1968

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## Recommended Citation

Vedder, Richard Charles, "Chemical precipitation of phosphorous with sodium aluminate and alum in the activated sludge aeration chamber" (1968). *Masters Theses*. 5191.
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# CHEMICAL PRECIPITATION OF PHOSPHORUS WITH SODIUM ALUMINATE AND ALUM IN THE ACTIVATED SLUDGE AERATION CHAMBER

BY

RICHARD CHARLES VEDDER, 1945

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THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI - ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING

Rolla, Missouri

1968

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(advisor)

# ABSTRACT

The purpose of this investigation was to study the removal of phosphorus by chemical precipitation with sodium aluminate and alum in the activated sludge aeration chamber, and determine the effect of the aluminum to phosphorus ratio and the mixed liquor suspended solids concentration on the phosphorus removal efficiency and the effect of the precipitants on the removal of organic pollutants in the activated sludge process.

The studies were conducted on settled domestic sewage in three bench-scale continuous flow activated sludge units supplemented with jar tests. Major parameters employed included influent and effluent total phosphorus and chemical oxygen demand (COD), mixed liquor total and volatile suspended solids, pH, and sludge volume index.

Both sodium aluminate and alum were found effective in reducing the phosphorus content of the sewage and aluminum to phosphorus ratios of 1.3 and 1.9 were required with alum and sodium aluminate to produce a minimum residual phosphorus concentration in the range of 1.0 mg/1 P (a reduction of approximately 90 percent). On an available aluminum basis, alum was more effective than sodium aluminate; however, when molecular weight and cost were considered, sodium aluminate cost about one-half as much as alum for equivalent phosphorus removal. Variation of the mixed liquor suspended solids concentration had no significant effect on the removal of phosphorus. The addition of chemicals did not adversely affect the removal of COD which averaged in excess of 90 percent throughout the studies; pH was also unaffected and remained in the 7.3 to 8.2 range.

# ACKNOWLEDGEMENT

The author gratefully acknowledges the guidance and comments of Dr. S. G. Grigoropoulos who served as his advisor in this work. He also wishes to thank Drs. J. C. Huang and K. Purushothaman for their helpful suggestions.

The author also wishes to recognize the Civil Engineering Department of the University of Missouri - Rolla for providing the facilities which made this investigation possible.

This investigation was supported by Training Grant No. 1T1-WP-86-01A1 from the Federal Water Pollution Control Administration.

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# I. INTRODUCTION

As human population increases and technology advances, environmental problems are beginning to arise which at one time were not considered important or whose immediate solution was not thought necessary. In the past, the removal of biochemical oxygen demand (BOD) and suspended solids has been the measure of efficient sewage treatment, and a treatment plant was to be complimented if it produced an effluent with low BOD and suspended solids. While these parameters remain important, today there is evidence to indicate that in many plants more thorough treatment is required if lakes and streams in this country, and for that matter in all population centers of the world, are to remain good sources of water supply and areas of recreation. In recent years, concern has been expressed over the excessive eutrophication which is taking place in some lakes and other bodies of water.

The word eutrophication is used to describe biological productivity changes occurring in all lakes and reservoirs during their life history (1). It can be referred to as the aging of a body of water and is caused by a prolific growth of algae and other phytoplankton resulting from an increased availability of plant nutrients. This aging process under natural conditions normally takes place over a period of tens of thousands of years; however, the activities of man can considerably increase the rate at which eutrophication occurs. In addition to trace elements which are present in water in nonlimiting quantities, algae require larger amounts of carbon, nitrogen, and phosphorus (2). A major portion of the nutrients which enter a body of water become incorporated into algae and other forms of life which eventually die and settle to the bottom. Through digestion by bacteria, protozoa, worms, and other organisms, a major portion of the nutrient material is solubilized and becomes available to support further growth (1, 3).

Eutrophication is characterized by increased algal growths, particularly the blue-green variety, larger populations of zooplankton, depletion of dissolved oxygen in the hypolimnion, and replacement of game fish with the scrap fish variety (2). The recreational use of the water is destroyed and problems such as tastes and odors, clogged filters, color and turbidity, and increased chlorine demand may develop where the water is used for domestic or industrial purposes (4). Several examples of excessive eutrophication have been reported. Lake Erie is a well publicized case. Swimming and water skiing have been curtailed in this lake because of high bacteria counts and dead plants and fish, some species of fish have died out and others are facing extinction, and during the summer months hundreds of square miles of bottom waters turn anaerobic (5). Cases of eutrophication are also being reported in Europe (6, 7).

Eutrophication can be controlled by limiting the supply of available nutrients. However, on the basis of Liebig's Law of the Minimum excessive algal growths may be controlled by limiting one essential element (8). Common elements needed by algae in relatively large amounts are carbon, hydrogen, oxygen, sulfur, potassium, calcium, magnesium, nitrogen, and phosphorus. Of these elements, all except nitrogen and phosphorus are normally found in water in sufficient quantities to promote good algal growth. Although conventional sewage treatment removes much of the carbon, little nitrogen and phosphorus are removed. Of the latter two, nitrogen has been reported to be available in nonlimiting concentrations naturally and to be fixed from the atmosphere by some species of blue green algae (9). These facts, along with the difficulty in removing nitrogen, have led researchers to select phosphorus as a reasonable limiting nutrient; however, it is recognized that phosphorus removal alone may not control eutrophication in all cases (10).

Algal growth has been maintained at phosphorus concentrations as low as 0.0025 mg/l P* (11), but quantities in excess of 0.01 to 0.1 mg/l P are considered necessary for an algal bloom (8, 12). The major sources of phosphorus are surface and ground water, urban and agricultural runoff, and domestic and industrial wastewater. Of these, domestic and some industrial wastes are considered to be the only sources in which the phosphorus concentration is sufficiently high to make removal feasible (13). Due to increasing use of synthetic detergents containing phosphate builders, the concentration of phosphorus in sewage has increased from 1.7 to 4.0 mg/l P in 1947 (14), to 4.0 to 5.5 mg/l P in 1951 (15), with an average of 10.7 mg/l P in 1961 (16). The low allowable concentration of phosphorus, coupled with its increasing concentration in sewage and the fact that water reuse is becoming more prevalent, necessitates some form of phosphorus removal.

A review of existing literature has shown that phosphorus removal is technically feasible through both chemical and biological methods and can take place during primary, secondary, or tertiary sewage treatment. Because of minimal additional equipment requirements, chemical precipitation in the aeration chamber of an activated sludge system was considered to be the most appropriate phosphorus removal process for use in existing activated sludge tretment plants. Since many plants of this type are already in operation in areas where eutrophication is a problem, it was felt that further investigation of the parameters involved in this process would be of value.

Previous investigations have shown that a number of chemicals will precipitate phosphorus in varying degrees when added to the activated sludge

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* Phosphorus may be determined in various forms; therefore, the form will be suffixed to the value reported.

aeration chamber. Two coagulants, alum and sodium aluminate, have been used to achieve residual phosphorus concentrations in treated sewage of less than 1 mg/l P. Alum has been investigated for the dual purpose of coagulating dispersed microorganisms and removing phosphorus in both batch (17) and continuous flow (18) laboratory units. Sodium aluminate has been studied primarily as a method of phosphorus removal in a 100 gpd pilot plant unit (19). A review of the experimental approach and findings of these studies (17, 18, 19) indicated several areas where additional work was needed. Questions were raised on the desirability of adding alum directly to the aeration chamber and the possible adverse effects of alum on the pH of the system; the continuous flow studies were conducted on a one unit basis without the benefit of a control unit run in parallel; and the effect of the total suspended and volatile suspended solids concentration was not investigated. In addition, the phosphorus removal efficiency at low coagulant concentrations needed to be investigated.

It was the purpose of this investigation to study the chemical removal of phosphorus with sodium aluminate and alum in the activated sludge system. The specific objectives of this study were to determine: the effect of the aluminum to phosphorus ratio on phosphorus removal, the effect of the mixed liquor total and volatile suspended solids on phosphorus removal, and the effect of the chemical additives on the removal of chemical oxygen demand (COD) in the system.

The studies were carried out in three continuous flow activated sludge units supplemented with "jar tests." Settled domestic sewage from a Rolla treatment plant was used to assure realistic results. The major parameters employed were the influent and effluent total phosphorus and COD, the aluminum to phosphorus ratio, the mixed liquor total and volatile suspended solids, pH, and the sludge volume index.

# II. REVIEW OF LITERATURE

Research findings and plant data pertaining to the removal of phosphorus by chemical precipitation, biological uptake, and chemical precipitation in the activated sludge aeration chamber are reported in this chapter.

## A. CHEMICAL PRECIPITATION

Considerable research work has been directed toward the chemical precipitation of phosphorus both in primary and tertiary treatment. The mechanism of phosphorus removal by chemical precipitation is not too well understood. Theoretically, phosphorus may be removed from solution through precipitation as an insoluble salt or by adsorption upon some insoluble solid phase. Early experimental evidence indicated that both mechanisms were operative. In the case of lime treatment it appeared that the principal mechanism was that of precipitation of phosphorus as insoluble calcium phosphate salts, while with iron salts and alum adsorption upon hydrated oxide floc particles appeared to play a major role (20, 21). More recent work, however, has indicated that phosphorus removal with polyvalent metallic ions occurred by precipitation rather than coagulation or adsorption (17).

### 1. Primary Treatment.

Lime, ferric chloride, alum, and sulfuric acid have been studied as agents for the removal of phosphorus from raw sewage. Stones (22) investigated the effect of lime, sulfuric acid, and alum on phosphorus removal by precipitation. One liter volumes of sewage were treated with 400 mg/l of each chemical and then allowed to settle for 18 hours. Several runs were made and the following results were reported:

| | Phosphate Content mg/l P | Removal % |
|---|---|---|
| Unsettled Sewage | 6.25 | -- |
| Settled Sewage | 4.38 | 29 |
| Precipitation | | |
| lime (CaO) | 0.75 | 88 |
| sulfuric acid | 4.58 | 27 |
| alum $[Al_2(SO_4)_3 \cdot 18H_2O]$ | 0.40 | 94 |

While alum and lime effected good phosphorus removal, sulfuric acid solubilized part of the phosphorus that would have been removed by sedimentation alone.

Karanik and Nemerow (23) conducted jar studies and found that an optimum dose of 300 mg/l lime $[Ca(OH)_2]$ raised the pH of raw sewage to 11.4 and caused a reduction of the phosphate content from 27.9 to 1.8 mg/l $PO_4$ or 93.5 percent. Suspended solids, volatile suspended solids, and biochemical oxygen demand (BOD) were also reduced by 95, 96, and 71 percent, respectively. In similar studies by Sawyer (24) total phosphorus was reduced from 3 to 4 mg/l P to 0.5 mg/l P with the addition of 50 mg/l ferric chloride.

On the basis of pilot plant studies, Buzzell and Sawyer (25) concluded that lime requirements were independent of phosphorus content but depended upon the alkalinity and pH. The optimum pH for chemical precipitation of phosphorus was found to be between 10 and 11 but had to be determined for each situation. Total phosphorus removals averaged 80 to 90 percent with an average residual of 1.2 mg/l P. Since 50 to 70 percent of the BOD was also removed by the addition of lime, the effluent was too weak for activated sludge secondary treatment; however, stabilization ponds were found suitable and were capable of removing 75 to 80 percent of the remaining phosphorus.

Neil (26) added 94 mg/l alum and 3.4 mg/l activated silica to the influent of the sedimentation tank of a 1.5 MGD primary treatment plant and obtained an effluent phosphate concentration of 3.15 mg/l $PO_4$ or a corresponding reduction of 81 percent. Filtered samples showed a concentration of 0.33 mg/l $PO_4$ or 98 percent removal.

2. Tertiary Treatment.

Malhotra, *et al.* (27) on the basis of laboratory studies concluded that the optimum pH of secondary treatment plant effluent for alum and lime precipitation of phosphorus was 5.57 ± 0.25 and 11.0, respectively. Total phosphorus removals of 95 percent with 250 mg/l alum $[Al_2(SO_4)_3 \cdot 18H_2O]$ and 99 percent with 600 mg/l lime $[Ca(OH)_2]$ were achieved, and 55 percent of the chemical oxygen demand (COD) was removed in the alum studies. Malhotra and his coworkers estimated that the chemical costs for removal of 95 percent of the phosphorus with lime and alum were $32 and $73 per million gallon, respectively.

Lea, *et al.* (20) obtained an 85 percent reduction in soluble phosphate concentration by including tertiary treatment in a 10 gpm pilot plant. Tertiary coagulation with 200 mg/l alum $[Al_2(SO_4)_3 \cdot 14H_2O]$, precipitation, and sedimentation resulted in an effluent concentration of 2.23 mg/l $PO_4$. Filtration of this effluent removed additional phosphate and resulted in a final effluent containing 0.14 mg/l $PO_4$ for a 99 percent overall phosphorus reduction. Alum recovery was also investigated by Lea and his coworkers. The aluminum hydroxide floc was recovered and purified by removing the adsorbed phosphates in the form of tricalcium phosphate, and reused for further phosphorus removal in the form of sodium aluminate. When the recovered alum was employed, 77 to 89 percent of the soluble phosphate could be removed.

