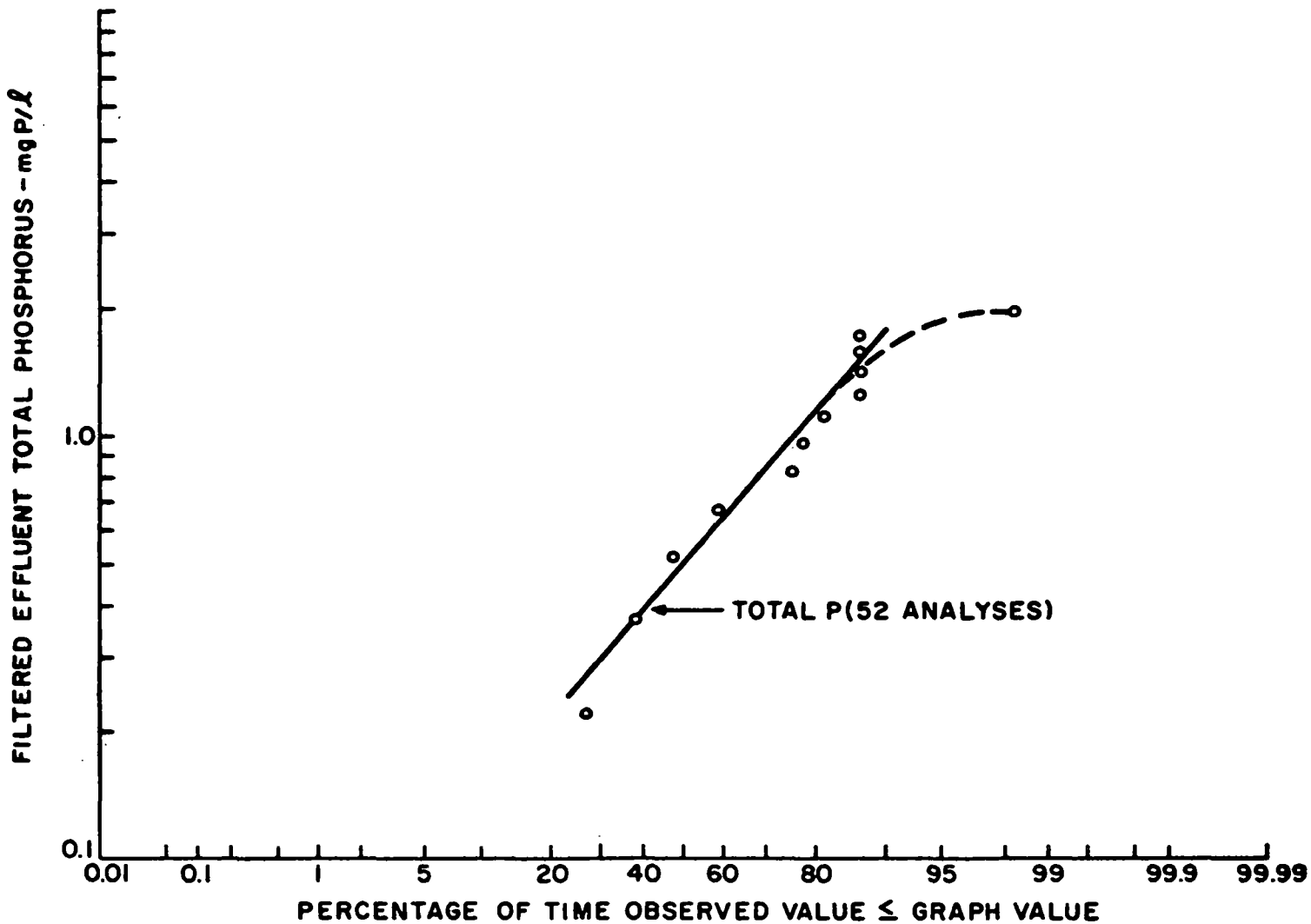


Figure 11. Statistical Distribution of Filtered Effluent Total Phosphorus Tank 1 Flow $\geq$ 1.041 MGD

high loss of solids with resulting carry-over of precipitated phosphorus simply rendered the whole process ineffective without filtration of the effluent. Figure 12 shows the statistical distribution of the unfiltered effluent phosphorus data for this category.

ALL FLOW DATA

General

Table 8 includes all data collected during Phase II operation beginning on August 21, 1969 and terminating on August 20, 1970. During this period, one occasion occurred where chemical addition was interrupted for about twelve hours when heavy snows prevented needed delivery of alum. On at least one other occasion a plant operator failed to make a scheduled feed pump rate change and underdosing occurred for a period of about three hours. These are the only known occasions during the one year run when chemical addition was interrupted or reduced from scheduled feed rates except for brief periods of less than one-hour duration to permit maintenance work on pumps and chemical feed lines. These data reflect results obtained on these occasions as well as those obtained during periods of flow adjustment when major changes in student population were occurring. All data included in Table 10 were used also in the data analyses for Tables 8 and 9.

Influent Waste (Trickling Filter Effluent)

As noted previously, the influent waste is characteristic of domestic wastewater and presents no unusual problems in treatment. The mean daily flow for all days on which data were collected was 0.96 MG which is below the design average flow of 1.040 MG. Prior discussion has pointed out the variability of flow experienced and the effect of this variation on results obtained.

The influent wastewater has a moderately high alkalinity and approximately equal calcium and magnesium content.

It should be pointed out again that approximately 90% of the unfiltered influent phosphorus and virtually 100% of the filtered influent phosphorus was in the ortho form. The phosphorus data for filtered samples frequently showed higher values for orthophosphate than for total phosphorus on both influent and effluent samples. There was no apparent explanation for this observation which has also been noted by others (3).

General Effluent Quality

Because of the extremely wide variation in results obtained for most of the parameters measured as a result of hydraulic overloading, the median values reported offer a better basis for comparison than do mean values. Therefore, unless otherwise noted the ensuing discussion will involve comparison of reported median values.

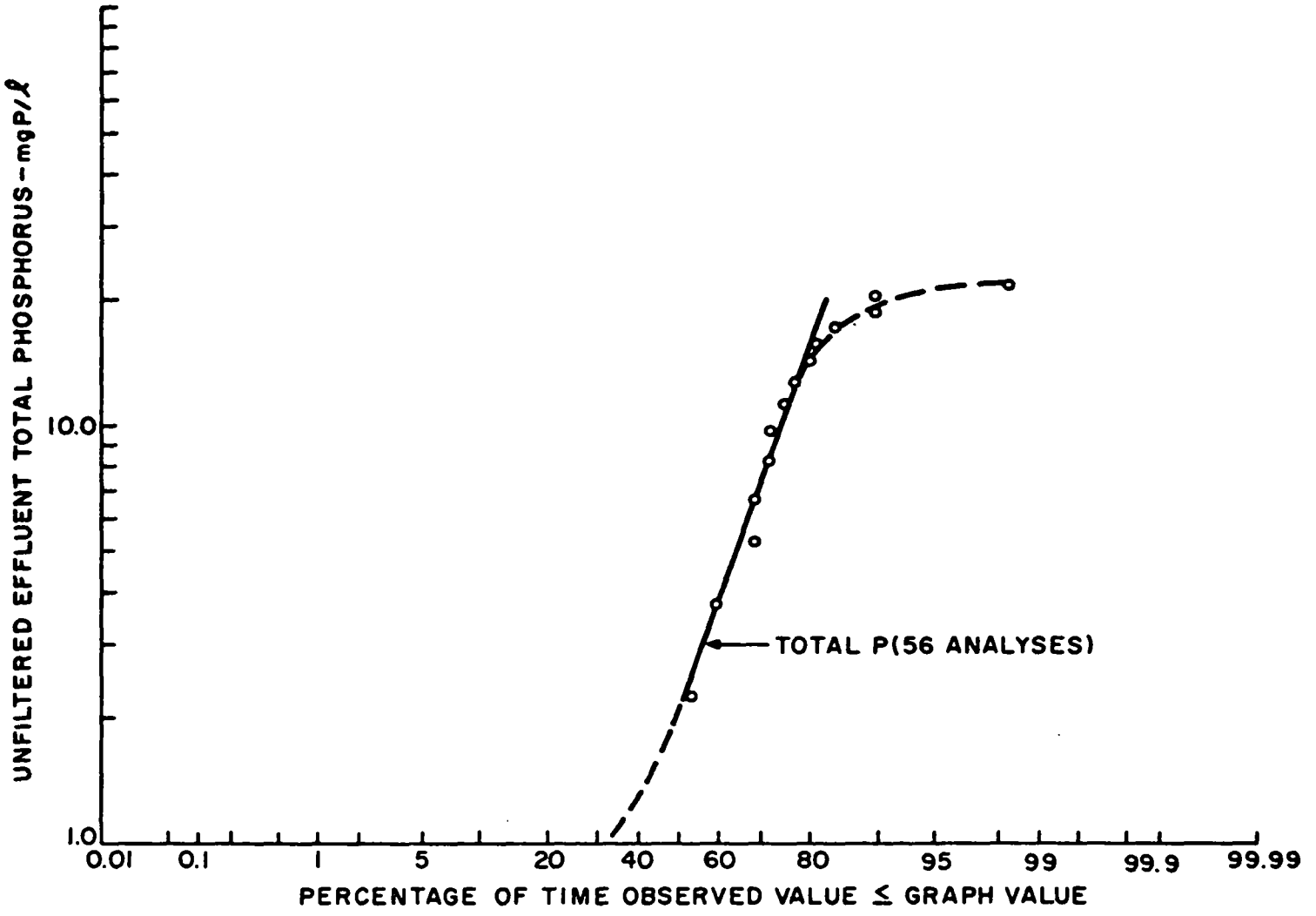


Figure 12. Statistical Distribution of Unfiltered Effluent Total Phosphorus Tank 1 Flow ≥ 1.041 MGD

Table 8. Summary Data from Phase II One Year Full Scale Study for All Flow Data

A. Trickling Filter Effluent Characteristics

Parameter[a]	Median	Mean	Std. Dev.	Range	No. of Observ.
Suspended Solids					
Total	110	114	55	38 to 448	132
Volatile	85	91	47	21 to 396	130
Unfiltered BOD_5	81	83	36	15 to 222	111
Unfiltered COD	193	195	73	32 to 436	116
Phosphorus - P					
Filtered					
Ortho	7.0	7.1	1.8	2.6 to 14.2	129
Total	6.5	6.6	3.2	3.1 to 13.6	117
Unfiltered					
Ortho	9.5	9.3	2.4	2.9 to 21.2	128
Total	10.8	10.3	3.2	3.6 to 21.6	120
Nitrogen - N					
Ammonia	17.6	15.7	5.7	1.8 to 23.9	111
Oxidized	0.8	1.4	1.8	0.0 to 9.3	97
T. Kjeld.	26.3	24.7	9.7	5.8 to 49.0	110
Alkalinity - $CaCO_3$	190	182	36	85 to 256	114
Calcium - Ca	24	25	4	18 to 34	88
Magnesium - Mg	25	24	6	11 to 35	87
pH - Units	7.60	7.60	0.20	6.90 to 8.05	122
Color - Units	50	45	5	30 to 50	73
Flow - MGD	0.98	0.96	0.28	0.33 to 1.37	141

Continued

Table 8 (Continued)

B. General Performance and Effluent Quality

Parameter[a]	Tank 1[b]			Tank 2[c]		
	Median	Mean	Std. Dev.	Median	Mean	Std. Dev.
Suspended Solids						
Total	26	59	98	25	28	17
Volatile	18	36	55	22	22	13
Unfiltered BOD_5						
mg/ℓ	10	16	22	15	14	4
% Removal	88.1	77.8	36.6	83.0	81.3	7.9
Unfiltered COD						
mg/ℓ	52	92	101	64	72	43
% Removal	77.6	66.3	33.3	69.2	65.7	17.4
Nitrogen						
Ammonia	15.7	14.1	5.7	11.5	10.5	5.3
Oxidized	2.3	3.0	2.4	4.0	5.5	3.2
T. Kjeld.	18.2	18.2	9.2	14.3	13.5	7.5
Alkalinity - $CaCO_3$	116	99	40	147	139	34
Calcium - Ca	28	28	3	26	25	3
Magnesium - Mg	25	23	6	25	23	6
pH - Units	6.90	6.95	0.45	7.40	7.40	0.20
Color - Units	20	20	10	30	30	5

Continued

Table 8 (Continued)

C. Final Effluent - Phosphorus Removal Performance

Parameter[a]	Tank 1[b] Median	Tank 1[b] Mean	Tank 1[b] Std. Dev.	Tank 2[c] Median	Tank 2[c] Mean	Tank 2[c] Std. Dev.
Phosphorus - P						
Filtered						
Ortho	0.26	0.51	0.76	7.0	6.9	1.3
% Removal	97.1	95.0	7.9	31.2	30.0	16.1
Total	0.29	0.53	0.69	6.5	6.6	1.6
% Removal	97.0	94.7	7.2	35.5	33.4	13.3
Unfiltered						
Ortho	1.30	3.7	6.8	7.5	7.7	1.8
% Removal	88.2	66.2	71.9	25.4	23.3	18.0
Total	1.44	4.3	8.5	7.9	7.7	2.1
% Removal	88.1	67.8	52.8	22.0	20.8	14.3
$A\ell/P_{filt.\ ortho}$ Ratio	2.39/1	2.61/1	1.05	--	--	--
Alum Dose $A\ell_2(SO_4)_3 \cdot 14\ H_2O$	190	178	94	--	--	--

[a]All units are mg/ℓ except as noted.

[b]Alum addition to effluent end of tank.

[c]Control unit - no chemical addition.

The data on effluent suspended solids show there was virtually no difference in suspended solids removal as a result of chemical precipitation of phosphorus within the activated sludge system. As expected, the untreated unit has a significantly higher percentage of volatile solids (88% compared to 69%).

The BOD data presented in Part B, Table 8, show a significant improvement in BOD removal as a result of alum addition. The effluent BOD from the chemical-biological system was only 67% as high as that from the control system.

The loading factors (LF) for each of the units for the entire period of study covered by Phase II were as follows:

LF (lb BOD_{5A}/lb MLVS/day)

	Average ± std. dev.	Range
Tank No. 1	0.567 ± 0.277	0.086 to 1.290
Tank No. 2	0.668 ± 0.363	0.099 to 1.920

These data show that organic loadings were generally in the normal range for conventional activated sludge operation.