Owen (28) added lime to the influent channel of the final clarifier of a 0.77 MGD trickling filter plant. Lime added at the rate of 545 mg/l (CaO) reduced the effluent phosphate concentration from 22.6 to 5.2 mg/l

$PO_4$ (0.40 mg/l with filtration) giving 77 percent phosphorus removal for the total plant.

Curry and Wilson (29) treated 4000 gallons of secondary treatment plant effluent with 200 mg/l alum [$Al_2(SO_4)_3 \cdot 18H_2O$], mixed for 10 minutes, and allowed to settle for 2 hours. This system reduced the influent phosphorus, which ranged from 3.61 to 4.62 mg/l P, by 97 percent.

Slechta and Culp (30) recently reported good phosphorus removals using coagulation followed by filtration. Effluent from secondary treatment in a 4 MGD plant was treated with 200 mg/l alum [$Al_2(SO_4)_3 \cdot 18H_2O$] added ahead of two mixed media filter beds which were operated in series and were followed by granular activated carbon filters. This set-up reduced the phosphate concentration from 25 to 30 mg/l to a residual of 0.1 to 1 mg/l $PO_4$. The cost of alum was reported to be $48 per million gallon of effluent. To reduce costs, chemical recovery of alum was investigated; however, it was found that recovery of a suitable form of alum was more expensive than the initial cost of alum. Lime was, therefore, investigated as a coagulant and resulted in a residual phosphorus content ranging from 0.2 to 1 mg/l P or a reduction of about 98 percent. With lime recovery, chemical costs, including recovery costs, were reduced to $42.70 per million gallon; $10.90 of this sum represented the cost of fresh lime. Due to the anticipated savings with lime, Slechta and Culp reported that it was planned to replace alum with lime coagulation at this plant.

## B. BIOLOGICAL UPTAKE

In theory, it is possible to use biological systems to remove nutrients from sewage. Cell tissue composition together with the mineral content of sewage will determine the amount of phosphorus which can be extracted. Assimilation of 1 mg/l phosphorus requires 25 to 50 mg/l carbon and 2 to 12 mg/l nitrogen (21). Ordinary domestic sewage does not provide a balanced diet, being deficient in carbon and nitrogen with respect to phosphorus. Phosphorus removal by means of biological uptake has been investigated in both algal and activated sludge systems.

### 1. Algal Systems.

Investigators at the University of Michigan (31,32) have studied algal growth characteristics as related to phosphorus removal using a synthetic secondary treatment plant effluent and a small laboratory unit in which pH, light, temperature, mixing, nutrient concentration, and density of the algal culture were controlled. These studies revealed that the amount of radiant energy available to each cell, the nutrient concentration, and the temperature were important factors in the metabolic uptake of nutrients (31). Additional studies (32) were conducted to provide information on phosphorus requirements and uptake by algae; cultures of *Scenedesmus* and *Chlorella* at a density of 50 mg/l were used. Algae were found to require certain amounts of phosphorus for basic cell growth and a minimum content in the cell mass (3 percent $PO_4$ on a dry weight basis) was necessary for cell growth to be independent of phosphorus. Algae were also found capable of storing excess quantities of this nutrient (up to 9 percent $PO_4$). On the basis of their findings, these investigators classified phosphorus uptake by algae into the three zones: the growth dependent zone (0 to 3 percent $PO_4$), the zone of storage (3 to 9 percent $PO_4$), and the zone of saturation (above 9 percent $PO_4$). Build-up of phosphorus in the algal cells over and above the level required for nonlimited growth was termed "luxury uptake." The bacteria functioning in the activated sludge were considered to have nutritional requirements similar to algae and, on the basis of the high phosphate concentrations present in today's sewage, to undergo luxury uptake during treatment.

Fitzgerald (33), at the University of Wisconsin, has investigated the removal of nutrients from secondary treatment plant effluent in tertiary ponds and found that the growth of algae was influenced by temperature and the level of nutrients available. Phosphorus was removed during periods of high pH, probably as the result of precipitation. During the winter months, the effluent phosphate concentrations frequently surpassed the influent levels; this was attributed to dissolution of phosphorus previously precipitated. In a similar study conducted in California using a tertiary pond with recirculation, Bush, et al. (34) obtained phosphate residuals of 2 to 9 mg/l $PO_4$ corresponding to 19 to 68 percent removal. Assenzo and Reid (35) have reported that phosphorus removal in seven oxidation ponds in Oklahoma varied from 30 to 90 percent; the influent phosphorus concentration in these ponds ranged from 135 to 41 mg/l $PO_4$ and the effluent content varied from 62 to 9 mg/l $PO_4$. Correlating these data with BOD, Assenzo and Reid concluded that the optimum BOD loading for effective phosphorus removal was 11.23 pounds per acre-foot per day.

The most comprehensive work relative to phosphorus removal by algal cultures has been carried out by Bogan, et al. (21) and Bogan (36). Using secondary treatment plant effluent, Bogan and his associates developed a high rate process whereby orthophosphate concentrations could be reduced to less than 1 mg/l $PO_4$ (equivalent to 90 percent removal) with contact times as brief as 6 to 12 hours. The system was similar to an activated sludge unit in that the algae were removed by sedimentation. Light intensity seemed to be the limiting factor with minimum requirements in the vicinity of 100 to 200 foot candles. Adsorption and coagulation appeared to play the major role where rapid removal of large amounts of phosphorus was involved; adsorption by the algae of insoluble calcium phosphate formed because of a photosynthetic shift to a pH of 9.5 or greater was found to cause coagulation of the algal cell tissue which resulted in the effective sedimentation of the cells. Artificial illumination at a cost of at least ten times that required for pH adjustment with lime was necessary to reach the desired pH photosynthetically.

### 2. Activated Sludge Systems.

Activated sludge has also been considered as a means of biological phosphorus removal. The phosphorus content in activated sludge has increased in recent years along with the increase of phosphorus in sewage. Anderson (37) reported in the mid 1950's the phosphorus content of dried activated sludge had increased from 1 to 2 percent in 1931-5 to 2 to 4 percent in 1951-5, while Greenberg, et al. (38) suggested that a BOD to phosphorus ratio of about 240 was necessary for the complete utilization of phosphorus by activated sludge.

Several studies have been conducted to determine the effects of various experimental parameters on the luxury uptake of phosphorus by activated sludge and some contradictory conclusions have been reported in the literature. Hall and Engelbrecht (39) have found phosphorus uptake to be influenced by the dissolved oxygen content and detention time in the aeration chamber but unaffected by mixed liquor suspended solids. With a minimum dissolved oxygen content of 2 mg/l, 50 percent of the soluble phosphorus was removed in 6 hours. Phosphorus uptake was independent of mixed liquor suspended solids in the 750 to 8000 mg/l range. On the other hand Rains and Ryckman (40) have concluded on the basis of laboratory studies that the uptake of soluble phosphorus was affected by pH, mixed liquor suspended solids concentration, initial phosphate concentration, and dissolved oxygen. The optimum pH for biological phosphorus uptake was found to be between 7.0 and 8.0. Phosphorus removal was found to increase and the required detention time to decrease as the suspended solids were increased; this was in contradiction to the findings by Hall and Engelbrecht (39). Increased concentrations of phosphate in the sewage resulted in increased phosphorus removal by a given activated sludge. The minimum dissolved oxygen concentration for optimum removal was reported to be 1.9 mg/l. Levin and Shapiro (41) and Shapiro, et al. (42) have reported that pH, aeration rate, and redox potential affected the uptake and release of phosphorus by the activated sludge. The optimum pH range was again reported as 7.0 to 8.0; however, a minimum aeration rate of 17 ml/sec per 1500 ml of mixed liquor, rather than dissolved oxygen content, was reported; it was also stated that a redox potential greater than zero was required. Phosphorus uptake was found to be reversible, depending on the above conditions.

Vacker, et al. (43) recently reported variations in phosphorus removal at nine wastewater treatment plants in San Antonio, Texas. While one of these plants (Rilling Plant) was able to reduce total phosphate by 88 percent to a 4.1 mg/l $PO_4$ residual, the other plants effected reductions of only 14 to 50 percent. Sludge at this plant was found to contain as much as 20 to 22 percent $PO_4$, on a dry weight basis. This high removal at the Riliing Plant was attributed to high dissolved oxygen levels in the aeration chamber (2 mg/l at the midpoint and 5 mg/l at the outlet end) and to the fact that digester liquor was not being returned to the system.

## C. CHEMICAL PRECIPITATION IN ACTIVATED SLUDGE

Several investigators have combined chemical and biological phosphorus removal in the activated sludge process. Tenney and Stumm (17) by means of jar studies have investigated the use of alum to simultaneously coagulate dispersed microorganisms and precipitate phosphorus. They reasoned that since BOD removal in activated sludge treatment occurred in two phases, bioflocculation and substrate utilization, by chemically aiding flocculation the entire process could be accomplished in a "high rate, low solids retention unit." The optimum pH for both phosphate removal and microbial flocculation was found to be between 5 and 6 and removal by polyvalent metallic ions was considered to occur by precipitation rather than by coagulation or adsorption. Aluminum phosphate was the precipitate and stoichiometrically one mole of aluminum was required to precipitate one mole of phosphorus. Tenney and Stumm reported that settleable precipitates were formed only when the concentration of aluminum added was very nearly equal to the initial phosphorus concentration, and that when the aluminum concentration was less than that of phosphorus slow settling negatively charged $AlPO_4$ colloids were formed. The aluminum ion had a stronger affinity for phosphorus than for the ionogenic groups of the microbial surface; therefore, when it was added to a suspension of microorganisms containing phosphate most of the phosphate was precipitated before flocculation of the microorganisms took place.

Eberhardt and Nesbitt (18) have also studied combined phosphorus removal and microbial flocculation in a continuous flow bench scale activated sludge pilot plant using both synthetic and settled domestic sewage. A summary of the operational conditions and results of this investigation which are appropriate to the present study is presented in Table I. Good COD and phosphorus removals were obtained for the most part under the different experimental conditions. However it is interesting to note the considerable difference in phosphorus content of the filtered and unfiltered samples when alum was added directly to the aeration chamber in the domestic sewage studies. The lack of settleability of the precipitate in some of the domestic sewage studies was attributed by these investigators to the long mixing time in the aera-

# TABLE I

## PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION WITH ALUM IN THE ACTIVATED SLUDGE PROCESS*

| Condition or Parameter | Synthetic Sewage Studies | | | | | | | Settled Domestic Sewage Studies | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Length of run, days | 9 | 44 | 20 | 30 | 31 | 31 | 35 | 19 | 4 | 4 | 20 | 15 | 10 |
| $Al_2(SO_4)_3 \cdot 18H_2O$ added, mg/l | 149 | 224 | 224 | 261 | 224 | 261 | 261 | 261 | 298 | 335 | 335 | 335 | 261 |
| Al/P ratio | 1 | 1.5 | 1.5 | 1.75 | 1.5 | 1.75 | 1.75 | 1.88 | 2.37 | 2.08 | 2.42 | 2.44 | 1.87 |
| Point of Chemical addition | Mix. Basin | Mix. Basin | Mix. Basin | Mix. Basin | Mix. Basin | Mix. Basin | Aer. Basin | Aer. Basin | Aer. Basin | Aer. Basin | Mix. Basin | Mix. Basin | Mix. Basin |
| Flocculation | Yes | Yes | Yes | Yes | Yes | Yes | No | No | No | No | No | No | No |
| pH of Chemical reaction** | 5.5 | 5.5 | 5.5 | 5.5 | 6.5 | 6.5 | 5.5 | 6.6 | 6.5 | 6.6 | 6.1 | 6.0 | 6.8 |
| Detention Time, Hr. | | | | | | | | | | | | | |
| Aeration | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.66 | 2.66 | 2.66 | 2.66 | 2.40 | 2.56 | 2.56 |
| Mixing | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 | N/A | N/A | N/A | N/A | 0.26 | 0.10 | 0.10 |
| Flocculation | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| Settling | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |
| Suspended Solids | | | | | | | | | | | | | |
| MLSS, mg/l | 6080 | 7420 | 6940 | 9110 | 7990 | 8270 | 8890 | 7510 | 8320 | 7030 | 7700 | 8020 | 7370 |
| VSS, % | 70.9 | 66.8 | 66.4 | 67.2 | 65.4 | 67.7 | 67.7 | 59.1 | 56.9 | 56.3 | 58.3 | 61.0 | 65.4 |
| SVI | 35 | 65 | -- | 25 | 33 | 113 | 22 | 110 | 54 | -- | 48 | 64 | 125 |
| COD, mg/l | | | | | | | | | | | | | |
| Influent | 372 | 372 | 372 | 372 | 372 | 372 | 372 | 324 | 314 | 323 | 346 | 421 | 401 |
| Effluent | 52 | 60 | 37 | 23 | 75 | 8 | 36 | -- | -- | -- | -- | -- | -- |
| Removal, % | 86.0# | 83.9# | 90.1# | 93.8# | 81.2# | 97.9# | 90.5 | -- | -- | -- | -- | -- | -- |
| Filtered Effluent## | 22 | 26 | 17 | 10 | 29 | 6 | 24 | 20 | 13 | 23 | 19 | 37 | 37 |
| Removal, % | 94.2 | 93.1 | 95.5 | 97.3 | 92.3 | 98.4 | 93.6 | 93.8 | 95.8 | 92.9 | 94.5 | 91.2 | 90.8 |
| Total phosphorus mg/l $PO_4$ | | | | | | | | | | | | | |
| Influent | 42.2 | 42.2 | 42.2 | 42.2 | 42.2 | 42.2 | 42.2 | 39.6 | 35.9 | 45.8 | 39.4 | 39.1 | 39.7 |
| Effluent | 9.9 | 7.3 | 2.8 | 3.2 | 11.3 | 1.3 | 1.6 | 19.6 | 20.8 | 38.8 | 3.5 | 1.6 | 4.8 |
| Removal, % | 76.5 | 82.7 | 93.4 | 92.4 | 72.0 | 96.9 | 96.2 | 50.5 | 42.1 | 15.3 | 91.1 | 95.9 | 87.9 |
| Filtered Effluent | 4.5 | 0.38 | 0.25 | 0.14 | 0.65 | 0.49 | 0.19 | 0.41 | 0.14 | 0.12 | 0.13 | 0.04 | 0.49 |
| Removal, % | 89.3 | 99.1 | 99.4 | 99.7 | 98.4 | 98.8 | 99.5 | 99.0 | 99.6 | 99.7 | 99.7 | 99.9 | 98.8 |

* A summary of the findings of Eberhardt and Nesbitt (18).

** pH was chemically controlled and constantly maintained at the desired level during the synthetic sewage studies.

\# Calculated from data presented by Eberhardt and Nesbitt.

\#\# Glass fiber filter pads were used.

tion chamber and in order to reduce this time alum was added just prior to sedimentation in the remaining runs; the removal of phosphorus was materially improved. On the basis of these studies, Eberhardt and Nesbitt concluded that nearly complete removal of soluble phosphorus was possible, the removal efficiencies depended upon the pH and the aluminum to phosphorus molar ratio, the phosphorus content of the unfiltered effluent varied with the suspended solids of the sample, biological performance was not adversely affected by alum concentrations as high as 335 mg/l, and the addition of alum caused a decrease in the sludge volume index. Since the aeration period was one third to one half that commonly used in activated sludge plants, Eberhardt and Nesbitt suggested that the chemical costs could be partially offset by the savings resulting from a shorter detention time.

Barth and Ettinger (19), at the Cincinnati Water Research Laboratory of the Federal Water Pollution Control Administration (FWPCA), conducted pilot plant studies to determine the removal of phosphorus by mineral control in the activated sludge aeration chamber. A 100 gpd pilot plant with a 6 hour total detention time (3 hour actual detention time when the return sludge rate is considered) was used with domestic sewage as the substrate. Various chemicals were added directly to the aeration chamber and their effect on phosphorus removal was determined. A summary of the results reported by Barth and Ettinger is presented in Table II. These investigators found sodium aluminate to be the most desirable precipitant because it did not lower the pH of the system as alum did, had no effect on COD removal, and added sodium rather than sulfate or chloride ions to the plant effluent. When sodium tripolyphosphate ($Na_5P_3O_{10}$) was added to increase the phosphorus content of the sewage, the phosphorus removal efficiency decreased. The dose of sodium aluminate needed

# TABLE II

## PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER*

| Chemical Added | | | Supplemental Phosphorus | Length of run, days | Pretreatment | Phosphorus content, mg/l. P | | Phosphorus removal, % |
|---|---|---|---|---|---|---|---|---|
| type | mg/l | to form | | | | Influent# | Effluent# | |
| None | -- | -- | None added | 14 (2 weeks) | No pretreatment was employed | -- | -- | 40 |
| CaO | 150 Ca | Hydroxy-apatite | | | | -- | -- | 64 |
| CaO<br>NaF | 150 Ca<br>6 F | Apatite | | | | -- | -- | 75 |
| $MgSO_4$ | 20 Mg | $MgNH_4PO_4$ | | | | -- | -- | 50 |
| $FeCl_3$ | 15 Fe | $FePO_4$ | | | | -- | -- | 75** |
| $Al_2(SO_4)_3$ | 20 Al | $AlPO_4$ | | | | -- | -- | 70** |
| $Al_2(SO_4)_3$<br>CaO | 30 Al<br>20 Ca | | | | | -- | -- | 90 |
| $Al_2(SO_4)_3$<br>CaO## | 5 Al<br>11 Ca | | | 4 | | 5.25 | 0.25 | 95 |
| $NaAl(OH)_4$ | 5 Al | | | 4 | | 3.00 | 0.20 | 93 |
| | 5 Al | | $Na_5P_3O_{10}$ Added | 18 | | 9.53 | 2.38 | 76 |
| | 10 Al | | | 11 | | 12.3 | 0.92 | 92 |
| | 10 Al | | | 18 | Primary sediment. | 11.1 | 0.50 | 95 |

* A summary of the findings of Barth and Ettinger (19).

\# Arithmetic average of values given by Barth and Ettinger.

** Turbid effluent.

\#\# Added for pH control.

to remove an equal amount of phosphorus was less when biologic solids were present than when they were absent. Barth and Ettinger concluded that a one to one aluminum to phosphorus ratio could be expected to produce an effluent with approximately 0.5 mg/l P residual phosphorus, but also recognized that competition from other ions in the waste would affect this ratio. It should be pointed out, however, that in later work by the FWPCA at a waste treatment plant located in Xenia, Ohio, it was found that an aluminum to phosphorus ratio of 1.8 to 1 was needed in order to remove 85 to 90 percent of the phosphorus with sodium aluminate (44).

# III. MODE OF STUDY

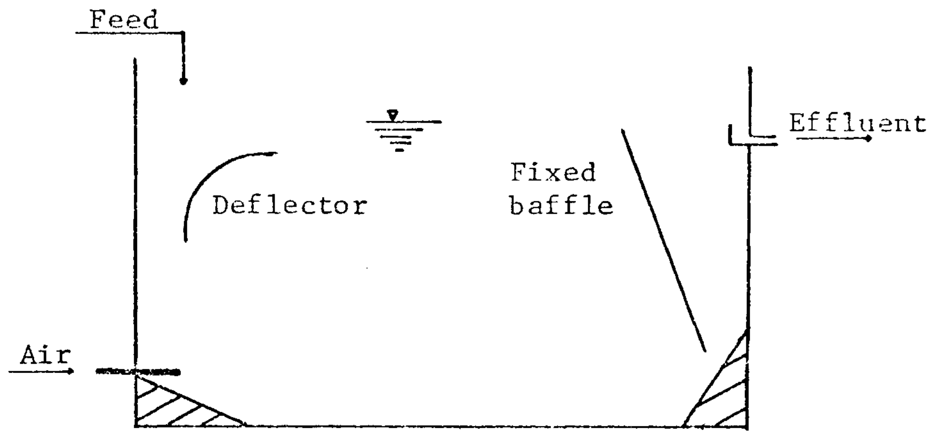
## A. EQUIPMENT

### 1. Activated Sludge Units.

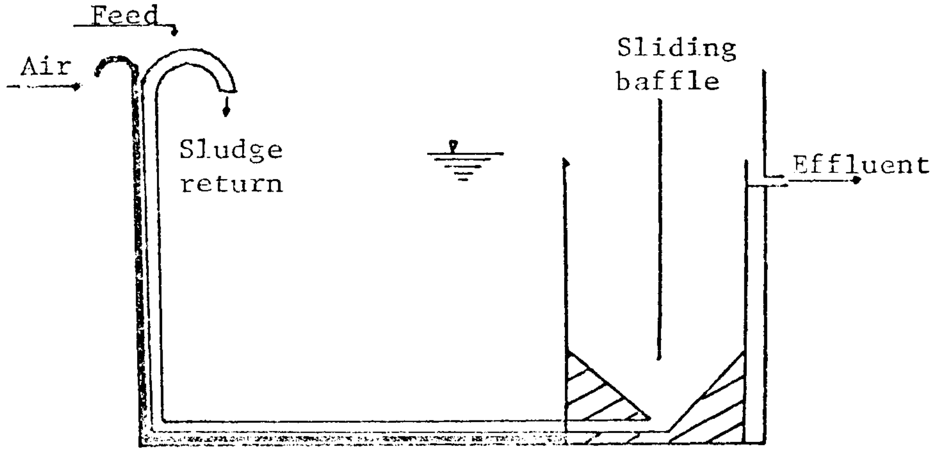
In order to simulate actual plant conditions as closely as possible, it was considered necessary to conduct continuous flow studies. A bench scale unit (Figure 1a) developed by Saxer (45) for studies on dairy wastes was evaluated for this purpose. It was found necessary to modify the design of this unit in order to improve its settling characteristics and serviceability.

The first modification (Figure 1b) provided for the continuous return of the settled sludge from the bottom of the sedimentation chamber to the head of the aeration chamber by means of an air pump. It was found, however, that the sludge adhered to the walls of the sedimentation chamber and was not drawn into the inlet of the air pump eventually clogging the pump.

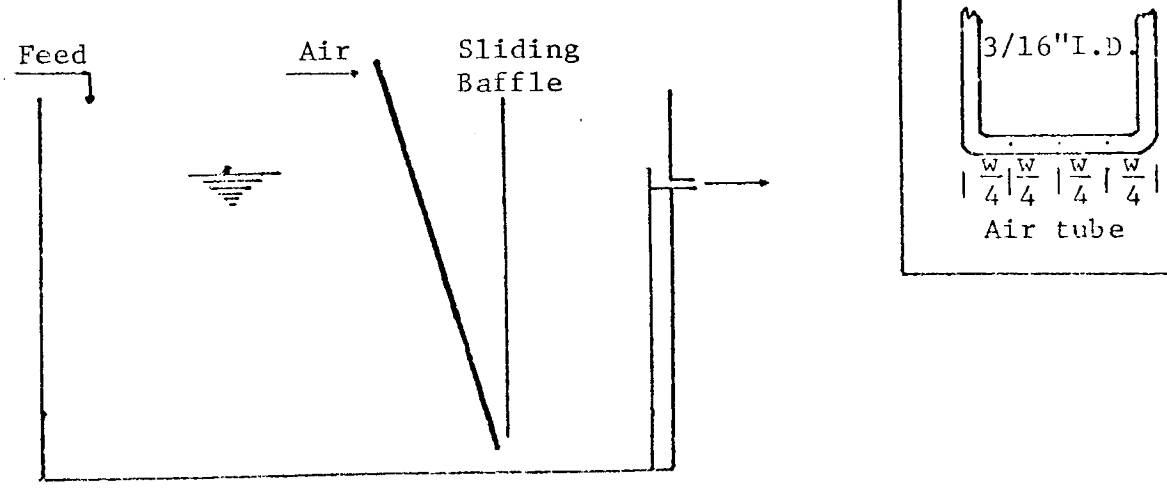
Since this modification was not successful, the design by Saxer was again considered and it was decided that the key to the effective return of the settled sludge was the location of the aeration tube and the height of the opening connecting the sedimentation and aeration chambers. Optimum settling conditions were achieved when the air tube was placed slightly in front of the baffle and midway in the opening (Figure 1c). A U-shaped air tube which had three 1/16 inches holes spaced at equal distance across the width of the aeration chamber facing the head of the chamber was used. By connecting air lines to both sides of the U tube and adjusting the pressure on one side, it was possible to achieve the same flow rate through all three air holes. When the aeration rate was properly adjusted, a rolling motion was achieved which effectively removed sludge from the sedimentation chamber while keeping the mixed



a. Design Employed by Saxer (45)



b. First Modification



c. Final Modification

Scale: 1 cm = 4.03 cm

Figure 1. DEVELOPMENT OF BENCH SCALE CONTINUOUS FLOW ACTIVATED SLUDGE UNIT

liquor suspended solids in suspension in the aeration chamber. A sliding baffle was also employed to enable adjustment of the height of the opening between the aeration and sedimentation chambers, as necessary. Because the dead corner in the sedimentation chamber showed some tendency to collect sludge, a slanting wall was added in the final design. Three identical continuous flow activated sludge units (Figures 2 and 3) were constructed of plexiglass sheets 1/4 inch thick and were equipped with plexiglass effluent and air tubes and aluminum V-notched overflow weirs. The volumes of the aeration and sedimentation chambers of each unit were 2.2 and 0.58 liters, respectively.

2. <u>Sewage Feed System</u>.

The sewage feed system consisted of three 3 gallon Pyrex bottles each serving as a feed reservoir for one activated sludge unit. The feed was distributed to each unit through an unrestricted siphon (Figure 3) and rate control was maintained by restricting the air flow into the reservoirs by means of capillary air inlet tubes. Cotton plugs were employed to protect the capillary tubes from dust and other foreign matter in the air thus securing uninterrupted air flow. Since sewage was the substrate, refrigeration was necessary to keep biological activity at a minimum. The feed bottles were, therefore, placed in the cold room* pictured on the left in Figure 3. The temperature in this room was maintained at 5°C.

The effluent from the units was collected in 2.5 gallon Pyrex bottles which were calibrated in order to allow determination of the volume collected during an appropriate period of time and the computation of the average flow rate through the activated sludge units.