The BOD removal characteristics (Sr) for the same period were:

Sr (lb BOD_{5R}/lb MLVS/day)

	Average ± 1 std. dev.	Range
Tank No. 1	0.527 ± 0.277	0.069 to 0.161
Tank No. 2	0.604 ± 0.304	0.070 to 1.274

Figure 13 shows the relationship between BOD loading and BOD removal for each tank for all of the data collected during Phase II. Regression analyses of the data yielded the following equations for the lines of best fit:

Tank No. 1 $\quad$ lb BOD_{5R} = 0.90 lb BOD_{5A} - 0.04 lb MLVS $\quad$ (5)

Tank No. 2 $\quad$ lb BOD_{5R} = 0.87 lb BOD_{5A} - 0.03 lb MLVS $\quad$ (6)

The correlation coefficients were found to be highly significant statistically. Although the differences between the constants for the BOD loading and removal regression equations for the chemical-biological

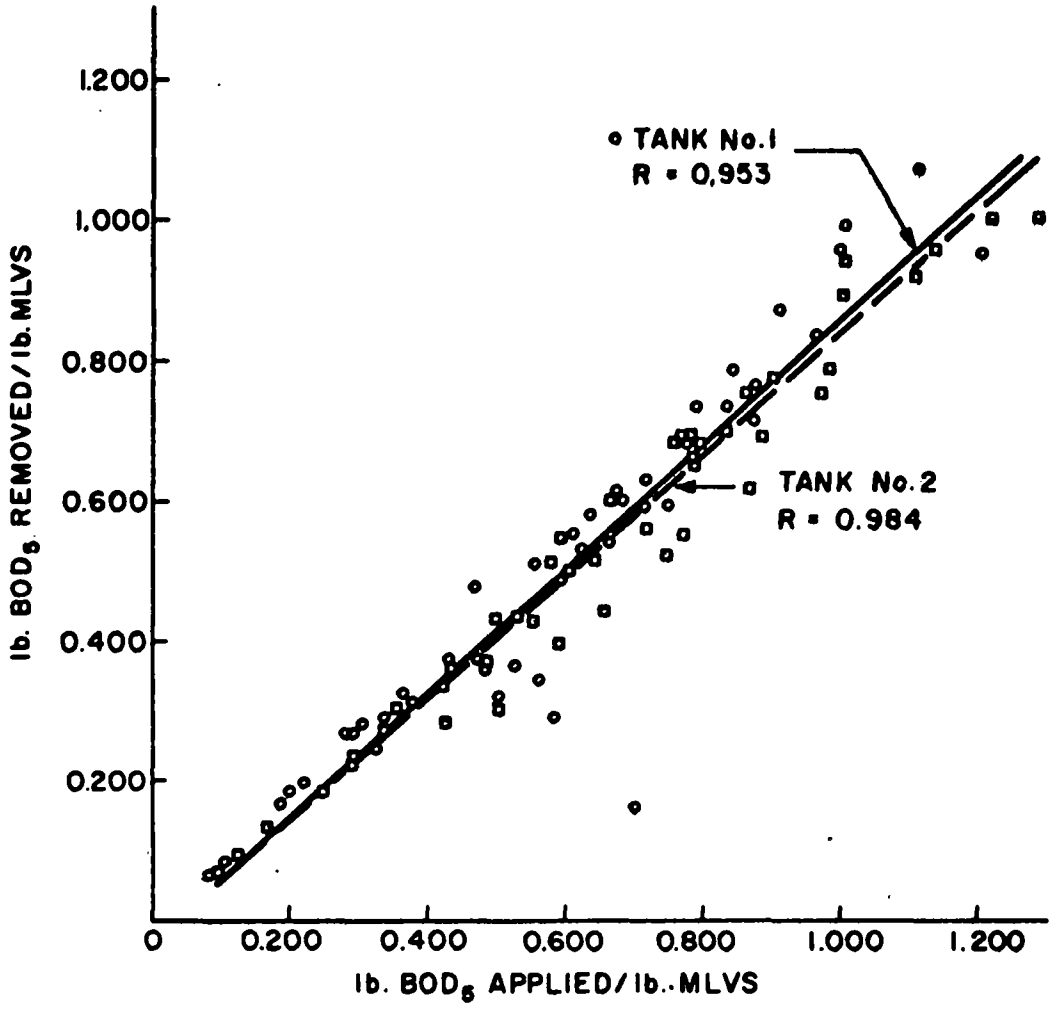


Figure 13. BOD Removal as a Function of BOD Loading Phase II All Flow Data

system and the control unit were small, they were statistically significant at the 1% level.

Figure 14 shows the relationship between unfiltered BOD and effluent solids for both units. A better correlation could have been achieved if sufficient data had been available to compute the insoluble BOD and these values used instead. Acknowledging this deficiency and the wide variability of data, these curves and the resulting regression equations also indicate that lower effluent BOD can be expected from the chemical-biological system. These curves also show the importance of suspended solids removal if optimum BOD removal is to be achieved.

The nitrogen data show a significant difference in the degree of nitrification which occurred in the chemical-biological system compared with that of the control unit. Table 9 shows the average results of nitrogen analyses performed on three occasions on samples of mixed liquor to see if the difference observed in effluent samples could be seen in samples taken prior to alum addition. The same difference was apparent indicating that alum addition does in some way reduce nitrification under the conditions of operation experienced during these studies.

As expected, the reduction in alkalinity in Tank No. 1 was much greater than that observed in the control unit. Brenner (4) reports a reduction in alkalinity from 182 to 67 mg $CaCO_3$ as a result of alum addition. This is significantly greater than the reduction observed in this study using mean or median values but such large reductions were observed on occasions where an overdose of alum occurred. Since Brenner did not include data on alum dosages, direct comparison is difficult.

Brenner (4) also reported in his analysis of chemical costs that "every 5 mg/l of alum added (as Al^{+++}) uses up 34 mg/l alkalinity (as $CaCO_3$)." The results of this study, using mean values, indicated that for the particular system studied, 26 mg/l of alkalinity were used up for each 5 mg Al/l added in the form of alum which closely agrees with the theoretical value of 27.8 mg $CaCO_3$/l.

Some increase in calcium in the effluent from Tank No. 1 was observed (3 mg/l from mean values) whereas no increase was noted in the effluent from the control unit. Menar and Jenkins (23) have postulated the release of calcium during activated sludge treatment. A possible explanation for the observed increase in calcium in Tank No. 1 but not in Tank No. 2 could be that the released calcium in Tank No. 2 precipitated out as calcium phosphate whereas in Tank No. 1 the phosphorus had already been precipitated with aluminum. This mechanism of phosphorus removal, i.e., precipitation with calcium under certain conditions within the aeration tank was the subject of an exhaustive investigation by Menar and Jenkins.

Color removal was significantly higher as a result of alum addition. On days where flows were low, the effluent from Tank No. 1 was crystal

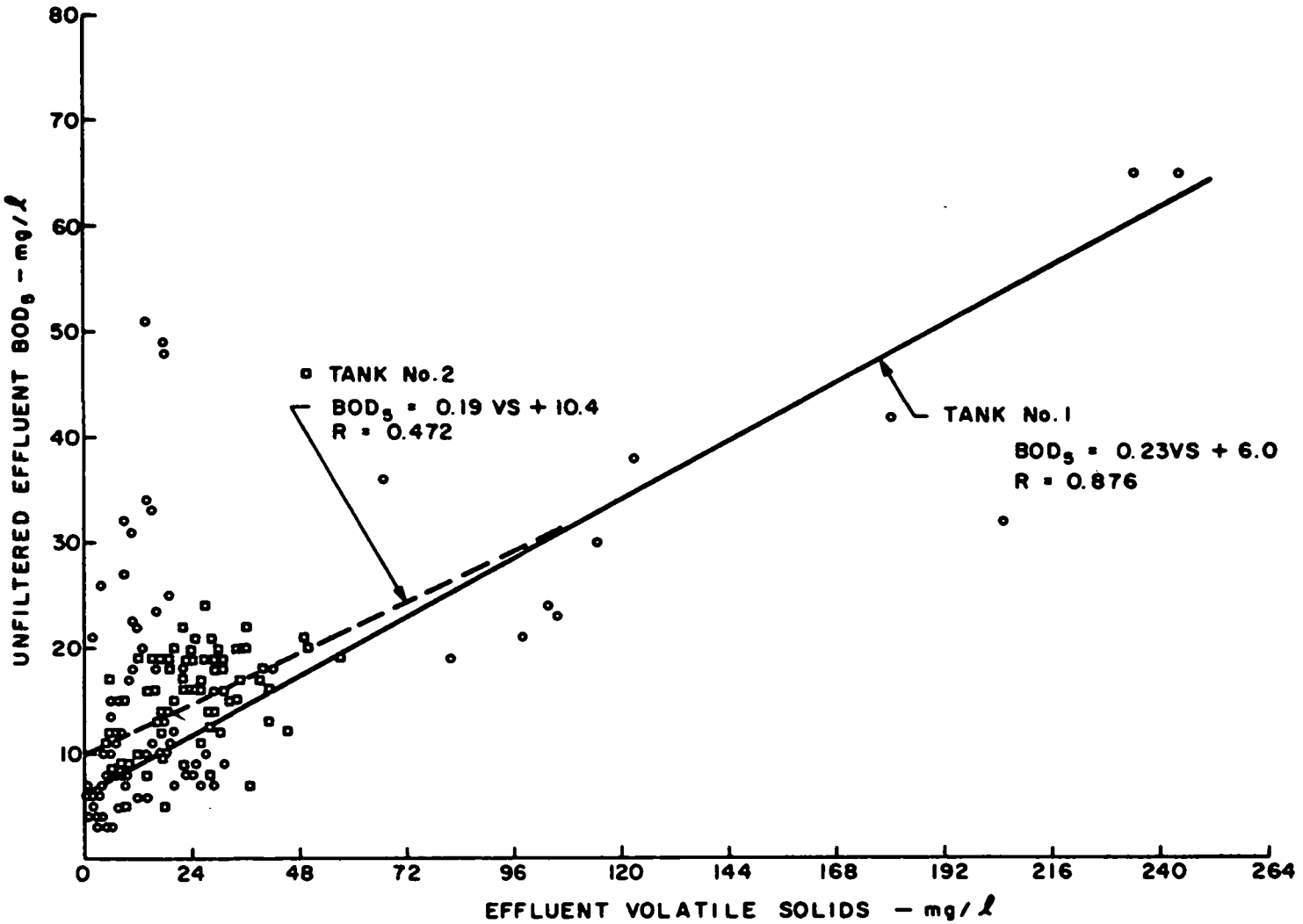


Figure 14. Effluent BOD as a Function of Effluent Volatile Solids Phase II All Flow Data

Table 9. Forms of Nitrogen in Mixed Liquor

Nitrogen mg N/ℓ

	Ammonia	Oxidized	Total Kjeldal
Tank No. 1	12.9	3.5	22.4
Tank No. 2	4.6	8.8	9.3

clear and sparkling whereas the effluent from Tank No. 2 had noticeable color even though suspended solids were often quite low.

Only a limited amount of data on aluminum and sulfate concentrations were collected during Phase II operation. The mean values for these data are as follows:

	Aluminum - mg Al/l	Sulfate - mg SO_4/l
Trickling Filter Eff.	0.17	48
Tank No. 1 Eff.	0.28	134
Tank No. 2 Eff.	0.14	40

The aluminum results are quite similar to those observed for the Phase I alum studies. The sulfate data for Phase I Run Code III (Table 1) showed the sulfate concentration of the trickling filter effluent and the final effluent during the period when no chemical was added to be only about one-half that observed for Trickling Filter and Tank No. 2 effluent during Phase II operation. There is no apparent explanation for this difference. The sulfate concentration of the alum treated unit was virtually the same as observed during Phase I studies. The sulfate data show that an average of 86 mg SO_4/l was added as a result of alum addition.

Each pound of aluminum added in the form of filter alum adds 5.33 pounds of sulfate ion to the water. If the observed increase in sulfate in the effluent from the treated unit is correlated with the mean flow (0.96 MGD) and mean alum dosage (178 mg/l), the observed increase represents an addition of 5.35 pounds per pound of aluminum added which verifies the accuracy of the sulfate data.

Phosphorus Removal

The effluent phosphorus data presented in Part C of Table 8 confirms the observations which have already been made regarding phosphorus removal. As was pointed out earlier, the reported results include all

data collected throughout Phase II operation including those obtained when alum feed was interrupted or when feed rate adjustments were being made in response to changes in flow or phosphorus concentration.

The overall removal percentages for filtered phosphorus of 97 to 95% depending on whether median or mean values are used for the chemical-biological system indicate a high degree of removal can be obtained over a long period of time. Figure 15 shows the statistical distribution of the filtered effluent total phosphorus for all data obtained.

Figure 16 relates effluent suspended solids and effluent insoluble phosphorus concentration and shows a high degree of correlation for the data (R = 0.978). Although not plotted in Figure 16, regression equations also were calculated for effluent insoluble phosphorus as a function of effluent volatile and inorganic solids (R = 0.971 for volatile solids and 0.957 for inorganic solids). The regression equations for the lines of best fit are:

$$\text{Eff P} = 0.06\text{SS} - 0.61 \quad (7)$$

$$\text{Eff P} = 0.11\text{VS} - 0.78 \quad (8)$$

$$\text{Eff P} = 0.14\text{IS} - 0.19 \quad (9)$$

This correlation further verifies the importance of effluent solids in determining effluent total phosphorus concentrations. These data show close agreement with the results obtained by Eberhardt and Nesbitt (9), particularly for the relationship between insoluble phosphorus and effluent inorganic solids. The comparable data from their study shows approximately 9.5 mg P/l with 70 mg/l of inorganic solids whereas the results of this study would indicate approximately 9.7 mg P/l would be expected at this same effluent inorganic solids concentration.

Figure 17 shows the statistical distribution of the unfiltered effluent total phosphorus for all data obtained.

ACTIVATED SLUDGE STUDIES

Mixed Liquor

Table 10 presents summary data from the activated sludge analyses performed during Phase II. As was the case in Phase I, volatile solids data were not corrected for apparent volatile solids production due to volatilization of inorganics during the analysis procedure.

The sludge volume index data show there was no decrease in SVI as a result of alum addition over those observed in the control unit. Eberhardt and Nesbitt (9) observed a significant decrease in SVI as a result of mineral addition into the high rate system used in their study. The work by Zenz and Pivnicka (52) in a full scale conventional activated sludge plant did not permit definite conclusions regarding

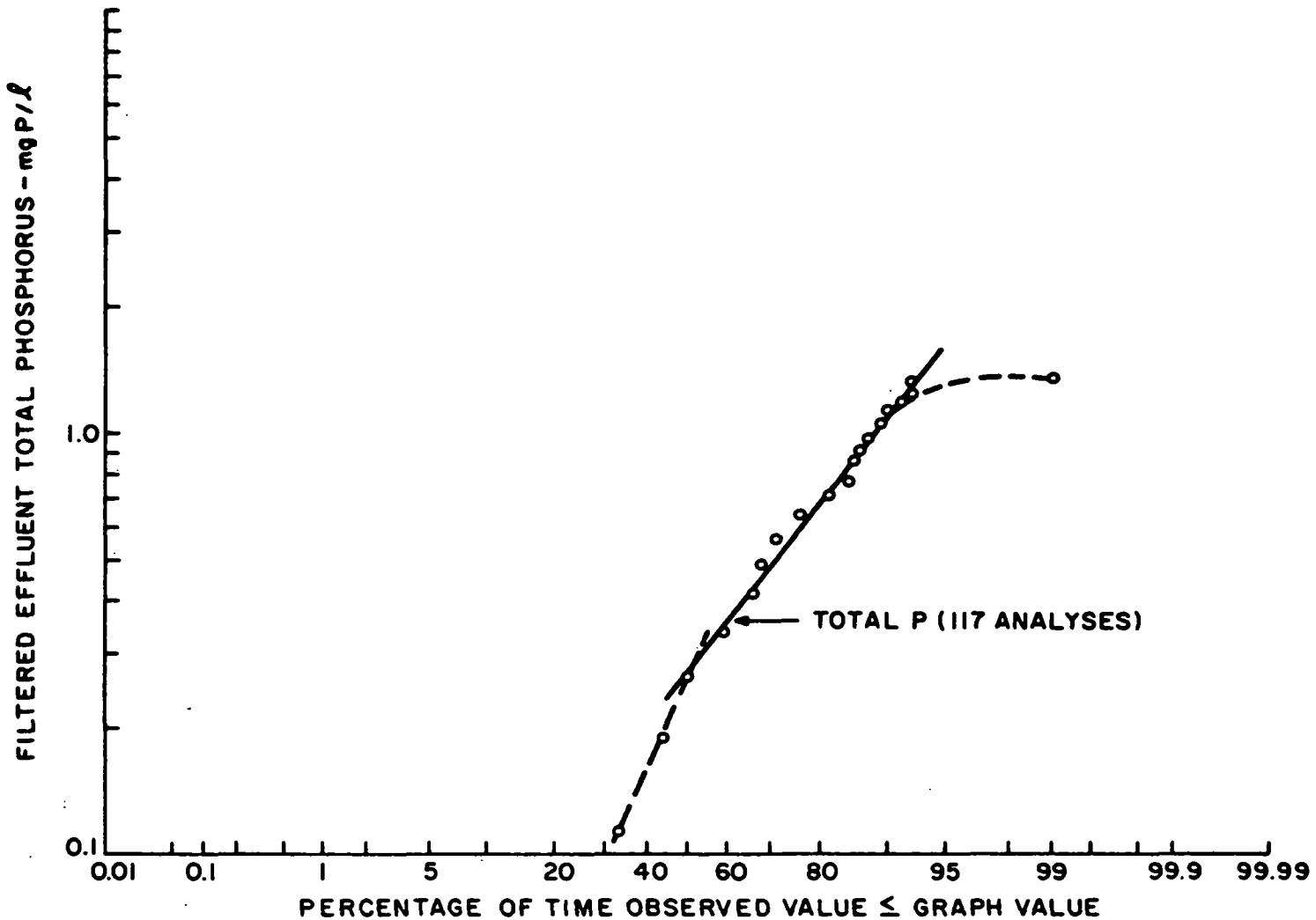


Figure 15. Statistical Distribution of Filtered Effluent Total Phosphorus Tank 1 All Flow Data