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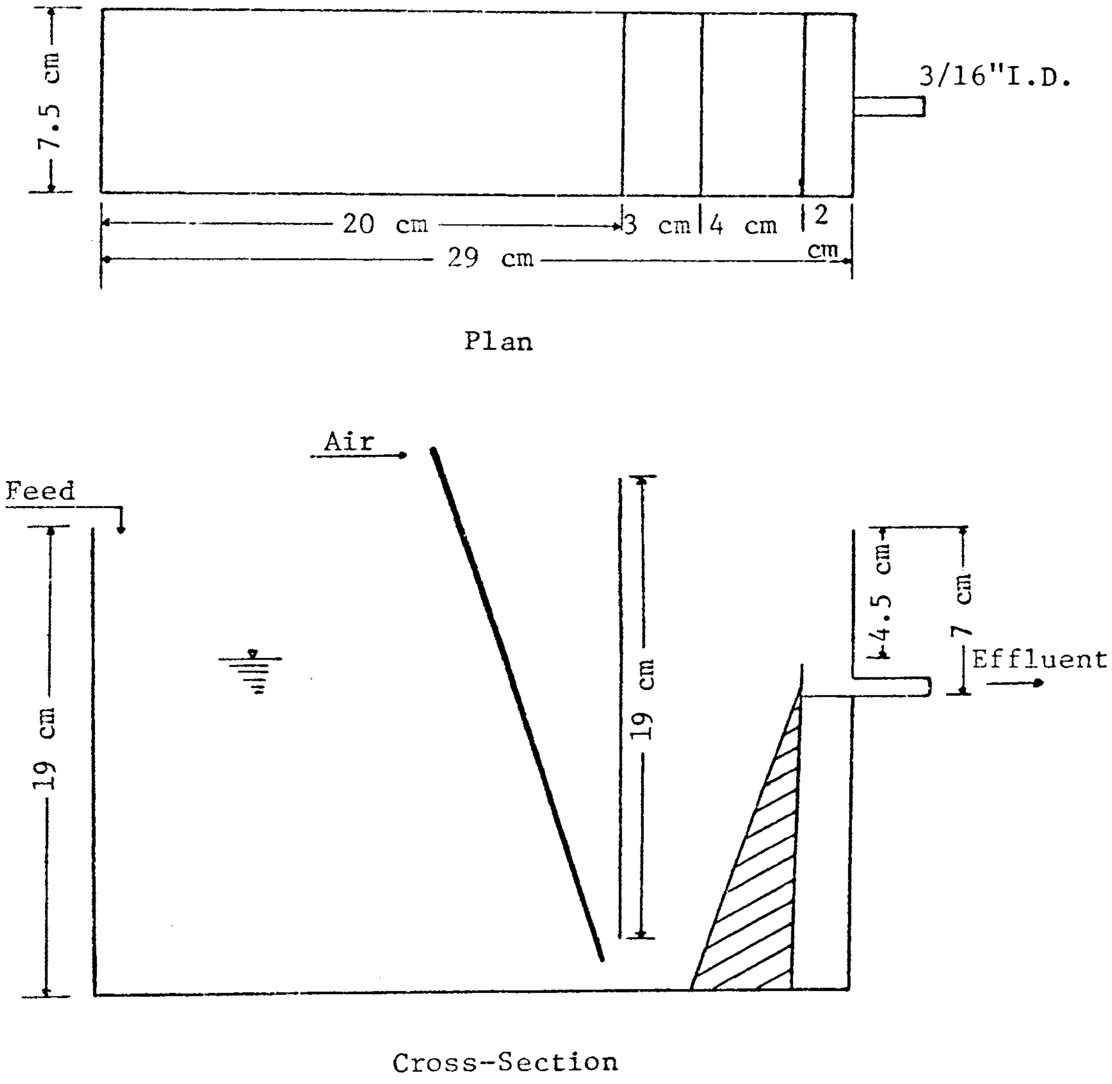
* Model 704A Constant Temperature Room, a product of Lab-Line Instruments, Inc., Melrose Park, Illinois .



Scale: 1 cm = 3.19 cm

Figure 2. BENCH SCALE CONTINUOUS FLOW ACTIVATED SLUDGE UNIT

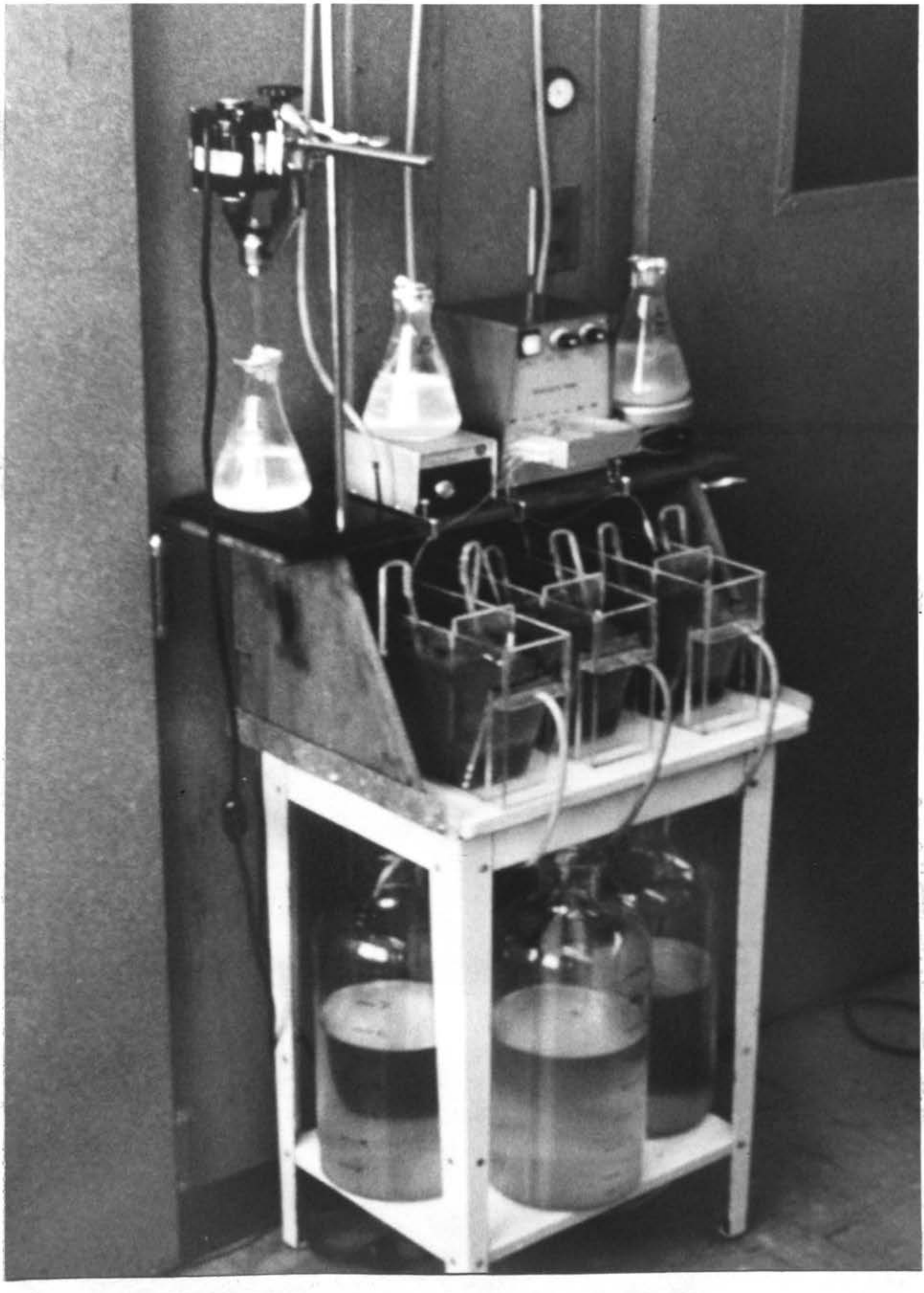


Figure 3. OVERALL ARRANGEMENT OF ACTIVATED SLUDGE UNITS

### 3. Chemical Feed Systems.

Two different methods were used in feeding the chemical precipitants. Flows of less than 20 ml/hr were required to keep the volume of the chemical feed small with respect to the sewage feed. This was accomplished during the early part of the investigation by using capillary tubes (1/32 inch I.D.) which were drawn to a point over a flame. Flow rates were regulated by adjusting the liquid level in the 2.5 liter feed bottles. Because of difficulties encountered with this system, a Buchler Dekastaltic Pump* (Figure 3) was obtained and used to regulate the chemical feed flow in the latter part of the study. By adjusting the speed and tubing size of this peristaltic action pump, it was possible to obtain flow rates in the range of 1.5 to 400 ml/hr. Three 500 ml Erlenmeyer flasks served as the chemical feed reservoirs and each was equipped with a stirring device. Constant stirring was necessary when alum was used because of the tendency of the alum suspension to settle; stirring was not needed when sodium aluminate was used.

### 4. Multi-Unit Variable Speed Stirrer.

Jar studies were conducted with a six unit Phipps and Bird heavy duty stirrer** commonly used for coagulation studies in water. Speeds from 20 to 100 rpm were possible with this unit. Samples were placed in 600 ml Pyrex beakers.

## B. MATERIALS

### 1. Sewage.

Settled domestic sewage was used as the substrate in these studies. It was obtained from the dosing tank of the new Rolla trickling filter

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* A product of Buchler Instruments, Inc., Fort Lee, New Jersey.

** Model 7790-300, a product of Phipps & Bird, Inc., Richmond, Virginia.

plant three times a week in 5 gallon carboys, 20 gallons at a time, and was kept under refrigeration to control microbial activity.

### 2. Activated Sludge.

A fill and draw unit was operated to provide a source of activated sludge for these studies. The sludge was initially developed in the laboratory by aerating raw domestic sewage and thereafter maintained on settled domestic sewage. The unit was aerated for a period of 23 hours daily and permitted to settle for one hour. The clear supernatant was then siphoned out, the unit was fed, and aeration was resumed.

### 3. Chemical Precipitants.

Both sodium aluminate and alum were used as the source of aluminum for the formation of an $AlPO_4$ precipitate. Sodium aluminate ($Na_2O \cdot Al_2O_3 \cdot 3H_2O$, ACS reagent grade) was used during the first part of this investigation and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, technical, ground, iron free) during the latter part.

## C. EXPERIMENTAL CONDITIONS IN THE CONTINUOUS FLOW UNITS

Throughout the studies, settled sewage fed at the average* rate of 375 ml/hr was employed as the sole source of carbon and phosphorus in order that actual sewage treatment plant conditions would be simulated in the closest possible manner. The strength of the sewage varied widely due to large amounts of infiltration into the Rolla sewer system during periods of rainy weather. Over the period of study, COD values ranged from 170 to 639 mg/l and averaged 385 mg/l, while total phosphorus values ranged from 4.5 to 18.4 mg/l P and averaged 11.6 mg/l. Sodium aluminate and alum were used as the precipitating agents and were added

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* A constant rate was not possible and the flow rate decreased as the static head decreased.

to the units in solution at the rate of 15.5 ml/hr (24 hour average*) when the capillary tube system was employed and 14.3** ml/hr when the Dekastaltic pump was used. The required chemical solutions were prepared every other day and the strength of each solution was computed on the basis of the flow rate of sewage and chemical feed through the units and the desired concentration of the precipitants in the units.

The mixed liquor suspended solids (MLSS) and the mixed liquor volatile suspended solids (MLVSS) were used as controlling parameters. Concentrations of MLSS in the range of 3000 to 5000 mg/l and of MLVSS of 1800 and 2000 mg/l were used at various times during this investigation. The level of solids in the units was adjusted when necessary by wasting a portion of the mixed liquor. No attempt was made to regulate the pH of the various systems; however pH measurements were made and recorded regularly in order to determine the effect of the chemical additives on the pH of the systems.

Throughout the studies, a 5.75 hour detention period was maintained; because of the gravity feed systems employed, this figure represents the average value for each 24 hour period. Air was obtained from the laboratory compressed air supply and was filtered through activated carbon to remove any oils or other materials present which might have interfered with the activated sludge. No attempt was made to regulate the rate of aeration other than necessary visual adjustments to obtain complete mixing and equal turbulence in all three units. The investigation was con-

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* A constant rate was not possible and the flow rate decreased as the static head decreased.

** In the first 4 days this pump was employed, a rate of 7 ml/hr was used but this was increased to 14.3 ml/hr to eliminate precipitation of sodium aluminate in the feed lines.

ducted at room temperature which remained at approximately 21°C. during the studies.

## D. EXPERIMENTAL PARAMETERS AND DETERMINATIONS

### 1. Phosphorus.

Total phosphorus was primarily measured in this investigation; however, total soluble phosphorus was also determined in one of the runs. There were two reasons for the measurement of total phosphorus. First, many of the complex inorganic and organic forms of phosphorus eventually may be broken down into soluble orthophosphates which would be available as plant nutrients (4); therefore, all forms of phosphorus are important from the standpoint of eutrophication control. Second, because of the nature of the determinations for the different phosphorus compounds, it is possible to get overlapping results; in other words, the determination for orthophosphate may measure a portion of the total inorganic phosphorus present, while the determination for total inorganic phosphorus may include some organic phosphorus. In addition, there seems to be some confusion in the literature as to the terms used to describe the various phosphorus compounds (46). The analytical determination, rather than the chemical formula, seems to govern the type of phosphorus being measured. These problems were eliminated in this investigation by oxidizing the test sample to convert all the phosphorus compounds present into orthophosphate which was then readily measured spectrophotometrically.

Since the Standard Methods for the Examination of Water and Wastewater (47) does not recommend a method for the determination of phosphorus in wastewater*, a method developed by Murphy and Riley (48) and Edwards, et al. (49) and modified by Jankovic, et al. (46) for use in

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* Methods are given for the determination of phosphates in water.

wastewater was employed. This method involved the formation under acidic conditions of an ammonium phosphomolybdate complex, reduction of this complex with ascorbic acid to give a blue colored sol, and measurement of the color intensity on a spectrophotometer. It was selected because of its accuracy and simplicity. According to Jankovic and his coworkers, the use of stannous chloride as reducing agent which is recommended in Standard Methods (47, p. 234) gave erroneous results when detecting known amounts of added phosphorus in domestic sewage. On the other hand, the use of ascorbic acid resulted in detection of all added phosphorus. Of equal importance, since a large number of phosphorus determinations was necessary throughout the course of this investigation, was the relative ease with which this determination can be performed. The blue colored sol was reported to be stable for at least one hour as opposed to 2 minutes for the stannous chloride method (47, p. 234) and the addition of only one reagent was necessary when preparing a sample.

The first step in performing a total phosphorus determination was the digestion of the sample using potassium persulfate as the oxidant. Two milliliters of 5 N sulfuric acid and one gram of potassium persulfate were added to a 125 ml Erlenmeyer flask containing 10 ml of sample* and a few boiling beads. The mixture was diluted to about 30 ml with deionized water and refluxed for 15 minutes on the COD apparatus. It was then cooled and diluted to an appropriate volume.

Phosphorus determinations were conducted using the reagents and procedure described by Jankovic, et al. (46), except that a wavelength of

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* When the total dissolved phosphorus was determined, the sample was first filtered through a 0.45 micron membrane filter (Catalog No. HAWG 047A0, a product of the Millipore Corporation, Bedford, Massachusetts).

725 mμ was employed. The optimum wavelength for the determination of the blue colored complex has been reported to be 880 to 882 mμ with another peak occurring at 725 mμ (46, 48, 49). However, the Hitachi Perkin-Elmer spectrophotometer* used in these studies had a wavelength range of 195 to 800 mμ necessitating the use of the lower wavelength. The digested sample was diluted with deionized water as needed** to obtain a spectrophotometric transmittance in the range of 50 to 100 percent. Eight milliliters of a mixed reagent*** were placed in a Nessler tube and enough diluted sample was added to provide a total volume of 50 ml. Ten minutes were allowed for color development and the percent transmittance was determined using the spectrophotometer. A blank prepared in a similar manner but using deionized water rather than diluted sample was employed to set the transmittance to the 100 percent value. The total phosphorus concentration in the sample was determined on the basis of the percent transmittance value from the calibration curve prepared using a standard phosphate ($KH_2PO_4$) solution and the results were reported as mg/l P.

2. <u>Chemical Oxygen Demand</u>.

Chemical oxygen demand provided a measure of the strength of the settled sewage fed to the activated sludge units and of the quality of the effluent produced; therefore, it enabled the evaluation of the treat-

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* Model 139 ultraviolet visible spectrophotometer, a product of the Coleman Instruments Corporation, Maywood, Illinois.

** A 25 fold dilution was employed with samples which had not received chemical treatment and a 10 fold dilution was used with treated samples.

*** Prepared by mixing 125 ml of a 5 N sulfuric acid solution with 37.5 ml of an ammonium molybdate solution (40g/1) and then adding 75 ml of a 0.1M ascorbic acid solution and 12.5 ml of a potassium antimonyl tartrate solution (0.2743 g/100 ml); this mixture was prepared daily.

ment efficiency of the various units under the experimental conditions employed. Chemical oxygen demand was determined according to the method described in Standard Methods (47, p. 510). A mixture containing 10 ml of sample, 5 ml of a 0.25 N potassium dichromate solution, 15 ml of a concentrated sulfuric acid, and 3 boiling beads was refluxed for a 2 hour period. The mixture was then cooled, diluted to approximately 70 ml, and titrated with a 0.05 N ferrous ammonium sulfate solution using ferroin as an indicator to determine the amount of dichromate remaining. Two blanks containing 10 ml deionized water were also run with each set of samples.

### 3. Mixed Liquor Suspended and Volatile Suspended Solids.

Mixed liquor suspended and volatile suspended solids were used as a means of controlling experimental conditions in the activated sludge units; in addition the effect of MLSS on phosphorus removal was evaluated. The procedure outlined in Standard Methods (47, p. 424) was employed, except that fiberglass discs* were used with the Gooch crucibles in place of the specified asbestos mats. A 25 ml volume of sample was filtered through a fired, preweighed crucible which was then dried in a 103°C. oven for one hour, cooled, and weighed to determine MLSS. The crucible was then ignited at 600°C. for 15 minutes in a muffle furnace, cooled, and reweighed to determine MLVSS.

### 4. Sludge Volume Index.

This index provided a measure of the settling characteristics of the activated sludge. It was determined as the ratio of the volume of sludge settled in 30 minutes divided by the MLSS. The procedure out-

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* Catalog No. 934AH, a product of H. Reeve Angel & Co., Clifton, New Jersey.

lined in Standard Methods (47, p. 541) was employed, except that a 100 ml graduated cylinder instead of the recommended 1000 ml cylinder was used to determine sludge settleability.

5. pH Value.

The pH of the mixed liquor in the various units was measured because pH has been reported to have an effect on the efficiency of phosphorus removal by various chemical additives; in addition, it was desired to determine the effect of these additives on the pH of the activated sludge units. A Beckman Zeromatic pH meter* was employed for this determination.

## E. EXPERIMENTAL PROCEDURES

### 1. Activated Sludge Studies.

The continuous flow activated sludge units were serviced once every 24 hours; the sewage and chemical feed reservoirs were refilled, the effluent bottles were emptied, and samples were taken. The following procedure was used when servicing the units:

a. The chemical and sewage feed systems were stopped.

b. The feed bottles were removed from the cold room and refilled with sewage. A 20 ml sample was drawn from each reservoir to form a composite sample used in determining the characteristics of the influent sewage. The bottles were returned to the cold room and the carboys, when empty, rinsed with water.

c. The volume of treated waste collected in each effluent bottle was recorded and a 50 ml representative sample was taken and used to determine the characteristics of treated effluent. The bottles were emptied, rinsed, and placed back into position.

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* A product of Beckman Instruments, Inc., Fullerton, California.

d. The chemical feed reservoirs were refilled with the appropriate soluions.

e. The sludge adhering to the sides of the aeration chamber was scraped back into the aerating mixed liquor with a rubber policeman and the effluent weir was rinsed with water.

f. The feed systems were placed back in operation.

g. The aeration rate was adjusted in each unit as needed to provide effective and uniform sludge return and turbulence in the aeration chamber.

Two day composite samples were used for the phosphorus, COD, and pH determinations. One half of the composite sample was kept under refrigeration until the following day when the remainder was added; analytical determinations were begun as soon as the composite sample was collected. Suspended and volatile suspended solids, sludge volume index, and pH determinations were made every other day using grab samples of the mixed liquor.

2. Jar Studies.

Jar studies were performed using a multi-unit variable speed stirrer and the following test procedure was employed:

a. The appropriate volume of settled sewage or settled sewage containing activated sludge solids was placed in six 600 ml beakers and the initial pH was determined.

b. The beakers were placed on the stirring device, the stirring mechanism was activated and its speed adjusted to approximately 90 rpm. The desired chemical dose was added to each unit (volumes less than 5 ml were always used) and rapid mix was continued for a period of 30 seconds after the last chemical addition.

c. The speed was reduced to 20 rpm and slow mix was continued for 20 minutes. The stirring blades were then removed and the mixture was allowed to settle for a 30 minute period.

d. The upper portion of the supernatant in each beaker was transferred into a 100 ml beaker and used for phosphorus and final pH determinations.

# IV. PRESENTATION OF DATA AND RESULTS

Sodium aluminate and alum were investigated as removal agents for the reduction of phosphorus in sewage. The main studies were conducted in three continuous flow laboratory activated sludge units and were supplemented with jar studies. The major experimental parameters employed were the influent and effluent total phosphorus and chemical oxygen demand, the aluminum to phosphorus ratio, the mixed liquor total and volatile suspended solids, pH, and the sludge volume index.

## A. ACTIVATED SLUDGE STUDIES

The continuous flow activated sludge studies consisted of four different experimental runs: a preliminary run to develop the operational characteristics of the units, two runs to investigate the phosphorus removal efficiency of sodium aluminate and alum, and a run to study the effect of mixed liquor suspended solids concentration on phosphorus removal. The three-and-one-half week preliminary run was undertaken to evaluate and adjust the sewage and capillary tube chemical feed systems in order to ensure reliable flow rates; general experimental information of value to the development of the remaining runs was also obtained. Two of the units were maintained as controls and the third received sodium aluminate. The data obtained in this run are not reported in detail due to the great fluctuation in experimental conditions. Total phosphorus residuals of 6.1 to 13.5 mg/l P and 6.2 to 14.3 mg/l P with corresponding average removals of 13.9 and 15.4 percent were obtained in the control units, while residuals of 1.1 to 7.3 mg/l P for a 73.9 percent average removal resulted in the unit to which sodium aluminate had been added at concentrations ranging from 10 to 70 mg/l. The influent COD was reduced by an average of 92.8 percent in the sodium aluminate unit and 89.1 and 89.2 percent, respectively, in the control units. A MLSS concentration as high as 5000 mg/l could be maintained in all units.

### 1. Effect of Sodium Aluminate.

The purpose of this run was to investigate the effect of sodium aluminate added at varying concentrations in the aeration chamber on the removal of phosphorus in and overall treatment efficiency of the activated sludge units. Sodium aluminate was added at concentrations ranging from 17.6 to 52.7 mg/l in Unit B and 35.2 to 70.2 mg/l in Unit C, while Unit A served as a control. In determining the coagulant dose, the theoretical one to one molar reaction ratio between aluminum and phosphorus to form aluminum phosphate ($AlPO_4$) was considered (17, 18, 19). On this basis, a solution containing 3.52 mg/l sodium aluminate ($Na_2O \cdot Al_2O_3 \cdot 3H_2O$) would contain enough aluminum to react stoichiometrically with 1.0 mg/l phosphorus. Sludge from the stock fill and draw unit was used to fill the three units. The data obtained from this study are presented in Table III. In the early part of the run, it was attempted to maintain the MLSS concentration in all units at 3000 mg/l; although the preliminary study had indicated that this suspended solids concentration could be supported, the strength of the settled domestic sewage during this period decreased significantly and it was found impossible to maintain the 3000 mg/l MLSS level in the control unit. At the same time the percentage of the MLVSS was observed to decrease in Units B and C. Therefore, in order to enable comparison of the three units from the standpoint of biological activity, it was decided to change the MLSS parameter to MLVSS and maintain the concentration at the controllable 1800 mg/l level; this change was effected after the 19th day.