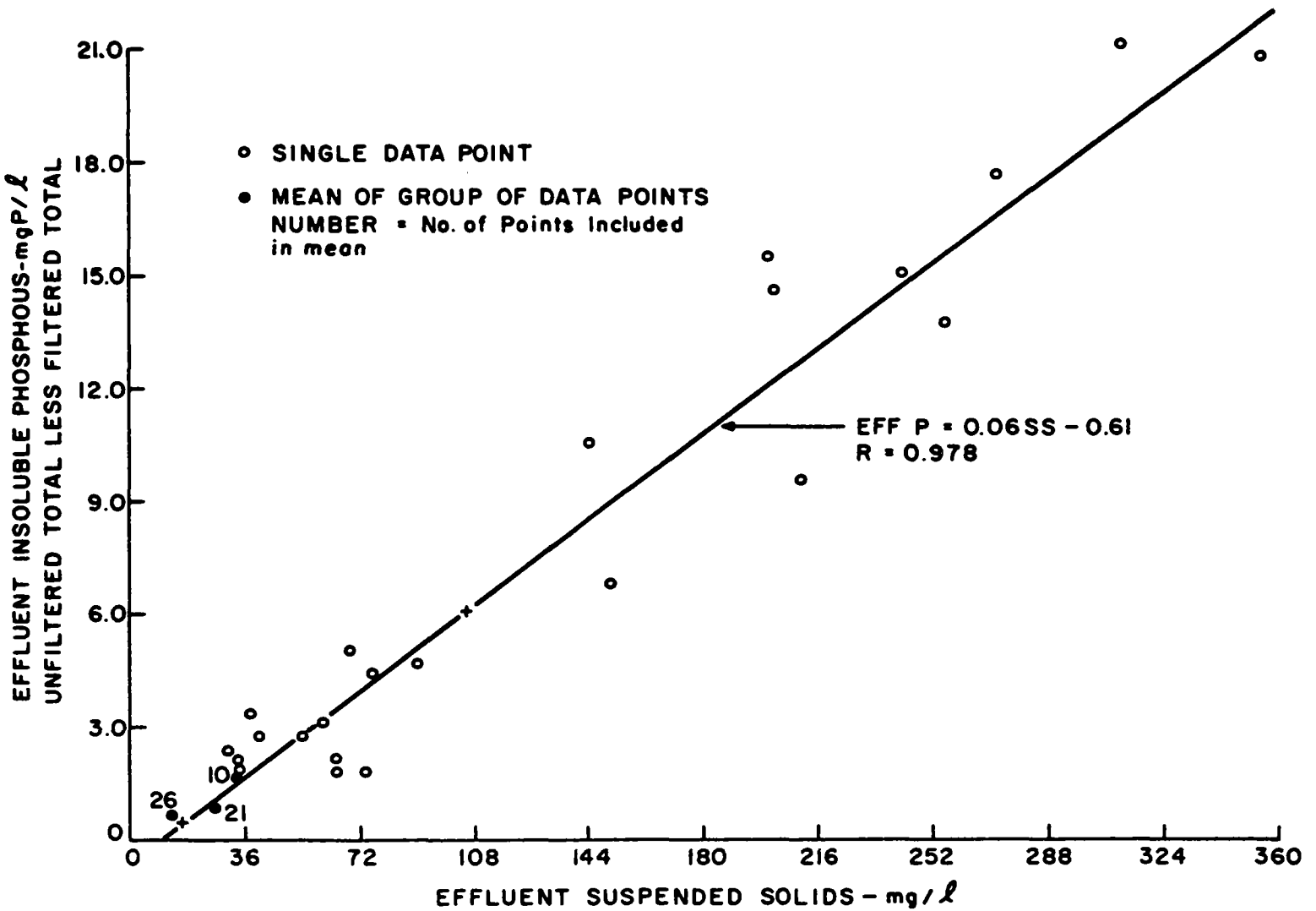


Figure 16. Insoluble Phosphorus as a Function of Effluent Suspended Solids Phase II Tank 1 All Flow Data

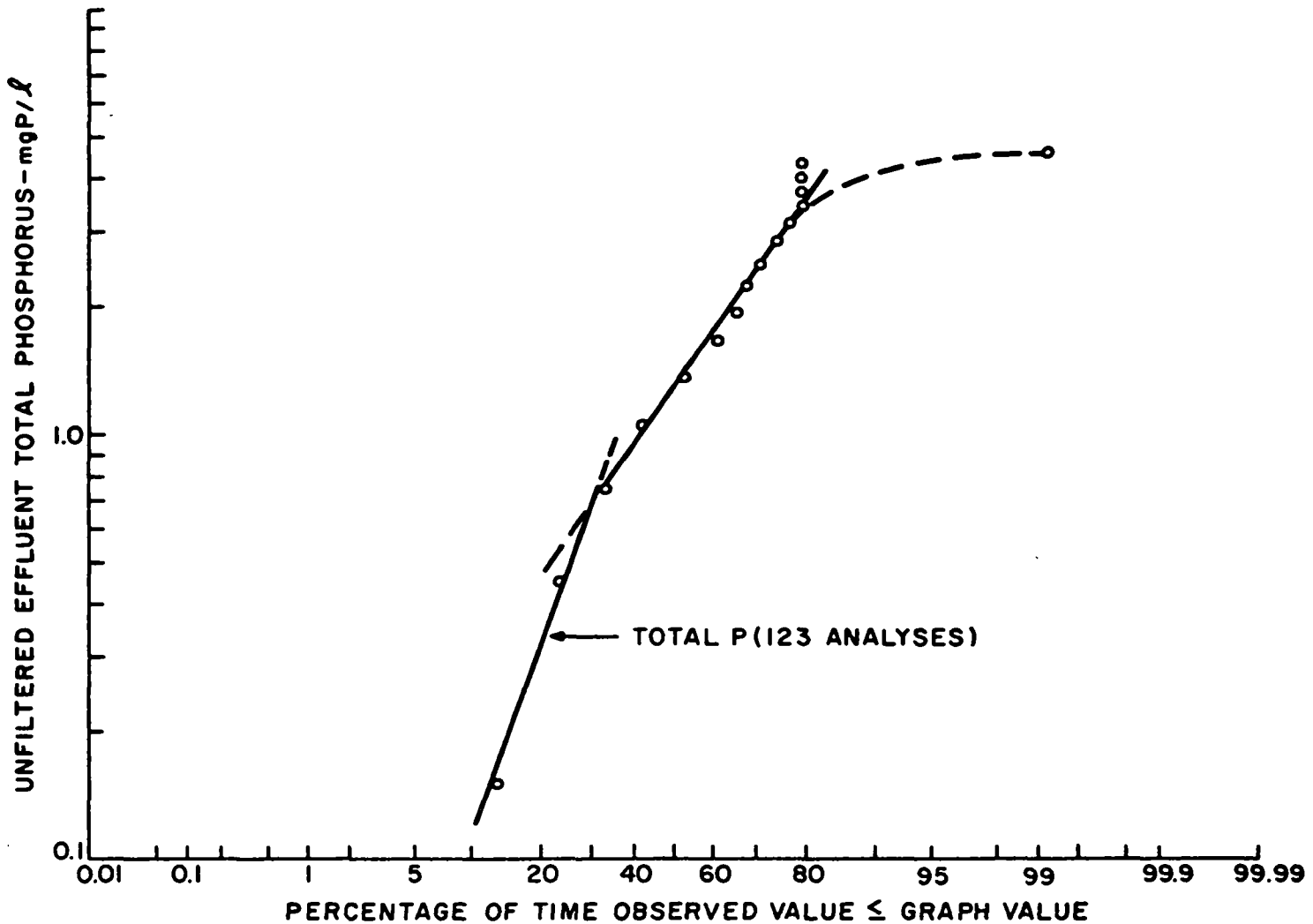


Figure 17. Statistical Distribution of Unfiltered Effluent Total Phosphorus Tank 1 All Flow Data

Table 10. Summary of Activated and Waste Sludge Data Phase II

Parameter	Tank No. 1		Tank No. 2	
	Mean	Std. Dev.	Mean	Std. Dev.
Mixed Liquor Solids - mg/ℓ				
Total	2500	480	1600	410
Volatile	1360	310	1150	320
SVI (Mohlman)	63	11	63	25
SDI[a]	1.59	--	1.59	--
Solids Age - days	1.58	0.76	2.09	1.17
MLVS Phosphorus - %	7.04	3.01	3.67	2.00
pH	6.95	0.30	7.00	0.20
Temperature °C	19.5	3.5	19.5	3.5
Waste Sludge				
Total - gal/day	16,870	4,300	5,670	2,490
- lb/day	1,077	436	513	282
Volatile - lb/day	575	237	368	208
- %	53.4	--	71.7	--

[a]Calculated from SVI: $SDI = \frac{100}{SVI}$

the effect of alum addition on SVI. However, the mean SVI of 63 for the control unit in the study reported herein is considerably lower than normally expected for a conventional activated sludge plant treating domestic wastes. The highest values recorded during the study were 96 and 172 for Tank No. 1 and Tank No. 2 respectively. The sludges from both tanks settled very readily as can be seen in Figure 18. This settling rate is particularly significant since even sludges with such excellent characteristics could not be handled under the conditions of hydraulic overload experienced without causing problems. As noted earlier, Tank No. 1 normally lost more solids in the effluent than Tank No. 2 but this unit (Tank No. 1) had to handle considerably more solids under the same hydraulic conditions.

The average solids age of the chemical-biological system was 1.58 days which was significantly lower than the average of 2.09 days for the control. This is probably most significant as it affects nitrification since BOD and COD removals were generally better in the chemical-biological system whereas nitrification was greater in the control.

Sludge Production

As indicated previously, solids handling is an important consideration in any wastewater treatment scheme. Hence, the solids production from the chemical-biological process is of prime concern. The data presented in Table 10 on waste sludge production were correlated with flow (mean flow for Phase II) and are shown in Table 11.

Table 11. Comparative Waste Sludge Production Phase II

Waste Sludge	Tank 1	Tank 2	Ratio Chem-Biol./Control
Gal/day/MG	17,600	5,830	3.02
lb total solids/day/MG	1,125	535	2.10
lb volatile solids/day/MG	600	385	1.56

The results showing the weights of sludge wasted are more directly comparable than are the volumes since the concentrations of the waste sludges from each tank were significantly different. The results of Phase II operation showed that for the system studied approximately twice as many pounds of total solids and one and one-half times as many pounds of volatile solids are produced in the chemical-biological system as in the control.

Eberhardt and Nesbitt (9) developed the following equation to describe the relationships between pounds BOD removed per day (BOD_{5R}), solids age in days (t_{SA}) and volatile solids production in lb per day (VS_p).

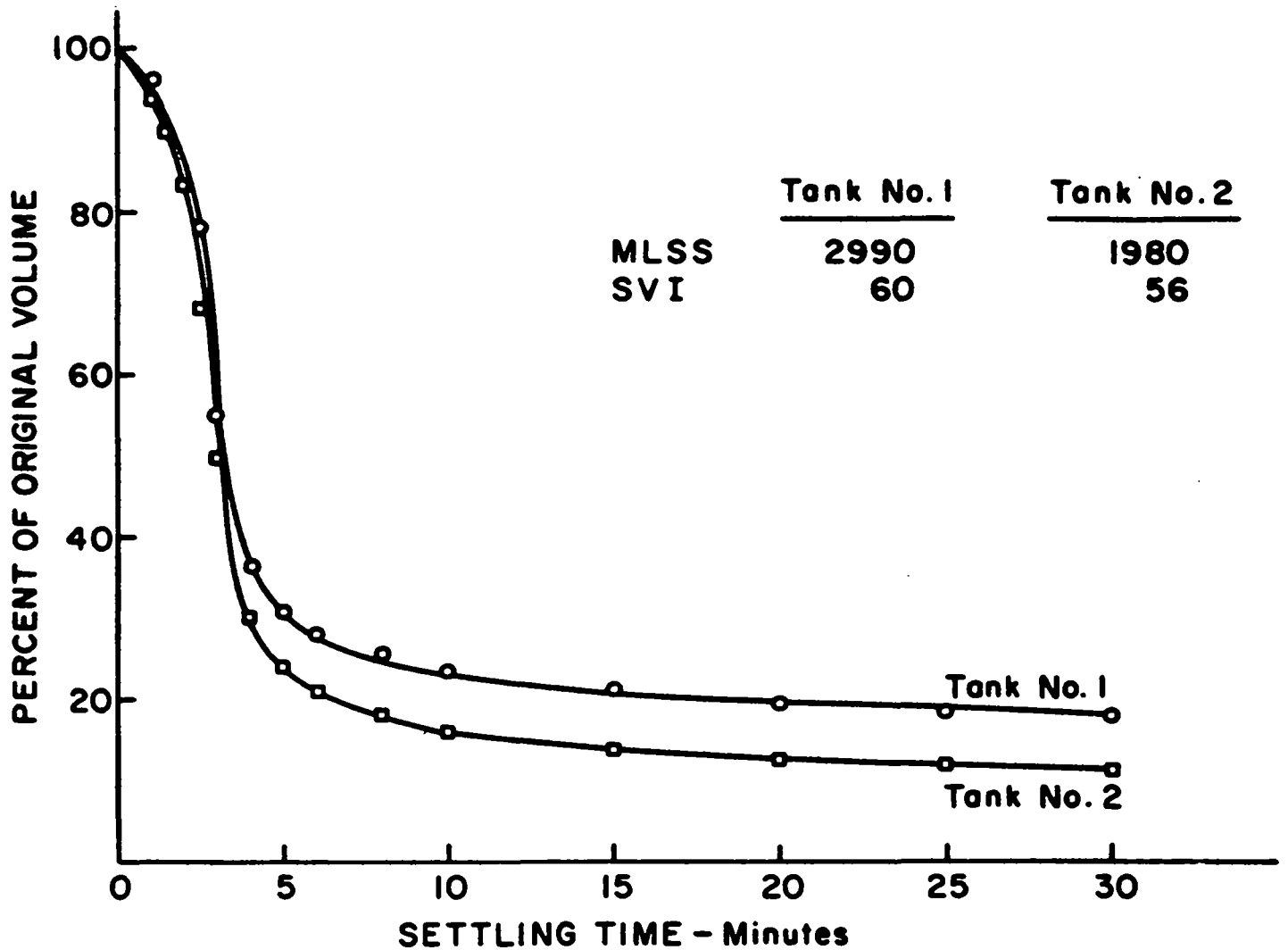


Figure 18. Mixed Liquor Settling Characteristics Phase II Alum to Tank 1

$$\log (100\ VS_P/BOD_{5R}) = -0.379 \log t_{SA} + 1.8761 \qquad (10)$$

Using this equation and mean values for BOD removal and solids age observed in this study, the predicted volatile solids production for each tank would be 452 lb/day for Tank No. 1 and 395 lb/day for Tank No. 2. The predicted total solids production would be 847 lb/day from Tank No. 1 and 550 lb/day from Tank No. 2 based on average volatile solids content of the waste sludges.