## TABLE III

## REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH SODIUM ALUMINATE IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit A - Control

| Time | Sodium Aluminate | | Mixed Liquor Solids | | Mixed | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|
| | Added | P Equivalent* | Total or VSS | VSS % of | Liquor pH | Influent | Effluent | Influent | Effluent |
| days | mg/1 | mg/1 | mg/1 | total | -- | mg/1 | mg/1 | mg/1 | mg/1 |
| 2 | 0 | N/A | --<br>Total | -- | -- | 341 | 20 | 8.0 | 5.7 |
| 4 | | | 2460 | 78 | 7.7 | 417 | 38 | 16.3 | 7.0 |
| 6 | | | 2080 | 79 | 7.7 | 326 | 15 | -- | 10.8 |
| 9 | | | 1840 | 79 | 8.1 | 232 | 30 | 10.5 | 7.4 |
| 11 | | | 2190 | 82 | 7.9 | 405 | 8 | 9.0 | 6.3 |
| 13 | | | -- | -- | -- | 302 | 24 | 13.4 | 8.0 |
| 15 | | | 2450 | 81 | 7.4 | 341 | 16 | 11.0 | 8.7 |
| 17 | | | 2330 | 83 | 7.0 | 216 | 47 | 7.7 | 7.0 |
| 19 | | | 2430 | 82 | 7.3 | 298 | 39 | 10.9 | 9.6 |
| 21 | | | 1800<br>VSS | 83 | 7.4 | 505 | 72 | 13.9 | 11.5 |
| 23 | | | | 83 | 7.6 | 435 | 20 | 14.1 | 10.6 |
| 25 | | | | 84 | 7.6 | 545 | 40 | 14.3 | 11.3 |
| 27 | | | | 83 | 7.8 | 498 | 12 | 17.5 | 13.1 |
| 29 | | | | 86 | 7.7 | 281 | 32 | 11.2 | 9.6 |
| 31 | | | | 85 | 7.4 | 226 | 8 | 10.0 | 7.8 |
| 33 | | | | 85 | 7.6 | 254 | 58 | 11.1 | 8.7 |
| 35 | | | | 83 | 7.8 | 304 | 27 | 12.6 | 10.1 |
| 37 | | | | 82 | 7.9 | 370 | 50 | 9.3 | 6.7 |
| 39 | | | | 83 | 8.0 | 340 | 15 | 9.8 | 6.8 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

## TABLE III (Continued)

## REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH SODIUM ALUMINATE IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit B - 17.6 to 52.7 mg/l Sodium Aluminate

| Time | Sodium Aluminate | | Mixed Liquor Solids | | Mixed Liquor | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|
| days | Added mg/l | P Equivalent* mg/l | Total or VSS mg/l | VSS % of total | pH -- | Influent mg/l | Effluent mg/l | Influent mg/l | Effluent mg/l |
| 2 | 17.6 | 5 | 3000 Total | -- | -- | 341 | 16 | 8.0 | 3.5 |
| 4 | | | | 72 | 7.7 | 417 | 45 | 16.3 | 3.9 |
| 6 | | | | 70 | 7.7 | 326 | 8 | -- | -- |
| 9 | | | | 68 | 7.9 | 232 | 37 | 10.5 | 4.5 |
| 11 | | | | 66 | 8.0 | 405 | 15 | 9.0 | 3.4 |
| 13 | | | | -- | -- | 302 | 12 | 13.4 | 5.6 |
| 15 | | | | 66 | 7.6 | 341 | 31 | 11.0 | 4.0 |
| 17 | 35.2 | 10 | | -- | 7.7 | 216 | 27 | 7.7 | 1.8 |
| 19 | | | 1800 VSS | 61 | 7.4 | 298 | 43 | 10.9 | 2.4 |
| 21 | | | | 62 | 7.5 | 505 | 12 | 13.9 | 4.1 |
| 23 | | | | 61 | 7.6 | 435 | 52 | 14.1 | 4.0 |
| 25 | | | | 61 | 7.6 | 545 | 32 | 14.3 | 3.9 |
| 27 | | | | 61 | 7.7 | 498 | 16 | 17.5 | 5.1 |
| 29 | 52.7 | 15 | | 59 | 7.7 | 281 | 12 | 11.2 | 2.0 |
| 31 | | | | 57 | 7.6 | 226 | 4 | 10.0 | 1.1 |
| 33 | | | | 57 | 7.7 | 254 | 8 | 11.1 | 1.6 |
| 35 | | | | 55 | 8.0 | 304 | 19 | 12.6 | 3.0 |
| 37 | | | | 55 | 8.0 | 370 | 30 | 9.3 | 1.1 |
| 39 | | | | 54 | 8.1 | 340 | 19 | 9.8 | 1.0 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

TABLE III (Continued)

REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH SODIUM ALUMINATE

IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit C - 35.2 tc 70.2 mg/1 Sodium Aluminate

| Time | Sodium Aluminate | | Mixed Liquor Solids | | Mixed Liquor pH | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|
| days | Added mg/1 | P Equivalent* mg/1 | Total or VSS mg/1 | VSS % of total | -- | Influent mg/1 | Effluent mg/1 | Influent mg/1 | Effluent mg/1 |
| 2 | 35.2 | 10 | 3000 Total | -- | -- | 341 | 28 | 8.0 | 1.5 |
| 4 | | | | 65 | 7.9 | 417 | 30 | 16.3 | 3.1 |
| 6 | | | | 66 | 7.8 | 326 | 30 | -- | 3.9 |
| 9 | | | | 60 | 8.1 | 232 | 30 | 10.5 | 3.0 |
| 11 | | | | 59 | 7.9 | 405 | 30 | 9.0 | 2.4 |
| 13 | | | | -- | -- | 302 | 27 | 13.4 | 3.8 |
| 15 | 0# | N/A | | 58 | 8.0 | 341 | 27 | 11.0 | 4.3 |
| 17 | | | | 77 | 7.4 | 216 | 24 | 7.7 | 6.8 |
| 19 | | | | 78 | 7.3 | 298 | 24 | 10.9 | 9.6 |
| 21 | 52.7 | 15 | 1800 VSS | 73 | 7.5 | 505 | 20 | 13.9 | 6.3 |
| 23 | | | | 67 | 7.6 | 435 | 16 | 14.1 | 2.7 |
| 25 | | | | 63 | 7.6 | 545 | 43 | 14.3 | 2.2 |
| 27 | | | | 63 | 7.9 | 498 | 59 | 17.5 | 4.1 |
| 29 | | | | 60 | 7.9 | 281 | 24 | 11.2 | 2.4 |
| 31 | 70.2 | 20 | | 57 | 7.7 | 226 | 4 | 10.0 | 1.3 |
| 33 | | | | 56 | 7.9 | 254 | 19 | 11.1 | 1.2 |
| 35 | | | | 57 | 8.2 | 304 | 15 | 12.6 | 1.6 |
| 37 | | | | 53 | 8.1 | 370 | 19 | 9.3 | 0.7 |
| 39 | | | | 51 | 8.2 | 340 | 15 | 9.8 | 0.6 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

\# Because of bulking, sludge in Unit C replaced with fresh sludge from stock unit; no aluminate was added during a 5 day acclimation period.

The total phosphorus data are plotted in Figure 4. Because of a bulking condition observed in Unit C, it was found necessary to replace the sludge in this unit on the 13th day with fresh sludge from the fill and draw stock unit. No sodium aluminate was added to this unit during a five day acclimation period and as a result the total phosphorus concentration in the effluent increased to the level in the control unit; after the chemical feed was again initiated the effluent phosphorus concentration rapidly decreased. The phosphorus content of the settled sewage fed to the units fluctuated throughout the run and had a noticeable effect on the residual phosphorus in all units. The chemical dose also affected the phosphorus removal efficiency.

The effect of sodium aluminate on COD removal is shown graphically in Figure 5. The COD values determined in the effluent from the three units were very comparable throughout the run and although the influent values ranged as high as 545 mg/1, the COD residuals in all units were in most cases less than 50 mg/1.

There was little difference in the mixed liquor pH between Units B and C and the control, indicating that the addition of sodium aluminate did not affect the pH of the system. The pH values ranged from 7.3 to 8.2 and were well within the acceptable limits for activated sludge. The pH of the settled domestic sewage was determined intermittently throughout the study and showed little variation; pH values varied from 7.3 to 7.9 and averaged 7.7.

2. Effect of Mixed Liquor Suspended Solids.

The primary objective of this run was to investigate the effect of suspended solids on the efficiency of phosphorus removal. Barth and Ettinger (19) have reported that better phosphorus removals were obtained with a lower dose of precipitant in the presence of biological

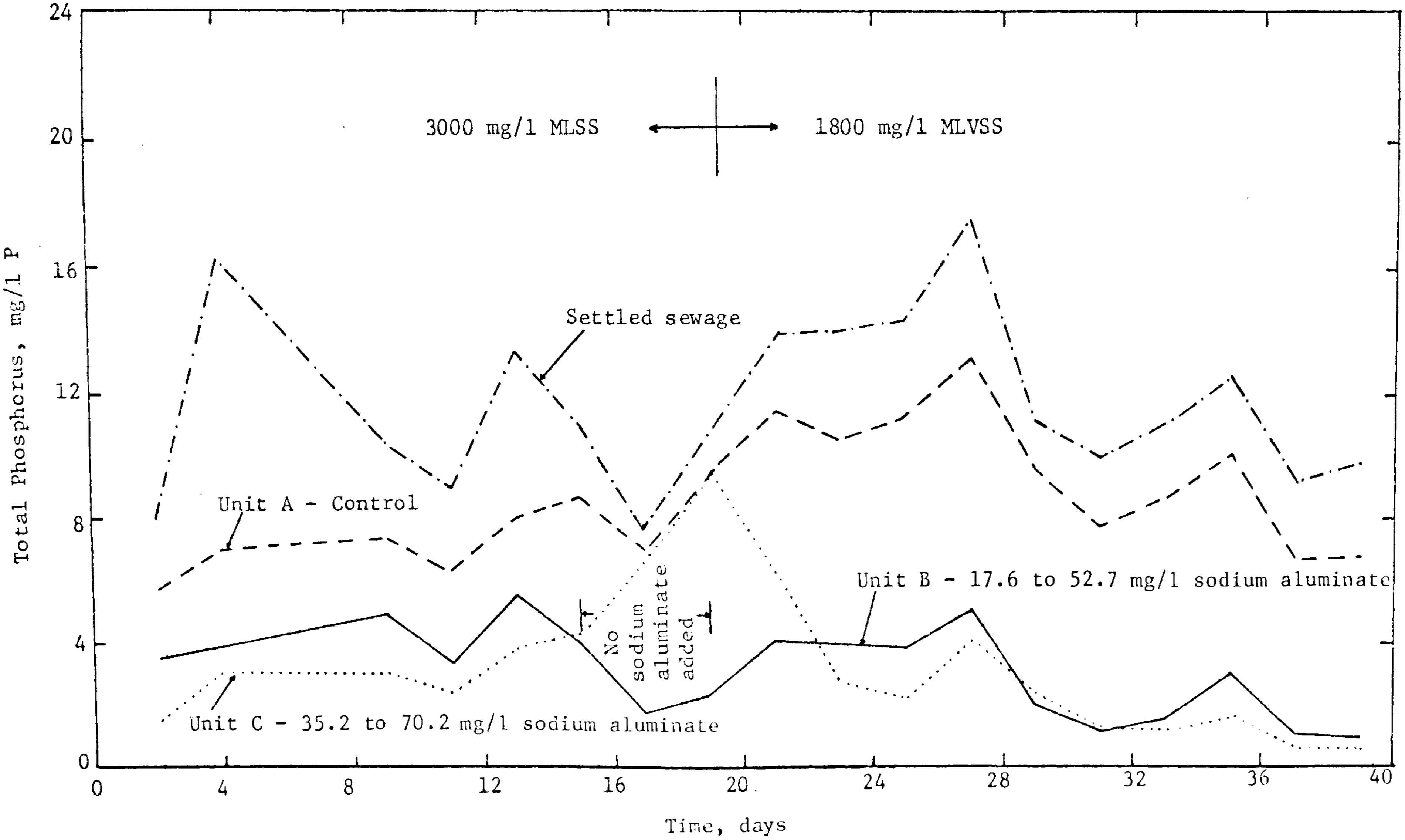

Figure 4. REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH SODIUM ALUMINATE IN THE ACTIVATED SLUDGE AERATION CHAMBER