The predicted and observed results show very close agreement for the sludge production from Tank No. 2. Tank No. 1 results show much more discrepancy, i.e., the predicted weight of sludge was only 78.6% of the observed weight of sludge. As pointed out earlier, the volatile solids test procedure used undoubtably reports results which are too high because of the probable volatilization of aluminum hydroxy-phosphate compounds. Eberhardt and Nesbitt (9) in referring to the work by others reported weight losses of as high as 21.6% for ster-rettite, an aluminum phosphate compound resulting from the reaction between aluminum and dihydroxy phosphate. Recht and Ghassemi (29) showed weight losses of 18.5% for the aluminum-orthophosphate precipi-tates obtained under the conditions employed in their work. While the results of these various studies are not directly comparable since con-ditions under which the precipitates were formed differ, they do show remarkably close agreement and suggest that approximately 20% of the reported weight loss in the volatile solids procedure used herein may have been due to volatilization of inorganic compounds. If the ob-served results for the volatile solids produced in Tank No. 1 are cor-rected on this basis, the corrected value of volatile solids would be 460 lb/day (575 x 0.80) which is very close to the predicted value of 452 lb/day. This then would suggest the actual inorganic solids pro-duction in the chemical-biological system was 617 lb/day (1077-460) or 0.43 lb per lb of alum ($Al_2(SO_4)_3 \cdot 14\ H_2O$) added.

Another estimate of the inorganic solids produced from phosphorus pre-cipitation with alum can be made by means of the following equations if it is assumed that all of the aluminum ion reacts only with phos-phate and hydroxide ions:

$$Al_2(SO_4)_3 + 2PO_4^{---} \longrightarrow 2AlPO_4 + 3\ SO_4^{--} \qquad (11)$$

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{--} \qquad (12)$$

Using values reported for this study, the weight of inorganic solids produced would be:

Flow = 0.96 MG Unfiltered Total P = 10.3 mg P/l

Alum dose = 178 mg/l as $Al_2(SO_4)_3 \cdot 14\ H_2O$

For Eq. (11) mg/l Alum = $1.0 \times 10.3 \times \frac{594}{54} = 113$

For Eq. (12) mg/l Alum = 178 - 113 = 65 (Excess)

Weight of solids produced:

From Eq. (11)

$$2 \times 113 \times 0.96 \times 8.33 \times \frac{122}{594} = 370 \text{ lb } AlPO_4/\text{day}$$

From Eq. (12)

$$2 \times 65 \times 0.96 \times 8.33 \times \frac{78}{594} = \underline{136} \text{ lb } Al(OH)_3/\text{day}$$

Total inorganic solids produced = 506 lb/day

This method predicts only 0.36 lb of inorganic solids per lb of alum added per day which is significantly less than the 0.43 lb per lb of alum calculated above. This difference probably results from the initial assumption above that aluminum reacts only with phosphate and hydroxide ions. This is probably not true and the other reactions if known could be incorporated into the calculation and could result in better correlation of results.

Several samples of waste sludge were subjected to X-ray diffraction analysis in an attempt to identify the precipitates which were formed but all samples showed the precipitates to be amorphous, hence identification was impossible. Other workers have reported similar results in their attempts to identify the compounds (29).

Mixed Liquor Phosphorus

The percentage of phosphorus in the mixed liquor from the chemical-biological system was about twice as great as that observed in the control system. Considerable variability was observed in this parameter in both systems. This variability was thought to be due in a large part to the difficulty in analyzing sludge samples for total phosphorus because of the high dilutions which must be made.

The phosphorus content of the control system of 3.67 percent was higher than expected based on the data collected during the limited period of no chemical addition during Phase I. It is also significantly higher than the 2.62 percent reported by Jenkins and Menar for activated sludge systems (14). Brenner (4) reported a phosphorus content in the waste activated sludge of 3.4% on a volatile solids basis prior to aluminum addition to the aerator. Barth and Ettinger (2) reported a value of 3.0% on a volatile solids basis prior to aluminum addition to their pilot plant.

Menar and Jenkins (23) in their work on the mechanism of enhanced phosphate removal by activated sludge were able to correlate percentage of calcium and percentage of phosphorus in the activated sludge (see Figure 19). A very limited amount of data collected during the latter part of Phase II are included in Figure 20, also taken from Menar and Jenkins (23). These data further indicate that the observed percentage of phosphorus in the control system was not unusually high.

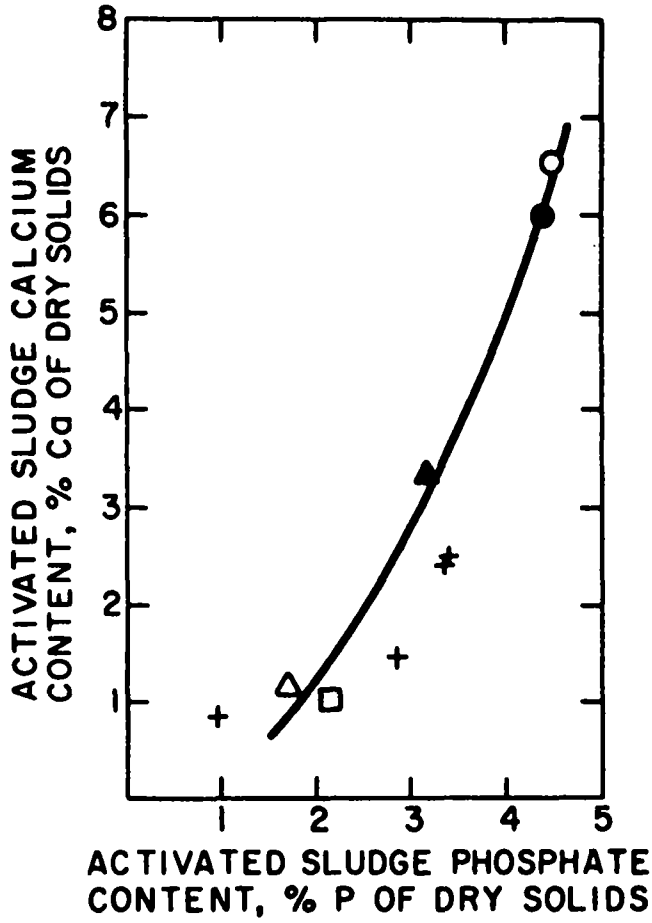
Perhaps the most interesting observation in the activated sludge data was the difference in the filtered total phosphorus concentrations in the mixed liquor from each of the two units. Mixed liquor samples were collected ahead of the point of chemical addition so it was expected the filtered phosphorus values would be approximately equal in each tank at the point of collection. The much lower values observed in Tank No. 1 (1.5 mg P/l compared with 7.0 mg P/l for Tank No. 2) indicate some precipitation or adsorbtion of phosphorus occurs as a result of contacting the chemical-biological sludge with the influent waste. However, continuous addition of alum is apparently necessary to keep effluent phosphorus concentrations low since they rose very rapidly when chemical addition was interrupted. Recht and Ghassemi (29) reported that freshly precipitated aluminum hydroxides possess little capacity to precipitate phosphates. The aging of the aluminum hydroxy-phosphate precipitates in the chemical-biological system during the time they are retained in the aerator may account for the observed difference in filtered total phosphorus concentrations between the two tanks.

SPECIAL STUDIES

Polyelectrolyte Addition

The heavy losses of solids from Tank No. 1 observed during periods of peak flow were of continuing concern throughout the study. In an attempt to apply corrective measures against this effluent degradation, a series of polymer additions were made into the influent to Final Settling Tank No. 1. The polymer selected for use on the basis of jar tests was a moderately cationic flocculant (Nalco 673). A 0.5% solution of the flocculant was made up fresh daily and was diluted after metering through a diaphram feed pump prior to application into the settling tank influent channel.

Samples of mixed liquor taken from the influent channel prior to and following polymer addition were allowed to settle in 1000 ml cylinders for visual comparison of settling rates and effluent clarity. The initial dosage of 0.25 mg/l was sufficient to produce a somewhat faster settling floc than was observed prior to polymer addition (see Figure 21). The flocs appeared to have a more grainy texture after polymer addition. The settling characteristics in the basin may have been better than those shown in Figure 21 since the floc would have had some additional mixing and time to build subsequent to the point of sampling. The supernatant liquor in the cylinder was much clearer as a result of



PILOT-PLANT EXPERIMENTS

● STANDARD RATE

○ LOW RATE

△ COMPARATIVE STUDY, VCSD PLANT

▲ COMPARATIVE STUDY, PILOT PLANT

OTHER DATA

□ SERL ACTIVATED SLUDGE PLANT AND GOLDEN GATE PARK ACTIVATED SLUDGE PLANT

+ PSU CONTROL

Figure 19. Correlation of Activated Sludge Phosphate and Calcium Contents [After Menar and Jenkin (23)]

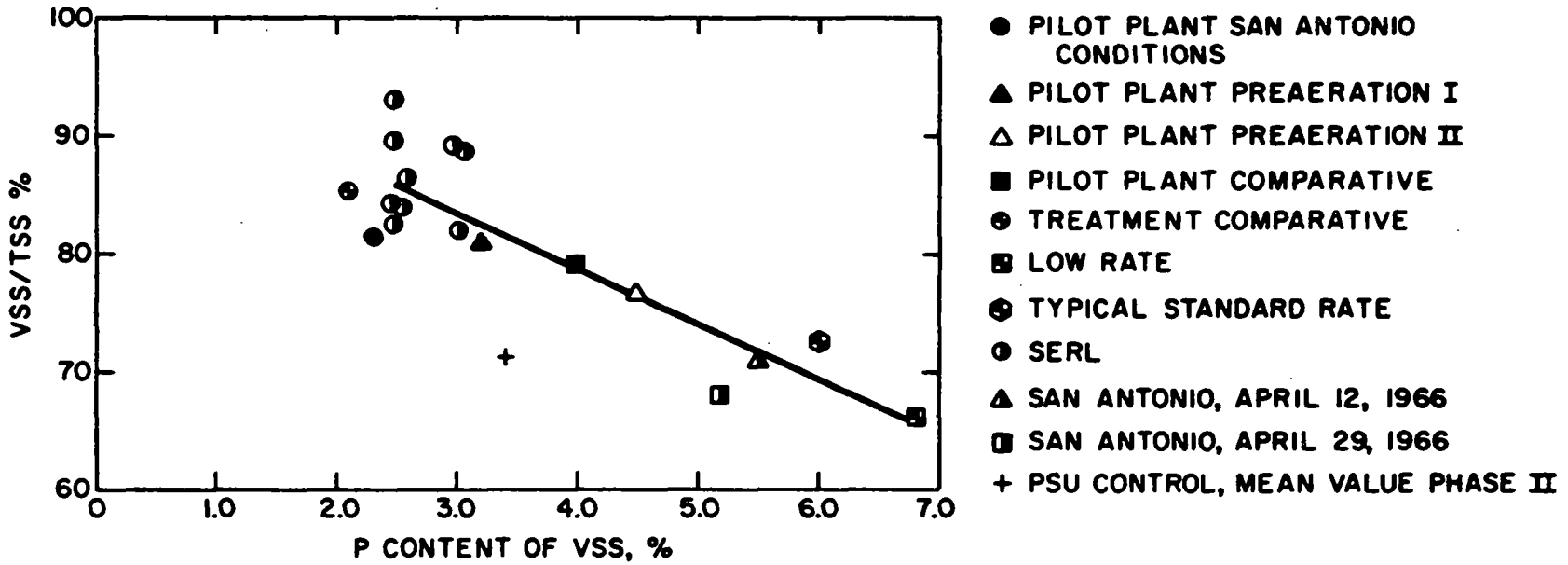


Figure 20. Correlation of Activated Sludge Phosphate Content and Volatile Fraction [After Menar and Jenkin (23)]

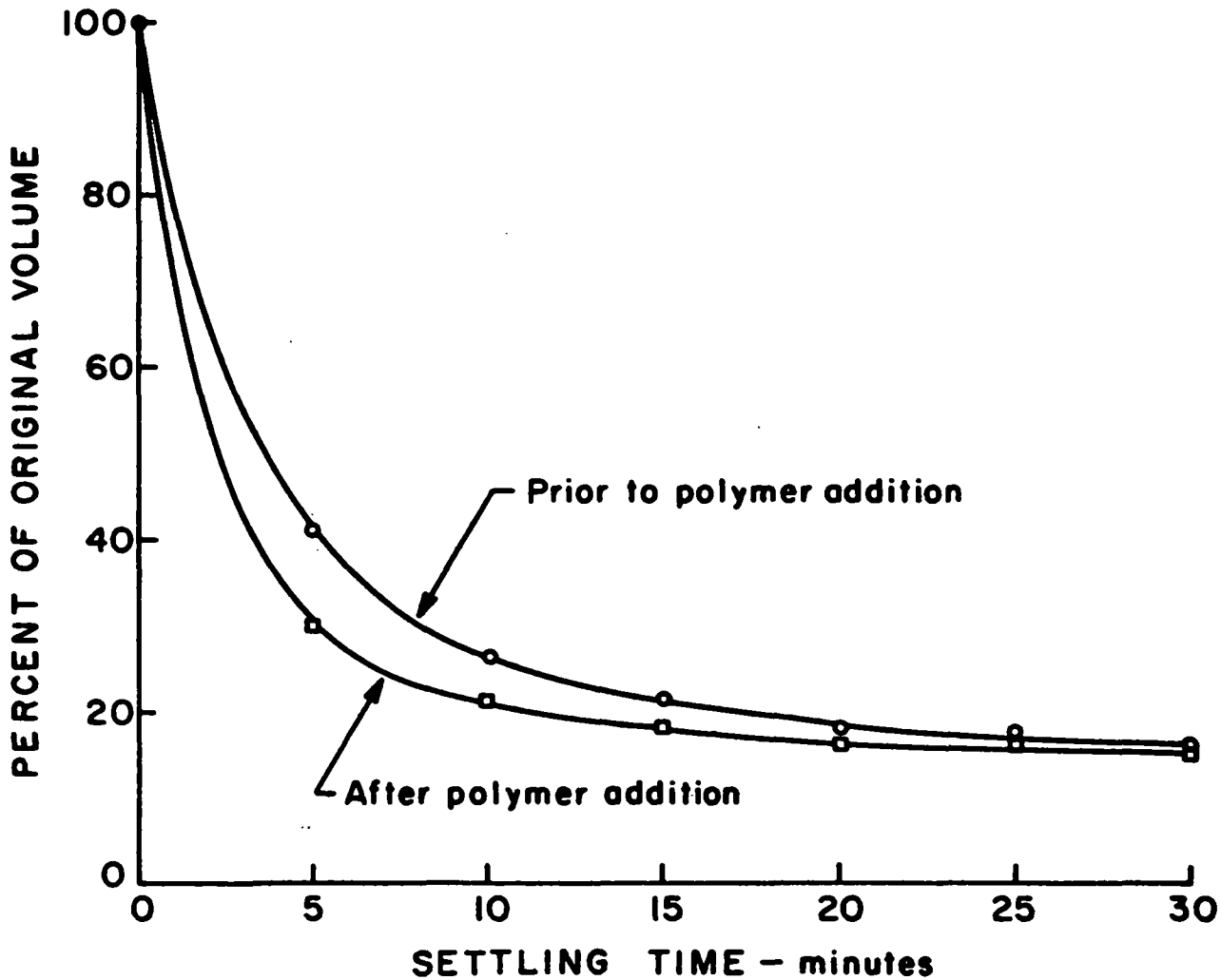


Figure 21. Comparative Settling With and Without Polymer Addition to Tank 1 Mixed Liquor

polymer addition although the sample taken prior to polymer addition was more clear than normal activated sludge effluent as a result of alum addition.

Visual inspection of the tank during periods of peak flows did not show any noticeable benefit from polymer addition. Polymer dosages were increased to 0.5 mg/l without any significant reduction in solids loss during peak flow periods. Because of limited storage capacity for polymer, polymer addition was restricted to those hours of the day when solids losses were heaviest, usually from 8:00 a.m. to 6:00 p.m. Although polymer addition did not significantly reduce the loss of solids from Tank 1, the resulting settled effluent was more clear and sparkling than normal. Figure 22 shows the typical variation in effluent suspended solids from Tank 1 during periods of hydraulic overload both with and without polymer addition. These data were taken on two different days so the flow patterns and hence the pattern of solids loss are not the same but similar. The data show conclusively that, even with polymer addition, the effluent suspended solids were too high for direct discharge to the receiving stream.

Since this was intended to be only a preliminary investigation of the effects of polymers on the reduction of suspended solids, the investigation was terminated after four days of operation because of the poor results obtained.

pH Studies

A series of jar tests were conducted in an attempt to yield some preliminary data on the effect of mixed liquor pH on the residual phosphorus concentrations and effluent clarity when alum was being added at the head end of the aeration tank. For the purposes of these studies, samples of the mixed liquor from Tank No. 1 were brought into the laboratory and six 1000 ml portions were set up on a jar testing apparatus. The initial pH's of the samples were recorded and the pH's of each of five samples were adjusted to the desired test pH with addition of 0.1 N H_2SO_4 or NaOH as required. The samples were mixed during the pH adjustment step and were then allowed to settle for 30 minutes. Phosphorus, turbidity and pH determinations were made on filtered and unfiltered supernatant samples from each jar. Table 12 shows the summary results from these studies.

As pointed out earlier, a haze or "carry-through" of what is thought to be very finely divided "aluminum phosphate" occurs when the precipitant is added at the head end of the tank. The data in Table 12 suggest this is partially a function of pH since lower effluent insoluble phosphorus and filterable turbidity results were obtained with a reduction in pH (see Figure 23). The pH adjustments were made after alum addition and mixing in the aeration tank so the fine precipitate should have been present in the samples brought back to the laboratory. Therefore, the data indicate that the fine precipitate was altered in some manner during the pH adjustment step which resulted in lower insoluble phosphorus concentrations in the effluent with a reduction in

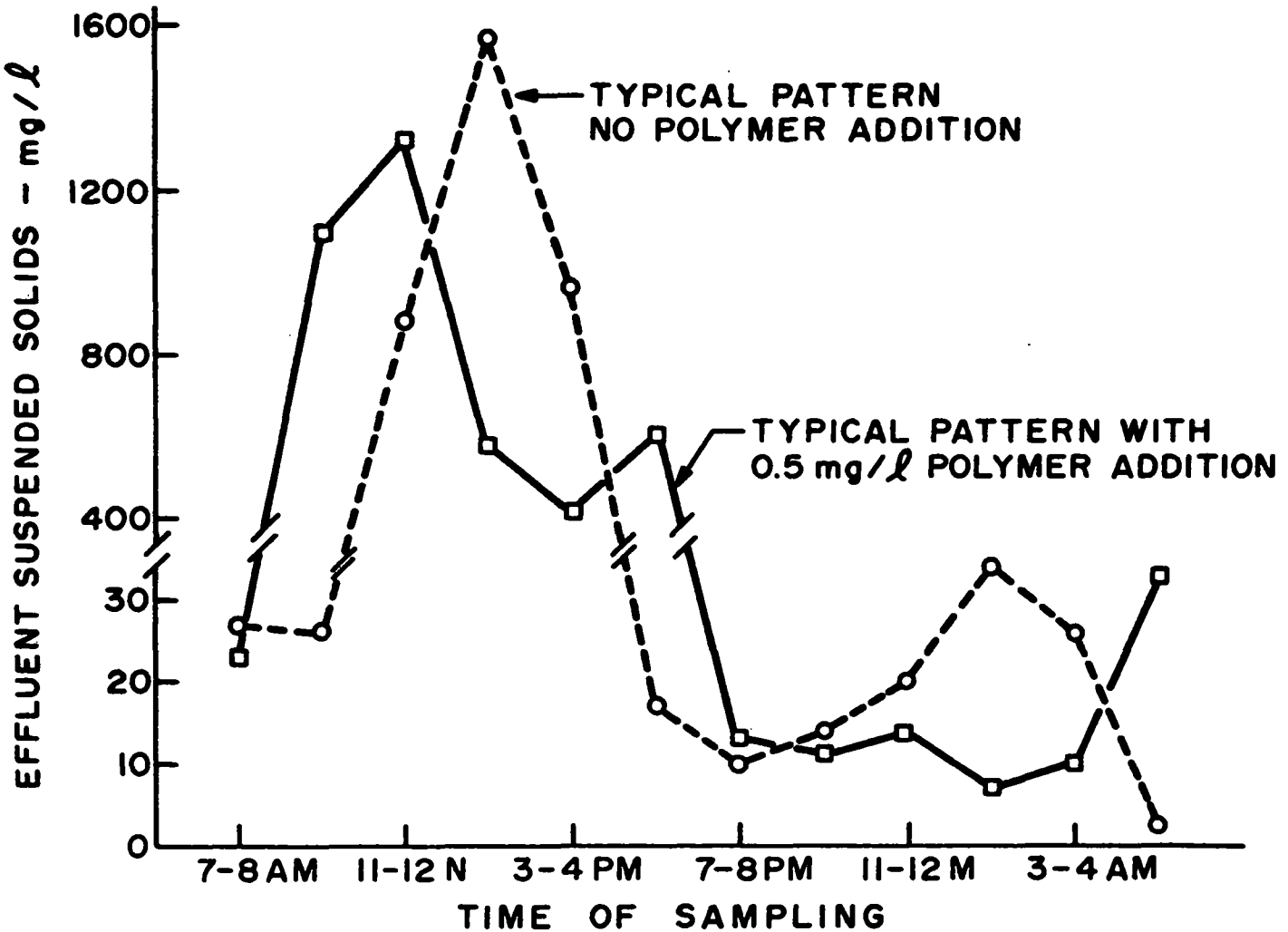


Figure 22. Variation in Effluent Suspended Solids With and Without Polymer Addition Tank 1 Flow $\geq$ 1.041 MGD

Table 12. Effluent pH Phosphorus and Turbidity Relationships

Parameter	Initial Test pH 5.30	5.80	6.30	6.80	7.30	Control[b]
Ortho P - mgP/ℓ[a]						
Filtered	0.26	0.30	0.27	0.32	0.53	0.36
Unfiltered	1.31	2.02	6.08	5.37	7.59	6.40
Turbidity - Units[a]						
Filtered	2.3	2.5	2.3	2.8	3.2	2.7
Unfiltered	10	16	25	30	34	31
pH[a]						
Filtered	6.00	6.20	6.65	6.95	7.20	6.95
Unfiltered	6.05	6.10	6.45	6.70	7.00	6.70
ml of 0.1N H_2SO_4 to reach test pH	13.1	9.0	1.8			
ml of 0.1N NaOH to reach test pH				2.4	6.9	-

[a]Data shown represent average values of analyses performed after 30 minutes settling following pH adjustment to test pH.

[b]pH of control was 6.60.

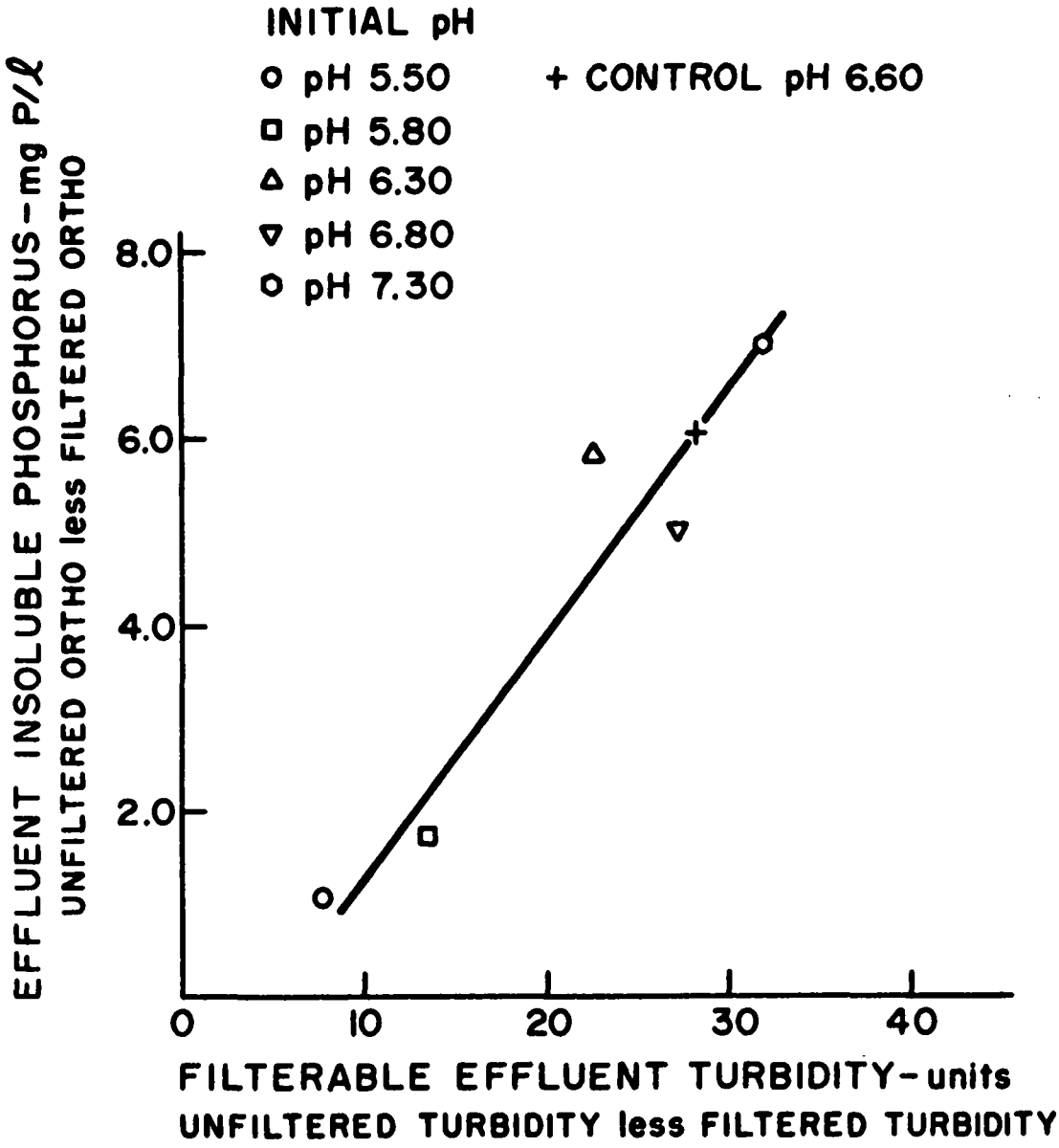


Figure 23. Correlation of Effluent Phosphorus and Turbidity with pH Adjustment

pH. Additional study would be needed to determine if this has any practical significance in terms of operating performance and procedures.

A series of in situ pH measurements were made in each of the two aeration and settling tanks to determine actual pH profiles through the tanks during normal operation. Figure 24 shows the pH profile during normal operation with alum addition into the effluent channel from the aeration tank as described earlier. These data show a very severe depression of pH immediately following the alum addition (pH 6.65 reduced to 4.65) with an increase to pH 5.9 after mixing is completed. The pH stays about 5.9 through the final tank. This pH is near optimum for phosphorus removal and is the result of the alum addition alone. These results were significantly different from the effluent pH's observed during regular collection of routine data and reported in Tables 6, 7 and 8 which showed values of 6.8 to 7.2 for Tank No. 1 effluent depending on the flow category. Further investigation showed the pH of the sample increases with time apparently as a result of loss of entrained CO_2. The sample which showed a pH of 5.85 at the time of in situ measurements showed a pH of 7.10 twenty hours later. The results of the jar tests reported in Table 12 also show this increase in pH upon standing. Therefore, the composite samples collected on a routine basis did not accurately reflect the pH in the final tanks but rather some sort of equilibrium pH depending on the length of time the sample had been standing. This same observation was made in the data from Tank No. 2 except the pH was essentially the same throughout the aeration tank and clarifier. The sample from Tank No. 2 which showed a pH of 6.95 at the time of in situ measurements showed a pH of 7.80 twenty hours later.

Figure 25 shows the pH profile data taken in a similar manner with alum addition at the influent end of the tank. These data show no measureable reduction in pH occurred as a result of alum addition under these operating conditions. The vast buffering capacity of the mixed liquor in the tank with the dispersion which occurred was able to buffer the alum addition at this point. In contrast, the relatively slow dispersion which occurred when alum was added into the effluent channel was not sufficient to buffer the system.

Recht and Ghassemi (29) also showed in their work on precipitation of phosphorus with aluminum that effluent residual turbidity is related to pH. They showed a minimum residual turbidity at about pH 5.5 with significant increases as the pH rises above 6. This observation may also help to explain the "carry-through" which occurred when alum was added at the influent end of the aerator since the pH then was about 7 through the aerator and final clarifier whereas it was decreased to about pH 6 through the final clarifier when alum was added into the effluent channel.

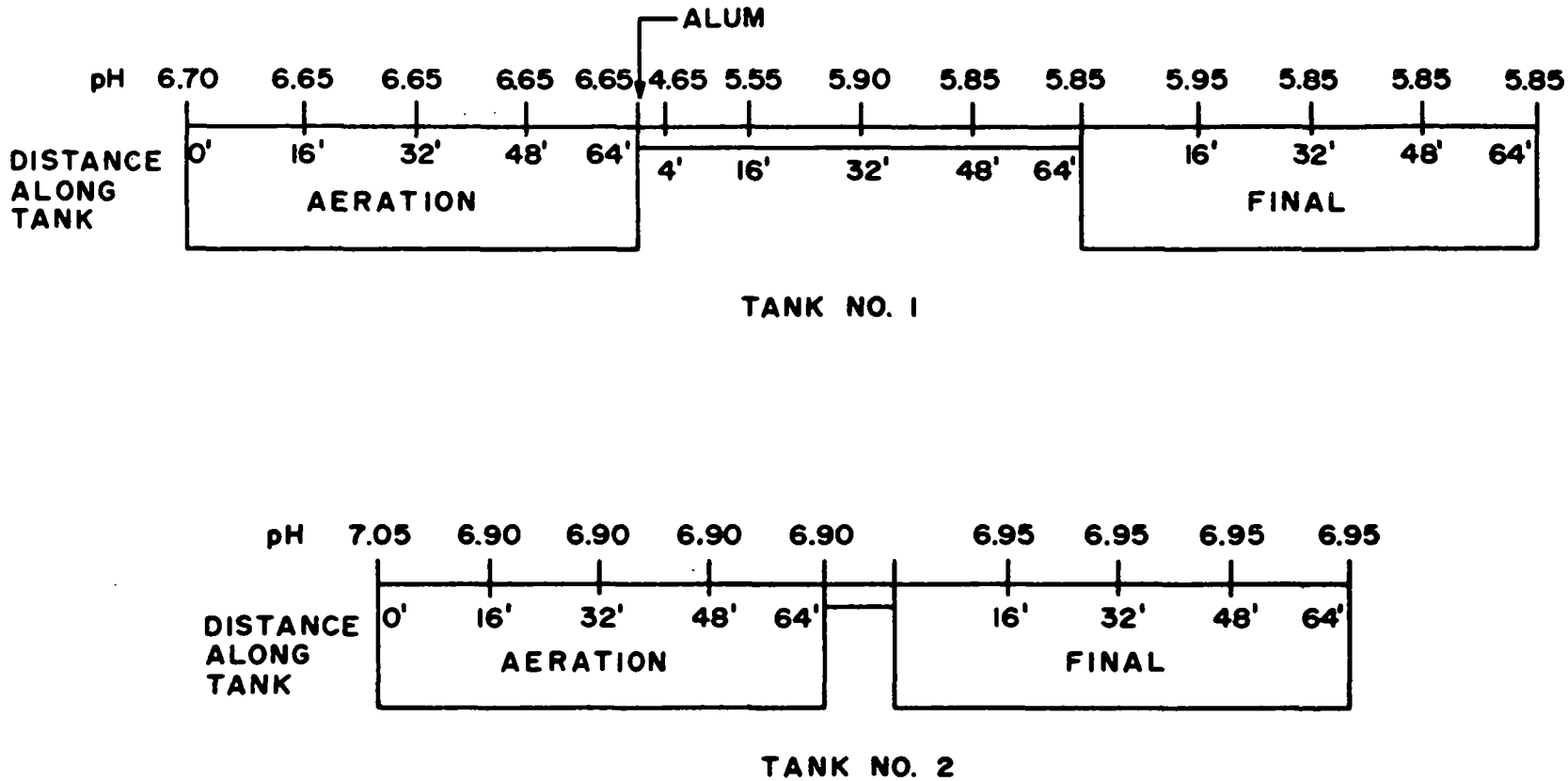


Figure 24. In situ pH Profile Alum Addition into Effluent Channel from Aeration Tank

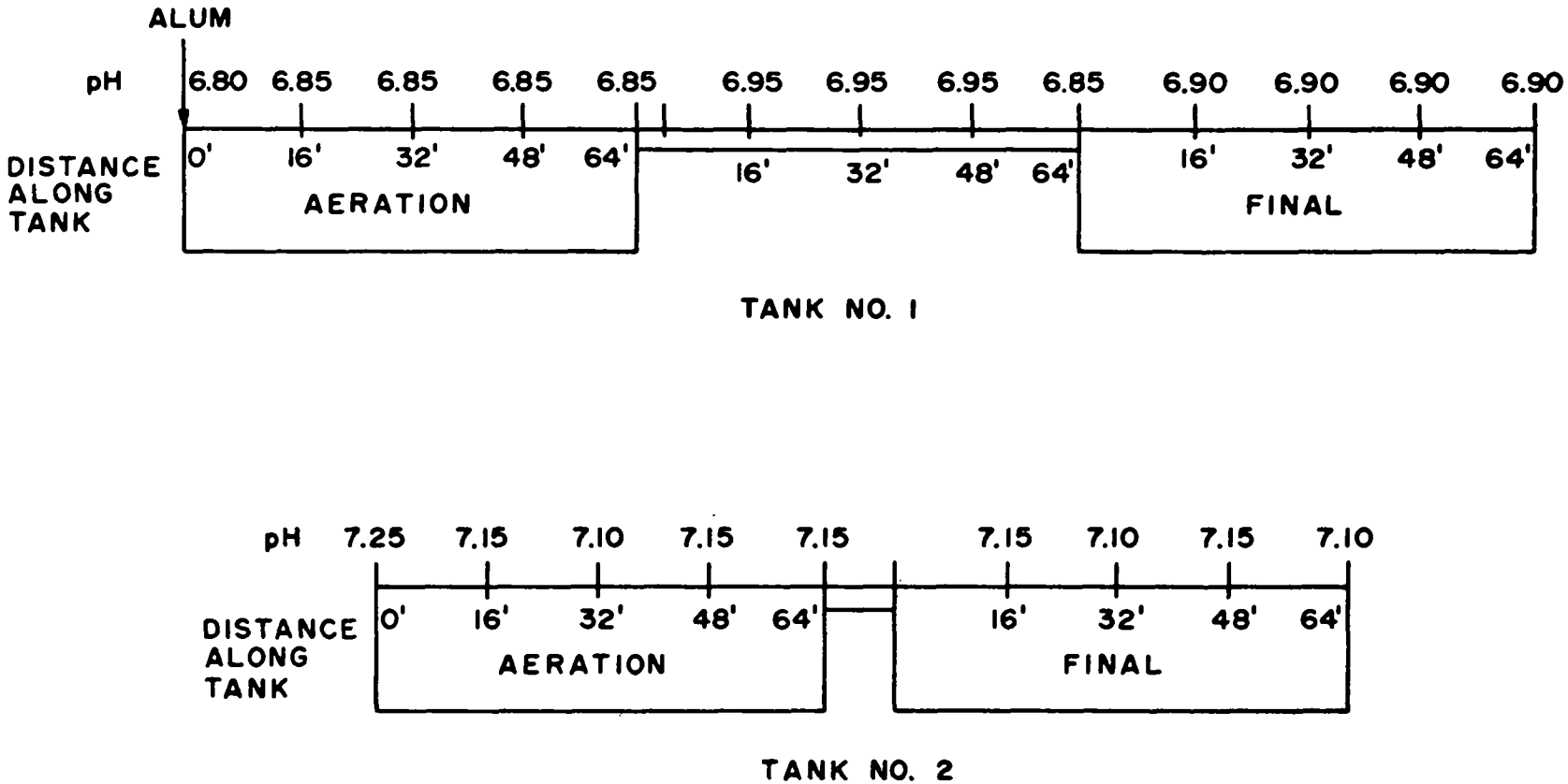


Figure 25. In situ pH Profile Alum Addition at Head End of Aeration Tank

Identification of "Carry-Through"

The attempts to characterize the "carry-through" which occurred when alum was added at the influent end of the aeration tank were not successful. A series of samples were analyzed by means of an atomic absorption spectrophotometer but no significant differences were observed between effluent samples obtained with alum addition at the influent end. Preliminary particle size determinations with an optical microscope did not show any discernible difference between effluents even with use of 0.1 μ pore size filter for purposes of particle retention. This similarity would suggest that many of the particles which make up the haze or "carry through" are extremely fine (pass through a 0.1 μ filter) and hence are not discernible except perhaps by means of electron microscopy. Because of limitations of time and the general lack of success in identifying or adequately characterizing the "carry-through," it was decided to abandon such attempts for the purposes of this project.

Nitrification

After the data collection for Phase II was terminated on August 21, it was decided to increase the mixed liquor suspended solids in Tank No. 1 to see what effect this would have on nitrification. Chemical addition during this period was at the influent end of the aeration tank for the purposes of a separate microbiology study and because of this the pH of the system following alum addition was higher than that observed during alum addition into the effluent channel as reported above. The effluent from the chemical-biological system during this period was more turbid than reported previously. However, on three occasions the effluent was visibly less turbid than usual and on all three occasions the pH of the mixed liquor sample was between 5.8 and 5.9 which was significantly lower than the average pH for the period of 6.40. Table 13 presents summary data for this period (Aug. 24, 1970 to Nov. 11, 1970) based on a limited number of analyses (approximately 17 for each parameter). The data on oxidized nitrogen show no significant difference between Tank No. 1 and 2 at the 5% level during this period of operation. These data can be compared with the results reported in Table 6, Part B, where the difference in oxidized nitrogen between Tanks No. 1 and 2 was significant at the 5% level and operation was quite similar except for mixed liquor solids level and point of chemical addition. It would appear that either the higher solids or the chemical addition into the influent end of the aeration tank or both negated the previously exhibited inhibitory effect of alum addition or nitrification. However, it is not possible from the data to determine whether the higher mixed liquor suspended solids (and resulting higher solids age) or the change in the point of alum addition was responsible for the change observed. It is the writer's opinion that the lower pH and greater pH shock which occurred with alum addition into the effluent channel was primarily responsible for the apparent inhibition of nitrification that was observed during Phases I and II. Therefore, while the higher solids age experienced during this special study did undoubtably increase the degree of nitrification which occurred, this same

Table 13. Summary Data from Special Nitrification Study

	Trickling Filter		Tank No. 1		Tank No. 2	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
A. Mixed Liquor						
MLSS - mg/ℓ	--	--	3030	360	1500	200
MLVS - mg/ℓ	--	--	1590	240	1050	160
SVI	--	--	84	12	58	9
pH	--	--	6.40	0.40	7.00	0.10
B. Effluent						
Oxidized Nitrogen						
mgN/ℓ	5.0	2.6	8.5	2.0	9.3	2.8
Phosphorus - mgP/ℓ						
Filtered						
Ortho	5.0	1.1	0.24	0.22	4.6	1.9
% Removal	--	--	96.8	--	38.7	--
Total	4.8	2.9	0.38	0.32	4.1	2.1
% Removal	--	--	94.9	--	45.4	--
Unfiltered						
Ortho	6.3	1.9	1.58	1.17	5.6	2.1
% Removal	--	--	79.0	--	25.4	--
Total	7.5	3.6	1.97	1.36	5.8	3.7
% Removal	--	--	73.8	--	22.7	--
C. Flow - MGD	0.75	0.16	--	--	--	--
D. $A\ell/P_{filt.\ ortho}$ Ratio	--	--	2.87/1	0.69	--	--

observation would also be true for Tank No. 2. However, it probably did not have a significant role in eliminating the inhibitory effect of alum addition. Insufficient data were available to calculate the respective solids ages for this period. Termination of project operation did not permit collection of comparative data with alum addition into the effluent channel.

Comparison of the phosphorus data in Table 13 with similar data in Table 6, Part C, illustrates the deterioration which occurs in effluent quality when alum addition is at the influent end of the aeration tank. These data show that average removals of unfiltered effluent total phosphorus decreased from 91.9% to 73.8% for operation under what was otherwise very similar operating conditions. This difference is most likely due to the "carry-through" which occurs with alum addition into the influent end of the aeration tank. The effect of filtered effluent phosphorus concentrations is much less since much of the mass of the "carry-through" is removed during the filtration step.

Effluent Fertility

Since the reason for removing phosphorus from wastewaters is to reduce the fertility of the effluent, samples of trickling filter effluent and effluents from the control unit and the chemical-biological system were subjected to the Provisional Algal Assay Procedure (PAAP) (28) by personnel from the FMC Corporation, Central Research Department, Princeton, New Jersey (19). *Selenastrum capricornutum* was used as the test organism and samples from Upper Spring Creek above the point of effluent discharge were used as the dilution medium for the tests.

Upper Spring Creek (USC) water alone showed significantly less growth of test cells than did 0.3 PAAP cultures with additions of 10% Upper Spring Creek water in one flask and 10% distilled water in another. There was no apparent difference in growth potential between the 0.3 PAAP plus 10% USC and 0.3 PAAP plus 10% distilled water. USC water with 1.0% addition of Tank No. 2 effluent showed about eight times more growth of test cells than did the same dilution with Tank No. 1 effluent. Increasing the addition of effluent to 10% resulted in about 130 times more growth with Tank No. 2 effluent than was obtained with Tank No. 1 effluent. Additional experiments showed that addition of dibasic potassium phosphate (K_2HPO_4) or sodium phosphate (Na_2HPO_4) to Tank No. 1 effluent to the same phosphorus concentration observed in Tank No. 2 effluent resulted in virtually identical growth curves for the two. The studies indicated that the lack of growth in the Tank No. 1 effluent was not due to aluminum toxicity.

While very limited in scope, these preliminary studies did show a significantly lower growth potential for effluents from Tank No. 1 when compared with the untreated control. Further, spiking of Tank No. 1 effluent with phosphorus resulted in a restoration of fertility thus substantiating to a degree the role of phosphorus in algal productivity for these test conditions. Considerably more work must be done to further define this role before the results can be projected to field

conditions but the results reported above do give some indication that conditions do exist where phosphorus removal from domestic wastewater may result in lower productivity in certain waters.

Data collection for Phase II operation was terminated on August 20, 1970. Operation of the chemical-biological system and the control unit were continued until December 1, 1970 to permit continued collection of data for a satellite project on the microbiology of the two systems and the special studies described above.

CHEMICAL-BIOLOGICAL PROCESS DESIGN AND OPERATION

DESIGN CONSIDERATIONS

Preliminary Data

The chemical-biological process is particularly well adapted for use in existing activated sludge wastewater treatment plants since it makes maximum use of existing unit processes and structures thus minimizing capital expenditures. The suggestions and recommendations contained herein are applicable for new treatment facilities as well as for modifications to existing plants. Some of the data on wastewater flows and characteristics will, of course, have to be estimated for new installations. Therefore, flexibility should be incorporated into the design so that reasonable changes from predicted values can be incorporated into plant operation without adversely affecting the results obtained. The following parameters must be evaluated in order to achieve an economical design that will provide the flexibility and capability to meet the effluent requirements established for the plant:

1. Flow - design average with due consideration of peak flow rates and daily, weekly and monthly variations.

2. Phosphorus concentration - variation in concentration with time is important as are the relative amounts of ortho and complex; soluble and insoluble phosphorus.

3. Alkalinity - higher alkalinity systems (125 mg $CaCO_3$/l or above) tend to favor usage of alum. If alkalinity is below 125 mg $CaCO_3$/l, sodium aluminate would probably be the chemical of choice although alum plus lime should also be considered

4. pH - related to alkalinity. If pH is 7.0 or above, alum is preferred whereas low pH would favor usage of sodium aluminate.

5. Sulfate - addition of appreciable amounts of sulfate to wastewaters already high in sulfate concentration or where effluents are to be discharged to stream used for potable water sources may be undesirable. In this event, sodium aluminate would probably be the chemical of choice.

Chemical Handling and Feeding

Liquid chemical handling and feeding systems are generally easier to operate and maintain than are dry feed systems. However, transportation costs and inaccessibility to liquid chemical sources may dictate use of dry chemicals in some instances. Chemical manufacturers should

be consulted for detailed recommendations on chemical storage and unloading facilities. Provision should be included for measuring the amount of chemical fed.

The point of chemical addition should be located as near to the effluent end of the aeration tank as is practical. Because of the severe pH shock which occurred when alum was added directly into the effluent channel during this study, it is suggested that addition be made into the aeration tank in order to take advantage of the greater buffering capacity at that point. Some deterioration in effluent quality can be expected as the point of addition is moved toward the influent end.

Excessive suction head on the chemical feed pumps should be avoided to prevent siphoning of chemical through the feed pumps at high tank levels. Pump manufacturers should be consulted for suction lift characteristics of their pumps and maximum suction heads which can be tolerated for the chemical involved. Exposed chemical feed lines and storage tanks should be insulated for cold weather operation.

Process Control

It is highly desirable for the chemical feeders to be paced from influent flow meters so that chemical feed rate adjustment is more responsive to flow changes. This is important both for economy of operation but perhaps even more to avoid underdosing which can result in intolerable increases in effluent phosphorus concentrations.

Since a proven reliable means for automated phosphorus analysis of effluents which could be used in compound loop control of chemical feed is not presently available, it is recommended that phosphorus concentration variations be incorporated into the chemical dosage calculations and the flow - feed rate schedule to compensate for the variations as much as possible. It is suggested that a planned slight overdose be practiced since this will help to ensure high quality effluent where this is required. Where phosphorus removal requirements are less stringent (90% removal or below), this is not nearly so critical as occasional underdoses do not have as serious an effect on the overall results.

Hydraulic Loading on Clarifiers

Based on observations made during this project, it is recommended that surface settling rates in final clarifiers should not exceed 600 $gal/ft^2/day$ for design average flow. Where unusually high peaks occur, consideration should be given to even lower overflow rates. In some instances it may be desirable to provide influent equalizing storage to dampen out surges. This would be of assistance also in optimizing chemical feed since many of the variations in flow and concentration which otherwise occur would be eliminated.

If hydraulic loads in existing treatment works are such that recommended overflow rates are exceeded, consideration should give to installation of tube settlers or other devices to improve the efficiency of the existing units. Severe cases of hydraulic overloading may require construction of new settling tanks or surge tanks to alleviate the problem.

Effluent Filtration

It will usually be necessary to provide filtration of effluent in order to meet very stringent phosphorus removal requirements. Filtration does provide a safety factor to protect the stream in the event of heavy solids losses from the clarifiers. Various filter devices are available and may be evaluated by the designer for the particular application involved.

Solids Handling

No special solids handling equipment or requirements are necessary for handling and disposal of the sludges resulting from chemical-biological treatment. Flexibility in pumping units should be sufficient to handle the greater weight of solids and volumes of sludges which result from chemical-biological treatment in instances. Sludge weights approximately twice those obtained without chemical addition can be expected.

Dewatering and disposal of the chemical-biological sludges should not present any unusual problems. These sludges are generally more easily dewatered than are biological sludges and may be handled by any of the normally employed unit processes. It is unlikely that recovery of the precipitating chemical will offer any economic advantage except under unusual circumstances.

OPERATIONAL CONSIDERATIONS

General

Operating experiences over the duration of the project resulted in the following suggestions on plant operation in order to realize maximum benefit from the chemical-biological process for phosphorus removal.

Process Control

It is recommended that filtered orthophosphate in the influent waste be used as the basis for process control. The orthophosphate test procedure is rapid and relatively simple to perform compared to the procedure for total phosphate. The data presented earlier on the relationship between Al/P (filt. ortho) ratio and effluent total phosphorus concentration indicate the ratios which can be used as guides for dosage

calculations. However, it is recommended that operating data from each individual plant be reviewed regularly and adjustments in dosage be made as needed to achieve the particular degree of removal required. Different wastewaters will undoubtably require different Al/P ratios to achieve a given effluent phosphorus concentration and these relationships can only be developed from actual plant operating data.

Once the relationship between ortho and total phosphorus has been determined for a given plant, the orthophosphate test can be used to predict effluent total phosphorus values with sufficient accuracy for control purposes.

Control of mixed liquor suspended solids must take into consideration the much lower percentage of volatile solids in the chemical-biological system. The mixed liquor volatile suspended solids should be maintained at the necessary level to achieve the desired organic loadings. Once the system has reached a balance, control can be based on total suspended solids with regular checks on volatile solids so that any changes can be incorporated into sludge wasting schedules.

Operators should check the amount of chemical actually fed each shift to detect underfeed or overfeed as soon as possible. Unless the chemical feed lines have a constant slope to the point of application, they should be checked frequently for entrapped air and vented as required.

Return of waste sludge from the chemical-biological system to the primary settling tanks during this study resulted in better concentration of primary sludges in the withdrawal hoppers. This reduces the amount of water which must be handled in the solids handling process and hence can be of advantage where piping flexibility permits.

Maintenance

Some additional corrosion can be expected as a result of the lower pH's which may occur in the chemical-biological system when alum is used. Visual comparison in September 1970 of collection mechanisms in the two final clarifiers used in the study revealed some additional corrosion occurred as a result of alum addition. However, the treatment plant foreman did not feel it was excessive for the length of time the units had been in operation without being taken down for maintenance. The most noticeable difference was in the color of the corrosion products. Those from Tank No. 1 were more rust colored whereas those from Tank No. 2 were more black in color. This corrosion problem can be taken care of by proper selection of protective coatings.

Less growth of slimes on weirs and tank walls was noted in Tank No. 1 than in Tank No. 2 during Phase II operation. This probably was due to the lower pH and perhaps to a lesser degree the lower amount of phosphorus in the effluent. Because of this, less routine cleaning of weirs and walls in Tank No. 1 was required which resulted in some savings in maintenance time.

No unusual operating problems developed during the duration of the study. Routine maintenance of equipment and structures is necessary to achieve optimum process performance and to avoid major breakdowns.

COST ANALYSIS

GENERAL

Process economics are as important as technical feasibility in the final selection of unit processes for the solution of a particular wastewater treatment problem. The chemical-biological process which served as the basis for this study offers two significant economic advantages over some of the other schemes which have been proposed for removing phosphorus from domestic wastewater. First, for application in existing wastewater treatment works, required capital expenditures are minimal since no new treatment units normally would be required. The addition of chemical storage and handling facilities are the only plant additions necessary in most instances. In some cases it may be necessary to modify waste sludge pumps and other solids handling facilities in order to accommodate the increased solids production which results from phosphorus removal. For new facilities construction, no additional treatment units over and above those required for activated sludge secondary treatment would be required. Chemical storage and handling facilities, of course, would be necessary also. Provision for handling the additional solids could often be incorporated into the design for little or no additional cost. These considerations should make the chemical-biological process an attractive alternative when considering the various phosphorus removal process schemes which are available.

CAPITAL COSTS

The major items requiring capital expenditures for the process include chemical storage tanks, chemical feed lines and provision for automatically pacing chemical feeders with flow. Housing for chemical storage and feeding equipment also would be required in most instances.

The type of chemical storage is dependent upon the type of chemical fed (liquid or dry) and the amount to be fed since this will influence the method of shipment. The cost comparisons presented herein were based on the use of liquid chemical for all three plant sizes shown since liquid systems are generally less costly and wide distribution of liquid alum producing facilities makes its use feasible in many different geographical locations.

The selection of chemical feeding equipment to be used also is dependent upon the form and amount of chemical to be fed. A diaphram feed pump such as the B-I-F, Series 1700, was used as the basis for the estimates for the 1 and 10 MGD applications and a volumetric feeder such as the B-I-F Rotodip feeder was used for the 100 MGD plant. Duplicate feeders were assumed to be provided in all instances and all were equipped for automatic pacing from the influent flow meter.

Complete housing of equipment and housing or insulation of storage tanks and feed lines was assumed for the purposes of this analysis.

OPERATING COSTS

Some additional operator time is required for checking chemical feeders and other routine operating duties in connection with phosphorus removal. Additional laboratory analyses would also be required for process control but in most instances these would not involve sufficient additional time to warrant additional cost allowances. While this is generally true, it should be pointed out that additional personnel costs can be significant in the smaller plant since the chemical-biological process is relatively more complex than those normally used for secondary treatment.

Additional power costs also would be incurred for chemical feed equipment and handling of the increased solids which result from phosphorus removal.

CHEMICAL COSTS

Alum is considerably less costly than sodium aluminate under present pricing structures. Liquid alum is also cheaper than dry alum where liquid alum is available within a reasonable haul distance. Figure 26 relates chemical cost to the effluent phosphorus concentration based on the results of this study. The chemical costs used to develop Figure 26 are bulk list prices F.O.B., the point of production, and are based on the following:

	Cents/lb as Alum or Aluminate	Cents/lb as Al^{+++}
Alum		
Liquid	1.13	25.7
Dry	2.89	31.8
Sodium Aluminate		
Liquid	5.80	40.9

Chemical costs for any particular installation will be affected by transportation costs. Since freight costs vary so widely, no allowance for these costs were included in the overall cost analysis. Table 14 presents cost data for delivery to the State College, Pennsylvania area and gives some idea of the effect of transportation costs where the delivery point is considered to be moderate to long distance from the point of production.

Transportation costs in this instance would increase the liquid alum costs presented in Figure 26 by approximately 35%. This is undoubtably higher than would be experienced for many other geographical locations.

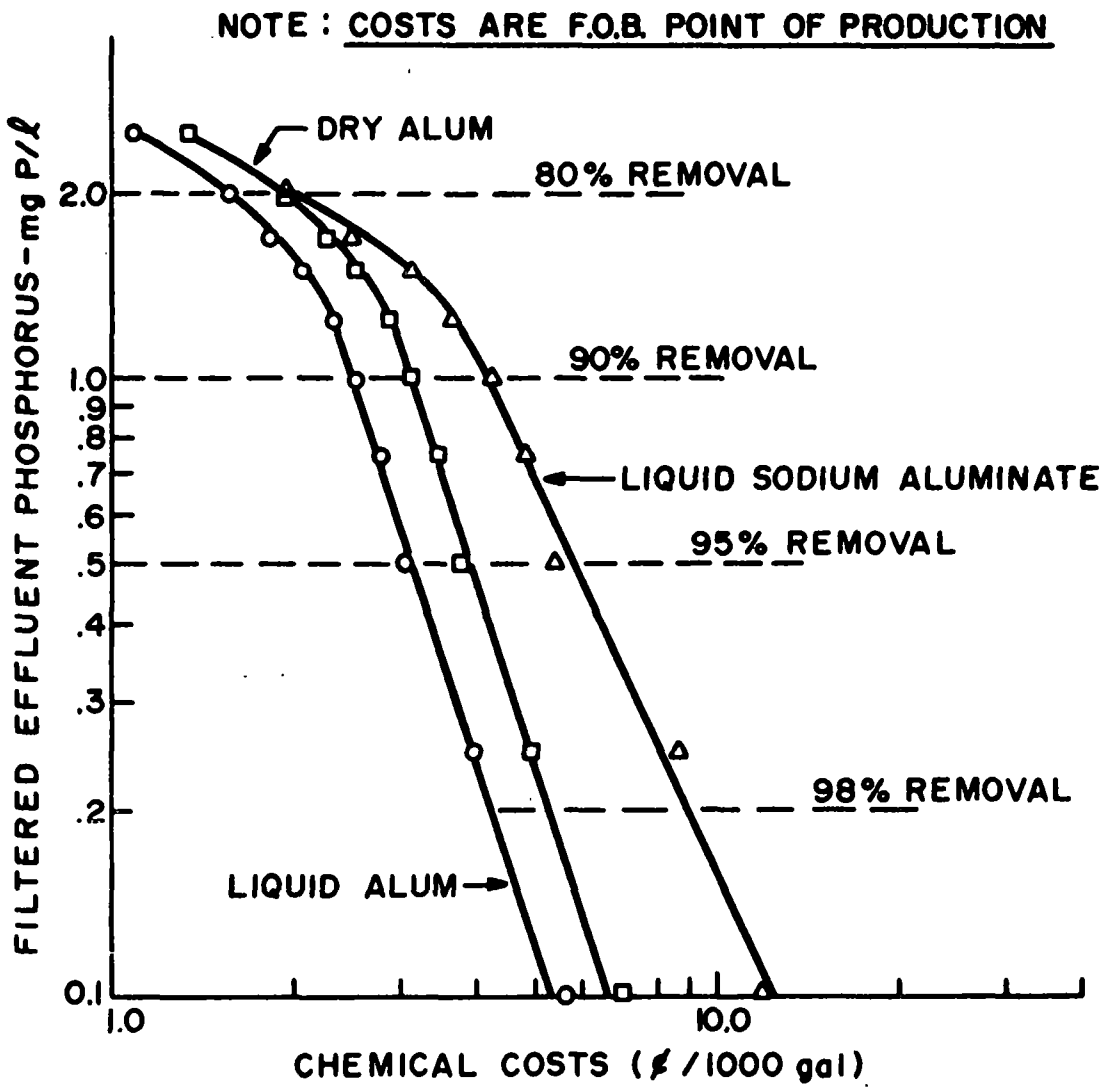


Figure 26. Chemical Costs as a Function of Filtered Effluent Total Phosphorus Concentration

Table 14. Cost of Chemicals Delivered to State College, Pennsylvania

	Cents/lb as Alum or Aluminate	Cents/lb as Al^{+++}
Alum		
Dry		
Bag		
Truck (30,000 lb)	3.90	42.9
Car (80,000 lb)	3.61	39.7
Bulk		
Truck (40,000 lb)	3.46	38.1
Car (40,000 lb)	3.71	40.8
Liquid		
Tank truck	3.14	34.5
Tank car	3.33	36.6
Sodium Aluminate		
Liquid		
Tank truck	8.45	59.9
Tank car	8.30	58.5

COST SUMMARY

Table 15 summarizes the estimated total costs of chemical precipitation of phosphorus using the chemical-biological process and based on the findings of this study. The influent waste in each instance was assumed to have 10 mg P/l unfiltered total phosphorus and 7 mg P/l soluble orthophosphate. Alum was the chemical of choice and capital cost estimates included only chemical storage and handling facilities. The basis for amortization was the same as that used by Smith and McMichael (38) in their recent work on costs of tertiary wastewater treatment (4.5% - 25 year period, 6.744% of capital cost). All costs are expressed in 1970 dollars based on the Environmental Protection Agency, average 1970 National Index of 143.64 (15).

Brenner (4) has estimated phosphorus removals costs of 4.3, 3.3 and 2.9 ¢/1000 gal for 1, 10 and 100 MGD plants respectively with use of the chemical-biological process. His costs were based on an assumed 90% removal of phosphorus. Data from this study would predict costs of 6.1, 4.1 and 2.9 ¢/1000 gal for 90% removal for 1, 10 and 100 MGD plants. The major differences between these two estimates occurs in the estimated amortization and operating costs (exluding chemical costs).

Table 15. Cost Summary for the Chemical-Biological Process to Precipitate 97 Percent of the Influent Phosphorus (1970 Dollars)

Costs \ Design Capacity MGD	1	10	100
Costs			
Capital, dollars			
Chemical Storage	$ 2,000	$ 6,000	$65,000
Chemical Feeders[a]	1,800	4,000	6,000
Housing and Insulation	5,200	15,000	15,000
Miscellaneous Plumbing and Equipment	3,000	5,000	8,000
TOTAL ESTIMATED CAPITAL COST	$12,000	$30,000	$94,000
Process Costs, cents/1000 gal.			
Amortization (25 yrs., 4.5%)	0.221	0.055	0.017
Alum (from Fig. 26 @ 97% Removal)[b]	3.7	3.7	3.7
Power	0.02	0.02	0.02
Operating & Maintenance Labor	2.40	1.01	0.11
Supervision & Payroll Overhead[c]	0.80	0.33	0.04
Maintenance Materials[d]	0.20	0.20	0.20
TOTAL ESTIMATED PROCESS COSTS, ¢/1000 gal.	7.341	5.315	4.087

[a]Duplicate units provided.

[b]Liquid alum was used for all three plant sizes and cost shown does not include transportation costs.

[c]Taken as 30% of operating and maintenance labor (after Smith and McMichael (38).

[d]Taken as 1/3 of maintenance and labor (after Smith and McMichael (38).

As stated earlier, the above costs only reflect the cost of precipitating the phosphorus. These costs would be in addition to the cost of activated sludge biological treatment. In addition, where phosphorus removal of more than 90% is required, it is recommended that filtration of effluent be provided. This too would be an additional cost. Table 16 summarizes the estimated costs for activated sludge treatment, chemical-biological treatment for phosphorus removal and multiple medium filtration of the effluent for the three plant sizes shown. The costs for sludge handling shown in Table 16 include costs for sludge thickening, digestion, elutriation, vacuum filtration and incineration for solids resulting from primary settling and conventional activated sludge. These costs do not reflect any adjustment for the additional solids which are produced as a result of phosphorus removal. Because of the wide variability in solids handling and disposal methods used in individual plants, it was decided not to refine sludge handling costs for this analysis. Cost refinements can be made on an individual basis and used to adjust the cost data presented in Tables 15 and 16.

Table 16. Estimated Total Treatment Costs (1970 Dollars)

Costs - ¢/1000 gal \ Design Capacity, MGD	1	10	100
Activated Sludge Treatment[a]	12.00	6.78	5.27
Chemical-Biological Phosphorus Precipitation[b]	7.34	5.32	4.09
Sludge Handling[a]	13.07	7.48	5.46
Multiple-Medium Filtration[c]	6.24	2.70	1.19
Chlorination[a]	0.95	0.74	0.66
TOTAL TREATMENT COSTS	39.60	23.02	16.67

[a]After Smith (37)

[b]From Table 15

[c]After Chen and Nesbitt (6)

GENERAL DISCUSSION

Results of the various investigations conducted during this study were discussed in detail in previous sections of this report. The general discussion presented in this section is not intended to repeat the earlier discussion but will focus on the general capabilities and applicability of the chemical-biological process of phosphorus removal.

The Phase I studies showed aluminum sulfate (alum) was a better precipitant than sodium aluminate with the moderately alkaline wastewater in this system. Uhler (45) in his pilot plant filtration study using treated effluent from Tank No. 2 (during Phase I operation when chemical was being added to both units) showed that a dual medium filter was capable of reducing the effluent total phosphorus concentrations to approximately 0.1 mg P/l when alum was used as the precipitant. He also showed that use of sodium aluminate resulted in filter effluent phosphorus concentrations of approximately 0.3 mg P/l at comparable Al/P ratios. The best effluent quality during this study was obtained when the precipitating chemical was added at the effluent end of the aeration tank. The exact point of addition is not considered to be critical so long as adequate mixing is provided since the precipitating reaction is virtually instantaneous. Excessive mixing such as occurs when the chemical is added at the influent end of the aeration tank results in the "carry-through" of material and a deterioration in effluent quality. The problem of "carry-through" which has been reported by other workers was not a problem in this study when the alum was added to the effluent end of the aeration tank. Some "carry-through" was noted with sodium aluminate even when it was added at the effluent end. This probably accounts for the higher effluent phosphorus observed by Uhler (45) in his filtration study and during Phase I of this study when compared to the results obtained from use of alum.

Overdosing of alum did not result in the adverse effects of higher effluent turbidity and phosphorus which have been noted by others (4, 52). Although Al/P ratios occasionally were as high as 6/1 or more when unexpected low flows or low phosphorus or both occurred in the influent waste, these high ratios actually reduced effluent turbidity and phosphorus. The absence of increased turbidities at these high Al/P ratios was probably due to the difference in the point of chemical application since, as far as is known, chemical addition was into the influent end of the aeration tank in the other studies referred to above.

Solids loss from the chemical-biological system as a result of hydraulic overload of the final clarifiers was a serious problem throughout much of the study. This was not anticipated prior to commencing the work and could not be eliminated during the course of the study. As was discussed previously, suspended solids losses from the chemical-biological system (Tank No. 1) were extremely heavy during periods of excessive flow and at such times the effluent could not be considered

acceptable for discharge to the receiving stream. This was contrasted with periods of low flow when suspended solids were significantly lower in the effluent from the treated system than they were in the control. Density currents apparently were established in the final clarifiers, at least during peak flow conditions. On several occasions, the sludge blanket was observed to be within approximately 3 feet of the water surface in Final Tank No. 1 moving toward the effluent end with an appreciable velocity. As it approached the end of the clarifier, it rose and went over the weirs of the effluent channels. The supernatant liquid over the sludge blanket was extremely clear with very few suspended solids. Solids losses from Final Tank No. 2 also increased during periods of peak flow but never in the magnitude observed in Tank No. 1. The sludge blanket in Tank No. 2 also never could be observed in the same manner as that in Tank No. 1. This observable difference in solids loss between the two tanks most likely is due to the greater amount of solids which must be handled in the chemical-biological system. Proper baffling of the clarifiers undoubtably would help to reduce this problem.

The results of the studies in both Phase I and Phase II demonstrated the enhanced removal of BOD_5 (unfiltered effluent, carbonaceous demand only) in the chemical-biological system. Eberhardt and Nesbitt (9) also demonstrated this capability as have several other workers (2, 4). The problems experienced with hydraulic overloading were also reflected in the BOD_5 data for effluent BOD's from the treated system often exceeded those of the control during periods of severe overloading. This cannot be considered typical process performance and under normal operating conditions improved organic removal should be realized. The study did not include investigations of oxygen uptake rates or other parameters which could identify relative biological activity between the two systems. Therefore, it was not possible to differentiate between biological and chemical removal of organic matter in the chemical-biological system. If it could be shown that a significant portion of BOD removal is by chemical means, a reduction in aeration tank capacity and air requirements could be made which would be reflected in lower costs for new facilities construction and operation. Operating costs would also be reduced in existing plants due to the lower air requirements which would help to offset chemical costs.

The data presented previously show that less nitrification occurred in the chemical-biological system under normal operating conditions than in the untreated control. Work still in progress on the microbiological study may yield additional insight into this phenomenon. Balakrishnan and Eckenfelder (1) have concluded that organic loading and sludge age are the most critical parameters affecting nitrification in the activated sludge process. They showed that the optimum organic loading was about 0.3 lb BOD/lb MLVS and a minimum sludge age of 3-4 days was recommended. The reported results from the present study show that normal operation did not fall within the limits recommended above, hence nitrification was not favored for either the control or the chemical-biological system.

The phosphorus removal results for unfiltered effluent samples were quite erratic because of the solids losses which occurred during periods of hydraulic overload. Filtered effluent phosphorus removals during Phase II were also somewhat erratic due largely to the difficulty of responding to changes in flow and influent phosphorus concentrations in settling chemical feed rates. Automatic pacing of chemical feed equipment from the flow meter would minimize this problem for most installations. The process is capable of continuously providing very high degrees of phosphorus removal under low flow conditions at relatively high Al/P (filt. ortho) ratios. Table 17 shows the phosphorus data for the period June 15, 1970 to August 12, 1970 when flows were lower than normal due to the smaller student population on campus during the summer term and flow variations were less severe. These results show the average removal of unfiltered effluent total phosphorus was 91.9%. Table 17 also shows that average phosphorus removal on filtered effluent was 98.9% for orthophosphate and 98.2% for total phosphorus during the period reported. The average Al/P (filt. ortho) ratio was higher than desired (2.71/1 instead of 2.25/1) since the influent phosphorus was lower than anticipated. However, the only adverse effect of this overdose was the increased chemical costs which resulted.

The average Al/P (unfilt. total) ratio for Phase II operation was 1.6/1 based on average values for aluminum fed and unfiltered total phosphorus for the trickling filter effluent. This is in the same range reported by others (2, 4, 9) as necessary to achieve phosphorus removals of approximately 95%. One of the difficulties in comparing results of this study with those of others is they ordinarily do not specify the phosphorus basis for the Al/P ratios reported. Most workers have apparently used unfiltered total phosphorus in the influent waste as the basis for calculating the reported ratios but it is not so stated in most instances.

Figure 27 shows the amount of Al^{+++} fed per day in relation to flow during Phase II operation. The desired dosage based on the average filtered orthophosphate and using an Al/P (filt. ortho) ratio of 2.25/1 is also shown and illustrates the problems of overfeed and underfeed which occurred due to inability to respond quickly to change in flow. As indicated earlier, pacing of chemical feed from the influent flow meter would minimize this problem.

Attempts to make acceptable phosphorus mass balances were generally unsatisfactory. This is thought to be due to the difficulty in obtaining reliable results for total phosphorus in the sludge samples. This same observation was made by O'Shaughnessy (26) in his digester studies. Since individual phosphorus mass balances yielded highly variable results, the mean values for the amount of phosphorus observed in the waste sludge from each aeration tank was compared with the amount of phosphorus which was predicted to be in the waste sludge based on observed phosphorus removal. These results are presented in Table 18 and show reasonable agreement between observed and predicted values.

Table 17. Summary Phosphorus Removal Data Phase II June 15, 1970 to August 12, 1970[a]

	Effluent			
	Tank No. 1		Tank No. 2	
	Mean	Std. Dev.	Mean	Std. Dev.
Phosphorus				
Filtered				
Ortho - mg P/ℓ	0.07	0.05	5.2	0.9
% Removal[b]	98.9	0.9	30.9	17.3
Total - mg P/ℓ	0.12	0.08	5.7	0.9
% Removal[b]	98.2	1.2	25.6	19.8
Unfiltered				
Ortho - mg P/ℓ	0.49	0.27	5.9	1.4
% Removal[b]	93.6	2.8	27.1	17.7
Total - mg P/ℓ	0.61	0.27	6.3	1.9
% Removal[b]	91.9	2.7	19.8	13.3
Al/P (filt. ortho) Ratio	2.71/1	0.57	--	--
Flow - MGD	0.71	0.05	0.71	0.05

[a]Sundays not included

[b]Based on unfiltered trickling filter effluent total phosphorus (mean value = 7.4 mg P/ℓ ± 2.0)

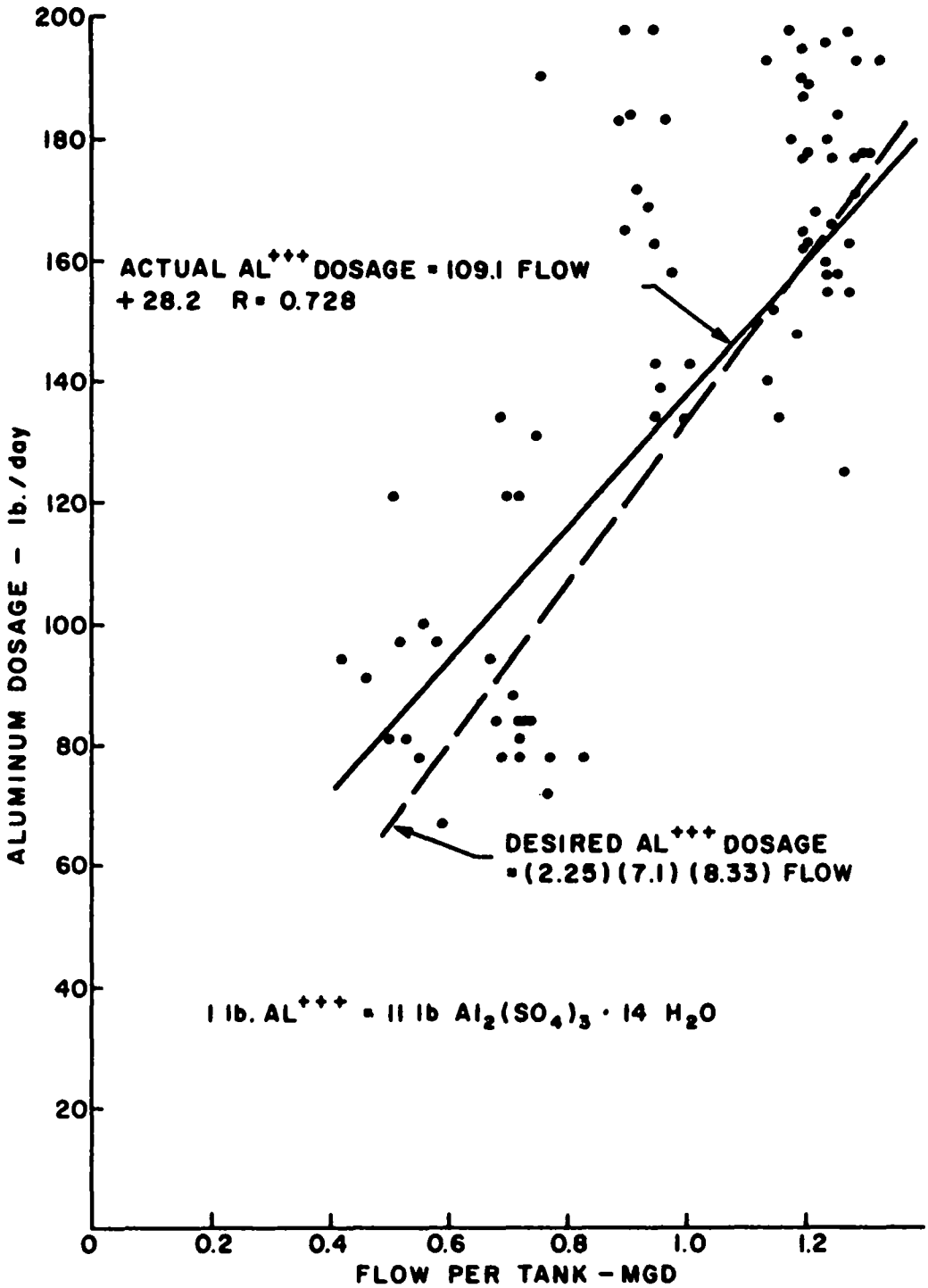


Figure 27. Aluminum Dosage as a Function of Flow Phase II

Table 18. Comparison of Observed and Predicted Amounts of Phosphorus in Waste Sludges

	Tank No. 1			Tank No. 2		
	Obs.[a] lb/day	Pred.[b] lb/day	Obs/Pred %	Obs.[a] lb/day	Pred.[b] lb/day	Obs/Pred %
Phase I Alum	56.2	72.7	77.1	55.9	78.3	71.4
Phase I Sodium Aluminate	31.6	36.8	85.9	36.8	40.1	91.8
Phase II Alum	50.2	47.9	104.8	--	--	--
Phase II Control	--	--	--	18.4	20.7	88.9

[a]Predicted P = (Ave. T.P. Unfilt. Inf. - Ave. T.P. Eff.) (Ave. Flow) (8.33)
(lb/day) (mg/l) (MGD) (lb/gal)

[b]Observed P = (Unfilt. T.P. Waste Sludge)(Waste Sludge Flow)(8.33)
(lb/day) (mg/l) (MGD) (lb/gal)

Sludge production and sludge handling continues to be a major concern with all phosphorus removal schemes. The results of this study have shown that significantly more solids are produced and hence must be removed from the chemical-biological system than from conventional secondary treatment. Although the results of this study did not indicate a reduction in SVI as a result of alum addition, this is considered to be atypical of what would be expected in most instances because of the unusually low SVI observed in the control system. Use of sodium aluminate did result in a significant reduction in SVI even in this system. Work by O'Shaughnessy (26) and others (2, 52) has shown that the precipitated phosphorus is not released during anaerobic digestion. Their work has also shown that waste sludges from the chemical-biological system are more easily dewatered than are waste sludges from conventional activated sludge treatment. Therefore, it does not appear that sludges from the chemical-biological system would create any unusual operating problems. However, due consideration must be given to the greater amount of solids which are produced.

No great differences in costs among the various process schemes using chemical precipitation for phosphorus removal which have been reported

by others and the chemical-biological process presented herein are apparent. This similarity occurs because the chemical costs are virtually the same regardless of which process scheme is selected and they represent the major portion of phosphorus removal costs. Costs are affected by the choice of chemical to be used and generally the least costly chemical which will give the required degree of removal should be chosen. Some cost advantage may be realized from use of aluminum or ferric compounds as the precipitating agents over use of lime since the dosages of the former are directly related to the phosphorus concentration whereas those of the latter are not. Therefore, any reduction in influent phosphorus would permit a reduction in the amount of aluminum or iron used and a net savings in cost. There does appear to be a definite cost advantage for the chemical-biological system when compared to a tertiary treatment system. Most of this advantage results from the lower capital costs for the chemical-biological process. Cost comparisons among the various processes which have been proposed is difficult because all are on different bases and none include all applicable costs.

Comparison of costs of the chemical-biological process with estimated costs of various chemical-physical process schemes which have been proposed (50, 53) also does not yield conclusive evidence in favor of any given process. The results of this study have shown the chemical-biological process is capable of effecting high degrees of removal of phosphorus and organic material by use of well proven, easily operated unit processes. Capital costs for use of the process in existing activated sludge plants are very low and they would not add significantly to capital costs for new facilities construction.

The problem of determining just what degree of phosphorus removal is necessary to control eutrophication in a particular instance still has not been resolved. Stream standards now being established show widely varying requirements for phosphorus removal by specifying different levels for the various forms of phosphorus (i.e., filtered or unfiltered, ortho or total) for different situations. This makes it necessary to match unit process performance to a specific standard which may well change in the near future as more results of research become available. A distinct advantage of the chemical-biological process is that varying phosphorus removal requirements can be met easily by controlling the amount of precipitating chemical added while still maintaining a high degree of organic removal.

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16. Abstract

It was the objective of this research to develop and evaluate, at full plant scale, the combined chemical-biological process of phosphorus removal. Phase I investigations indicated an Al/P (filt. ortho) weight ratio of 2.25/1 was necessary to reduce the influent phosphorus of approximately 10 mg P/l to approximately 0.3 mg P/l in the filtered effluent. Alum proved to be a more effective precipitant than sodium aluminate in the moderately alkaline wastewater available for this study. The best results were obtained when the chemical was added at or near the effluent end of the aeration tank. Total phosphorus concentration of the unfiltered effluent was dependent upon effluent suspended solids levels as well as on effluent soluble phosphorus concentrations. Removal of organic matter was improved as a result of chemical addition in the chemical-biological process. The chemical-biological process produced approximately twice as much weight of sludge as did the parallel control. Alum addition did not reduce the sludge volume index (SVI) of the mixed liquor whereas sodium aluminate addition resulted in significant decreases. Costs for chemical precipitation of phosphorus in the chemical-biological process are estimated to vary from 7.3 cents/1000 gal in a 1 MGD plant to 4.1 cents/1000 gal in a 100 MGD plant for 97% removal.

17a. Descriptors

*Phosphorus, *Chemical precipitation, *Activated sludge, *Aluminum, *Efficiencies, *Nitrification, Wastewater treatment, Effluents

17b. Identifiers

*Operations, *Alum, *Aluminate, *Chemical removal, Waste sludge, Dosages, Costs

17c. COWRR Field & Group

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Abstractor D. A. Long

Institution Dept. of Civil Engrg., Penn State University