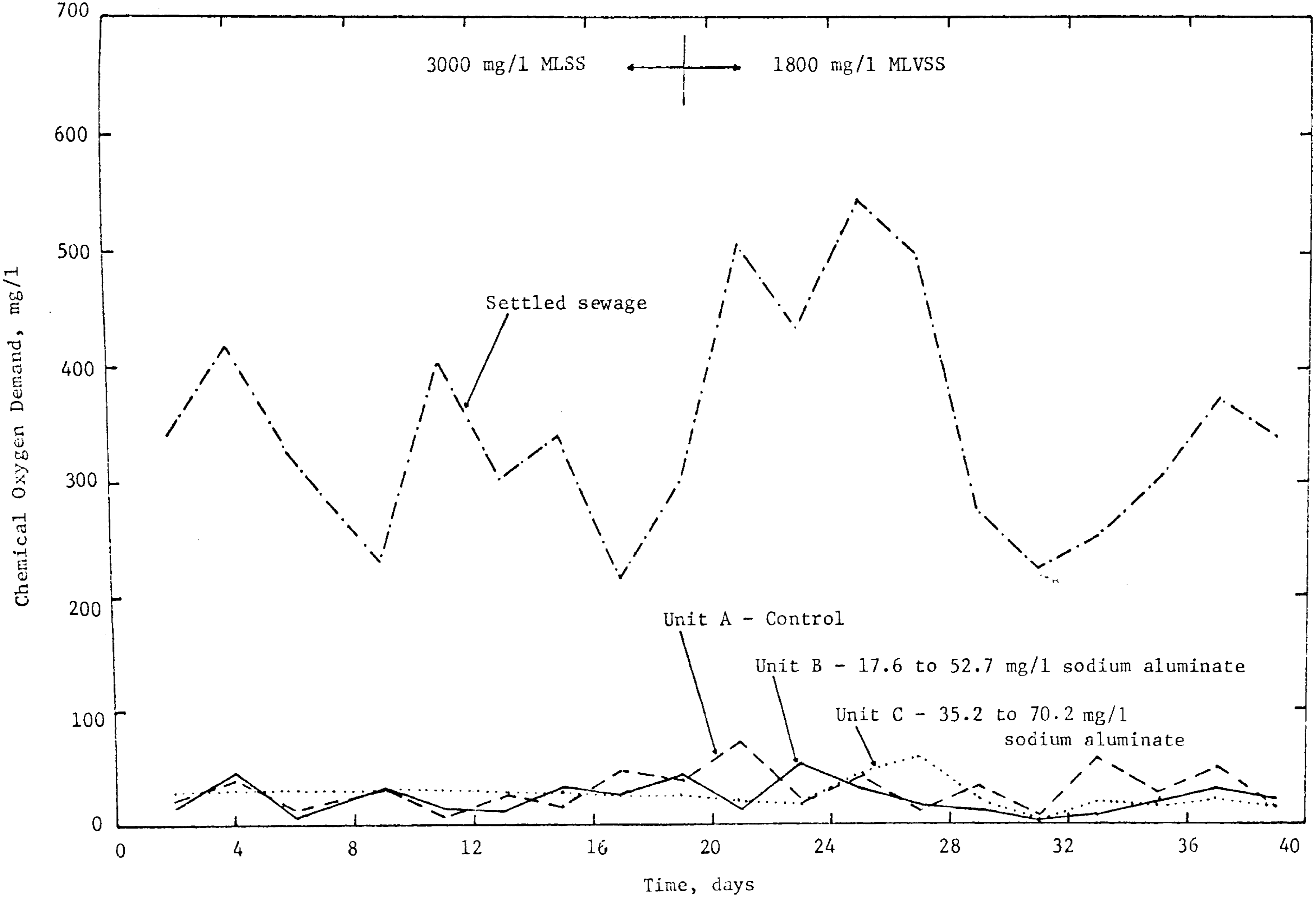

Figure 5. EFFECT OF SODIUM ALUMINATE ON CHEMICAL OXYGEN DEMAND REMOVAL

solids than were obtained with a higher dose when solids were absent, and attributed this to the large surface area of the biological floc. The effect of sludge mass was evaluated by maintaining the MLSS at 3000, 4000, and 5000 mg/l in Units A, B, and C, respectively; part of the sludge employed in the units had been previously exposed to aluminum. Since the previous runs had shown that the addition of sodium aluminate had no significant effect on COD removal, a control unit was not used. Both sodium aluminate and alum were investigated; sodium aluminate was added at a concentration of 52.7 mg/l during the first 10 days of the run and alum was added at 161 mg/l during the last 12 days. On a one to one aluminum to phosphorus reaction basis*, these precipitant concentrations should have been capable of removing 15 mg/l P.

The data obtained in this study are given in Table IV and the effect of the MLSS concentration on phosphorus and COD removal is presented graphically in Figures 6 and 7. The MLSS level had only a slight effect on phosphorus removal, except on the 7th and 8th day when an abrupt increase occurred in the influent phosphorus content. Unit A which had the lowest MLSS concentration was affected relatively more than the other units. In general, higher total phosphorus removals were obtained during the latter part of the study when alum was employed and the resulting phosphorus residuals were the lowest observed in any of the runs. A rapid rise in influent phosphorus concentration during this period did not significantly affect the phosphorus removal efficiency.

From the standpoint of COD removal, all units performed very satisfactorily (Figure 7). The effluent COD values in all three units were very nearly the same and, with one exception, less than 40 mg/l

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* On this basis a solution containing 10.74 mg/l alum [$Al_2(SO_4)_3 \cdot 18H_2O$] should contain enough aluminum to react stoichiometrically with 1.0 mg/l phosphorus.

## TABLE IV

## EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON PHOSPHORUS REMOVAL BY PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit A - 3000 mg/l MLSS

| Time | Chemical Precipitant | | | Mixed Liquor Solids | | Sludge | Mixed | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Added | | P Equivalent* | Total | VSS | Volume | Liquor | Influent | Effluent | Influent | Effluent |
| days | type | mg/l | mg/l | mg/l | % of total | Index -- | pH -- | mg/l | mg/l | mg/l | mg/l |
| 0 | Sodium Aluminate | 52.7 | 15 | 3000 | 61 | -- | 7.7 | -- | -- | -- | -- |
| 2 | | | | | 59 | 75 | 7.9 | 495 | 53 | 9.8 | 1.2 |
| 4 | | | | | 59 | 170 | 7.9 | 537 | 30 | 9.3 | 1.1 |
| 6 | | | | | 57 | 180 | 7.9 | 548 | 7 | 10.4 | 1.2 |
| 8 | | | | | 55 | 85 | 7.9 | 595 | 11 | 14.4 | 2.8 |
| 10 | | | | | 54 | 66 | 7.9 | 200 | 12 | 8.8 | 2.8 |
| 12 | Alum | 161 | | | 52 | 77 | 7.6 | 224 | 33 | 9.6 | 1.1 |
| 14 | | | | | 50 | 72 | 7.3 | 268 | 32 | 9.5 | 1.0 |
| 16 | | | | | 49 | -- | -- | 292 | 8 | 6.5 | 0.7 |
| 18 | | | | | 50 | 62 | 7.6 | 173 | 31 | 4.5 | 1.0 |
| 20 | | | | | 54 | 70 | 7.5 | 314 | 16 | 7.8 | 0.6 |
| 22 | | | | | 51 | 73 | 7.7 | 610 | 35 | 13.8 | 1.2 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

## TABLE IV (Continued)

## EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON PHOSPHORUS REMOVAL BY PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit B - 4000 mg/l MLSS

| Time | Chemical Precipitant | | | Mixed Liquor Solids | | Sludge | Mixed | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Added | | P Equiva-lent* | Total | VSS | Volume | Liquor | Influ-ent | Efflu-ent | Influ-ent | Efflu-ent |
| days | type | mg/l | mg/l | mg/l | % of total | Index -- | pH -- | mg/l | mg/l | mg/l | mg/l |
| 0 | Sodium Aluminate | 52.7 | 15 | 4000 | 61 | -- | 7.8 | -- | -- | -- | -- |
| 2 | | | | | 59 | 111 | 7.8 | 495 | 30 | 9.8 | 1.4 |
| 4 | | | | | 59 | 128 | 7.9 | 537 | 37 | 9.3 | 1.2 |
| 6 | | | | | 58 | 103 | 7.9 | 548 | 0 | 10.4 | 1.2 |
| 8 | | | | | 55 | 104 | 8.0 | 595 | 26 | 14.4 | 2.2 |
| 10 | | | | | 53 | 68 | 8.0 | 200 | 20 | 8.8 | 1.6 |
| 12 | Alum | 161 | | | 52 | 64 | 7.6 | 224 | 37 | 9.6 | 1.2 |
| 14 | | | | | 50 | 62 | 7.5 | 268 | 37 | 9.5 | 1.1 |
| 16 | | | | | 49 | -- | -- | 292 | 20 | 6.5 | 0.7 |
| 18 | | | | | 47 | 60 | 7.8 | 173 | 20 | 4.5 | 0.7 |
| 20 | | | | | 51 | 55 | 7.7 | 314 | 27 | 7.8 | 0.8 |
| 22 | | | | | 51 | 54 | 7.9 | 610 | 12 | 13.8 | 1.3 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

TABLE IV (Continued)

EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON PHOSPHORUS REMOVAL

BY PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER

Unit C - 5000 mg/1 MLSS

| Time | Chemical Precipitant | | | Mixed Liquor Solids | | Sludge | Mixed | COD** | | Total Phosphorus** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Added | | P Equivalent* mg/1 | Total | VSS % | Volume Index | Liquor pH | Influent | Effluent | Influent | Effluent |
| days | type | mg/1 | | mg/1 | of total | -- | -- | mg/1 | mg/1 | mg/1 | mg/1 |
| 0 | Sodium Aluminate | 52.7 | 15 | 5000 | 61 | -- | 7.7 | -- | -- | -- | -- |
| 2 | | | | | 58 | 127 | 7.8 | 495 | 23 | 9.8 | 1.2 |
| 4 | | | | | 58 | 134 | 7.9 | 537 | 23 | 9.3 | 1.1 |
| 6 | | | | | 57 | 121 | 7.8 | 548 | 11 | 10.4 | 1.1 |
| 8 | | | | | 55 | 65 | 7.9 | 595 | 30 | 14.4 | 1.8 |
| 10 | | | | | 53 | 48 | 7.9 | 200 | 29 | 8.8 | 1.8 |
| 12 | Alum | 161 | | | 52 | 53 | 7.7 | 224 | 8 | 9.6 | 1.1 |
| 14 | | | | | 50 | 54 | 7.5 | 268 | 32 | 9.5 | 0.9 |
| 16 | | | | | 49 | -- | -- | 292 | 24 | 6.5 | 0.6 |
| 18 | | | | | 48 | 51 | 7.9 | 173 | 20 | 4.5 | 0.7 |
| 20 | | | | | 51 | 50 | 7.8 | 314 | 12 | 7.8 | 0.6 |
| 22 | | | | | 51 | 52 | 7.9 | 610 | 27 | 13.8 | 1.2 |

* Based on stoichiometric reaction requiring a molar Al/P ration 1/1.

** Influent and effluent values correspond.

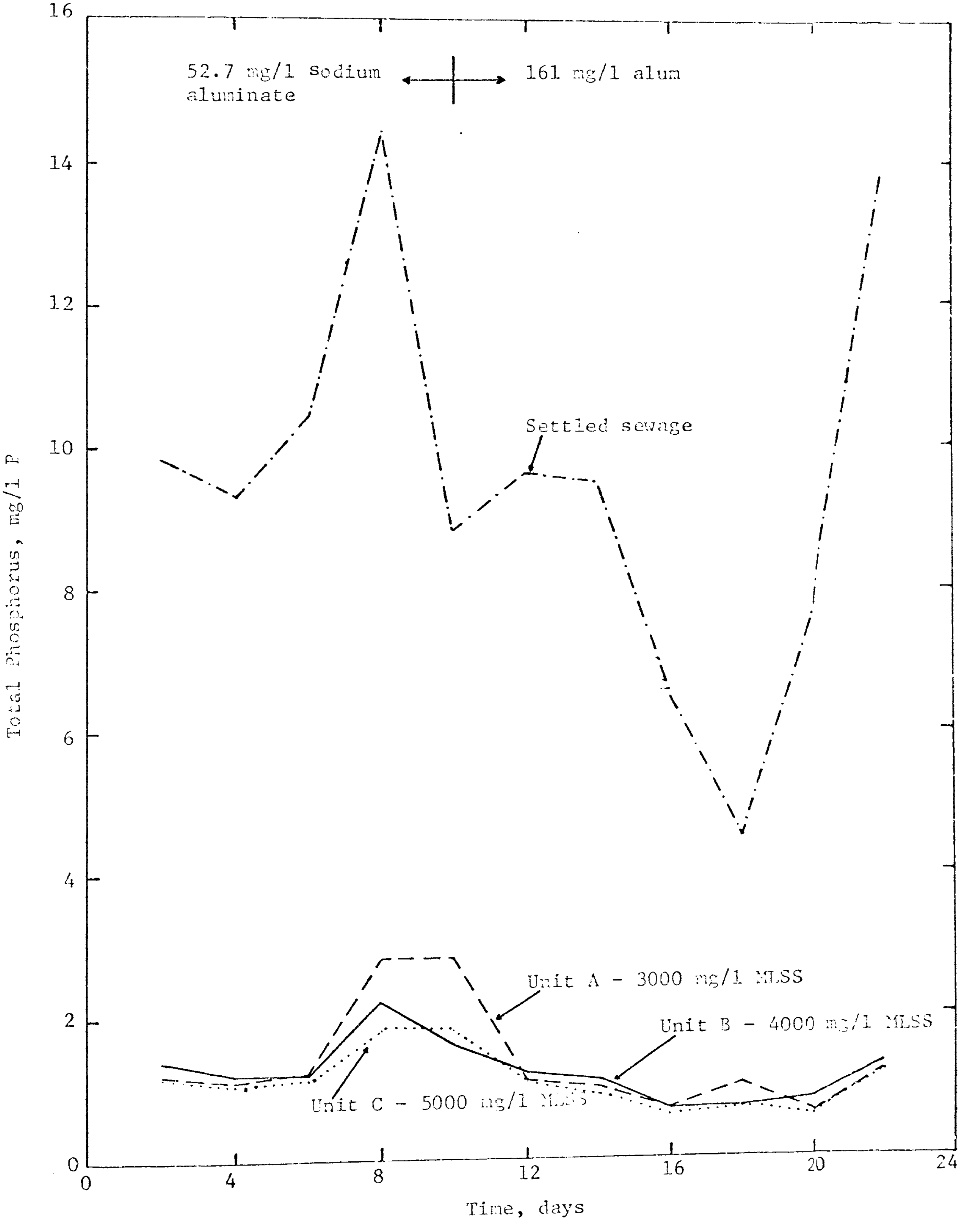

Figure 6. EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON PHOSPHORUS REMOVAL BY PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER

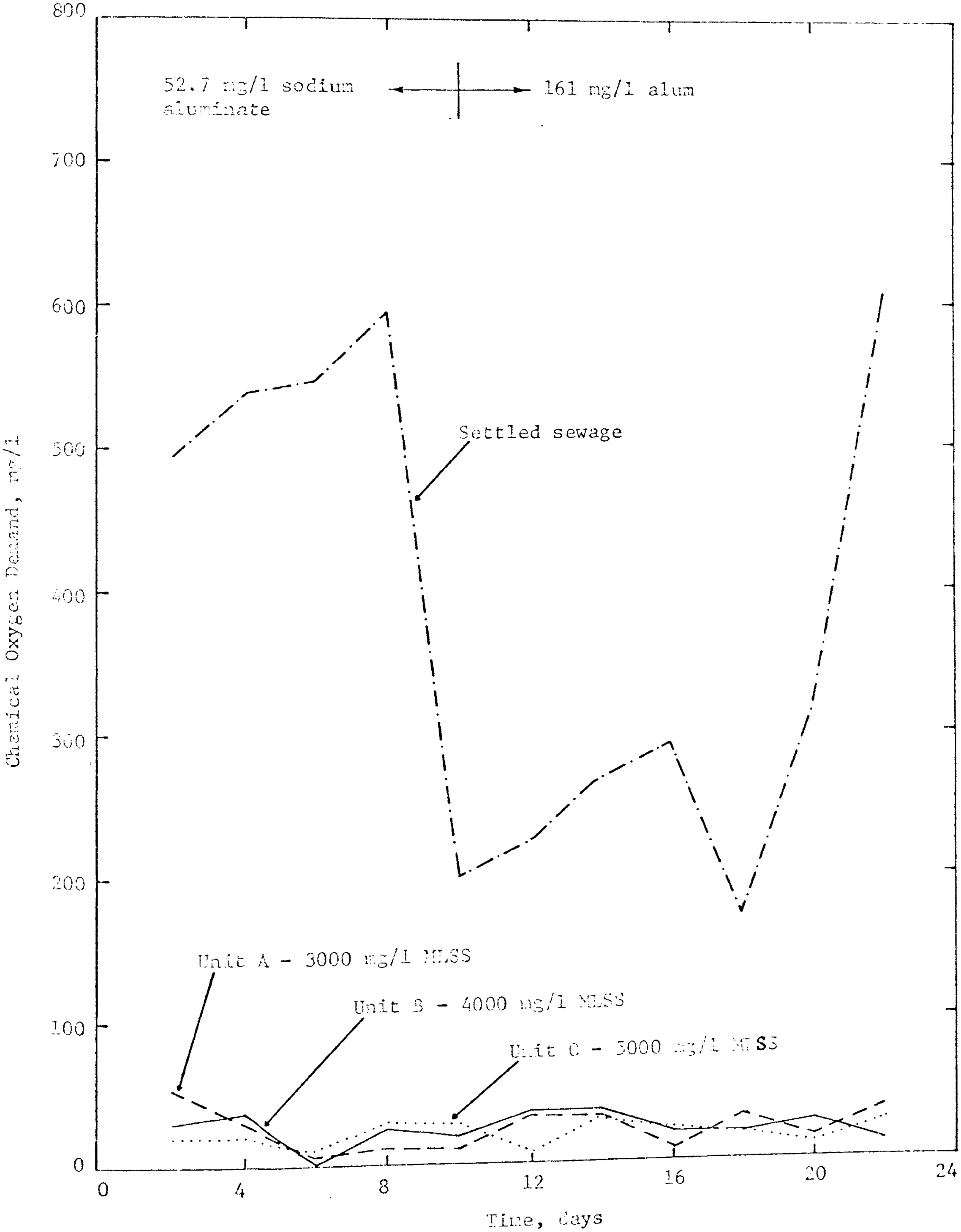

Figure 7. EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON CHEMICAL OXYGEN DEMAND REMOVAL IN THE PRESENCE OF SODIUM ALUMINATE AND ALUM

and in many instances less than 25 mg/1. The effluent COD values were similar when sodium aluminate and alum were employed and were not affected by the MLSS concentration.

The pH of the mixed liquor and the sludge volume index (SVI) were also determined and the values obtained are shown in Table IV. The mixed liquor pH ranged between 7.3 and 8.0 and generally remained at the same level when sodium aluminate and alum were used; however, when alum was first introduced the pH in all units first decreased and then began to rise to the previous levels. The SVI was initially above the 100 value but then fell and remained below 80 in all units for the entire period of alum addition; this was attributed to the reduced strength of the settled domestic sewage, as indicated by the lower COD values. The percentage of MLVSS was found to decrease in all units from an initial value of 61 percent to the vicinity of 50 percent at which level it was maintained for the remainder of the run.

### 3. Effect of Alum.

Because alum was found in the preceding run to remove phosphorus more effectively than sodium aluminate, its efficiency at various concentrations was investigated in this run. The addition of alum was again based on the theoretical aluminum to phosphorus ratio of one to one and concentrations of 134, 188, and 215 mg/1 alum were maintained in the three units. The sludge present in the units at the end of the previous run was mixed and returned to the units. The MLVSS concentration was held at the 2000 mg/1 level throughout this run in all three units and represented approximately 50 percent of the total MLSS present.

The experimental data pretaining to this run are summarized in Table V and the effect of alum on the removal of phosphorus is also shown in Figure 8. Both total and total filtered phosphorus were deter-

## TABLE V

## REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH ALUM

## IN THE ACTIVATED SLUDGE AERATION CHAMBER

| Time | Alum | | Mixed Liquor Solids | | Sludge Volume Index | Mixed Liquor pH | COD** | | Total Phosphorus** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Influent | | Effluent | |
| | Added | P Equivalent* | VSS | VSS % | | | Influent | Effluent | Unfilt. | Filtered | Unfilt. | Filtered |
| days | mg/l | mg/l | mg/l | of total | -- | -- | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l |
| Unit A - 134 mg/l Alum | | | | | | | | | | | | |
| 2 | 134 | 12.5 | 2000 | 53 | 60 | 7.7 | 484 | 8 | 13.9 | 9.1 | 1.9 | 1.4 |
| 4 | | | | 50 | 75 | 7.7 | 581 | 12 | 14.4 | 10.5 | 2.0 | 1.6 |
| 6 | | | | 52 | 81 | 7.8 | 608 | 35 | 18.4 | 12.1 | 2.8 | 2.5 |
| 8 | | | | 50 | 135 | 7.9 | 639 | 27 | 14.4 | 8.6 | 2.1 | 1.9 |
| 10 | | | | 50 | 107 | 7.9 | 624 | 12 | 15.6 | 9.6 | 1.9 | 1.5 |
| Unit B - 188 mg/l Alum | | | | | | | | | | | | |
| 2 | 188 | 17.5 | 2000 | 53 | 59 | 7.7 | 484 | 12 | 13.9 | 9.1 | 1.4 | 0.9 |
| 4 | | | | 50 | 77 | 7.7 | 581 | 20 | 14.4 | 10.5 | 1.4 | 0.9 |
| 6 | | | | 52 | 107 | 7.7 | 608 | 20 | 18.4 | 12.1 | 1.7 | 1.6 |
| 8 | | | | 50 | 148 | 7.7 | 639 | 27 | 14.4 | 8.6 | 1.1 | 1.0 |
| 10 | | | | 50 | 142 | 7.7 | 624 | 12 | 15.6 | 9.6 | 1.1 | 0.9 |
| Unit C - 215 mg/l Alum | | | | | | | | | | | | |
| 2 | 215 | 20.0 | 2000 | 53 | 56 | 7.8 | 484 | 12 | 13.9 | 9.1 | 1.2 | 0.5 |
| 4 | | | | 49 | 71 | 7.7 | 581 | 27 | 14.4 | 10.5 | 1.0 | 0.7 |
| 6 | | | | 51 | 85 | 7.7 | 608 | 27 | 18.4 | 12.1 | 1.2 | 0.9 |
| 8 | | | | 49 | 135 | 7.7 | 639 | 8 | 14.4 | 8.6 | 0.7 | 0.7 |
| 10 | | | | 49 | 135 | 7.7 | 624 | 15 | 15.6 | 9.6 | 0.7 | 0.6 |

* Based on stoichiometric reaction requiring a molar Al/P ratio of 1/1.

** Influent and effluent values correspond.

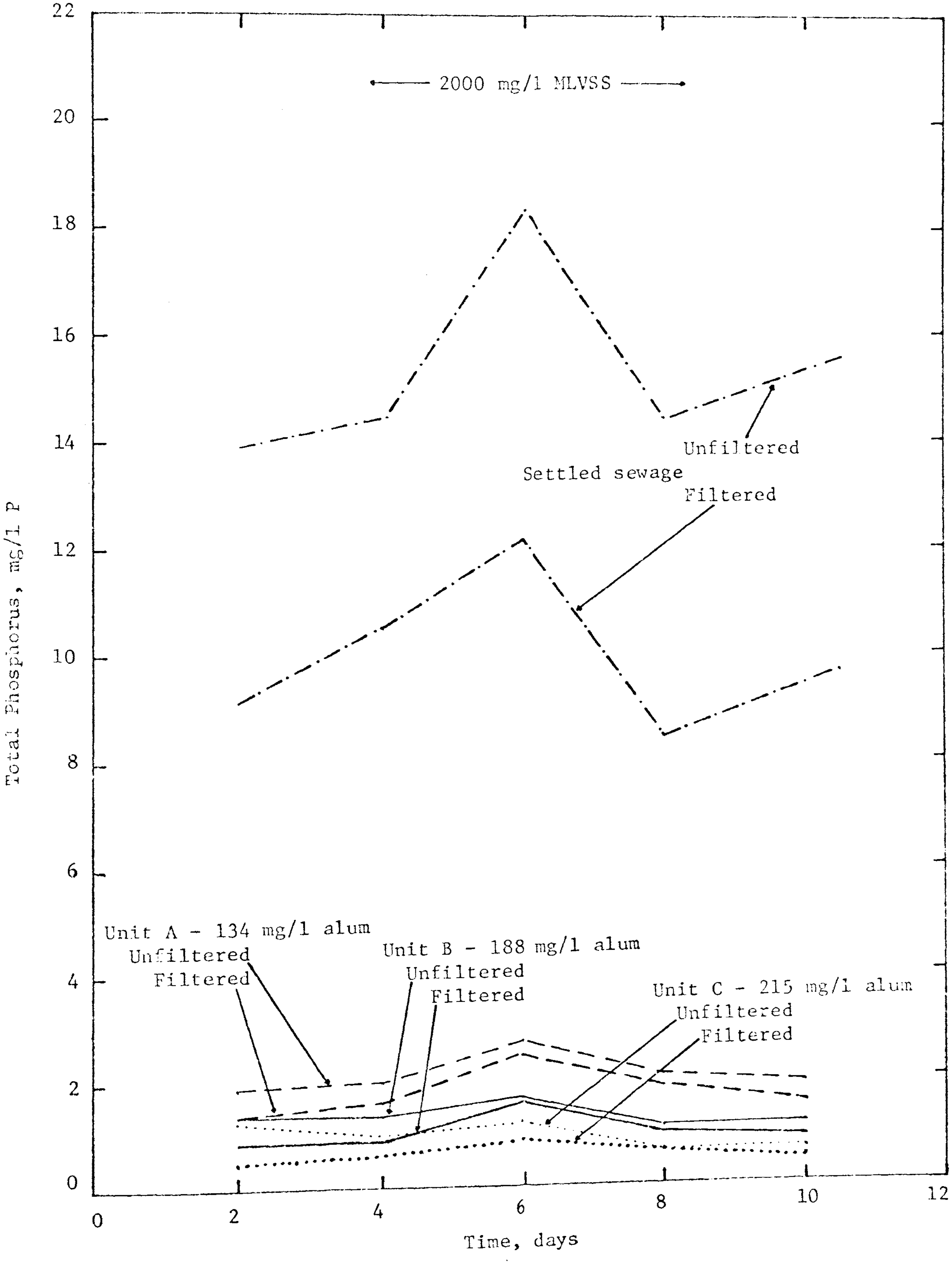

Figure 8. REMOVAL OF PHOSPHORUS BY PRECIPITATION WITH ALUM IN THE ACTIVATED SLUDGE AERATION CHAMBER

mined and are reported in order to give an indication of the amount of soluble phosphorus present in the effluent. According to Eberhardt and Nesbitt (18), when alum was added directly to the activated sludge aeration chamber a turbid effluent with a relatively high phosphorus content resulted; however, when samples were filtered a significant decrease in effluent concentration was noted. The total dissolved phosphorus averaged about 65 percent of the total phosphorus in the settled domestic sewage and the corresponding percentages in the treated effluents from Units A, B, and C were 83, 78, and 73 percent respectively. The total phosphorus removals obtained in this run were the highest observed in any of the studies and again, as in the case of sodium aluminate, the higher alum concentrations effected greater phosphorus removals. The deterioration in the quality of the effluent in terms of suspended solids reported by Eberhardt and Nesbitt (18) did not occur and the effluent remained clear throughout the run.

The COD data are plotted in Figure 9. The activated sludge units continued to treat the waste effectively and the effluent COD values were very similar to those obtained in previous runs, although the COD of the settled domestic sewage was high throughout the run ranging from 484 to 639 mg/l. As a result of the higher food to microorganisms ratio maintained in this run, the SVI increased in all units from a value of approximately 60 at the beginning of the run to well over 100. On the other hand, the MLVSS remained at approximately 50 percent of the MLSS. The addition of alum did not appear to exert any effect on the pH of the activated sludge systems which remained at the 7.7 to 7.9 range.

## B. JAR STUDIES

Eight sets of jar tests were conducted to provide supplemental information on the removal of phosphorus by sodium aluminate and alum

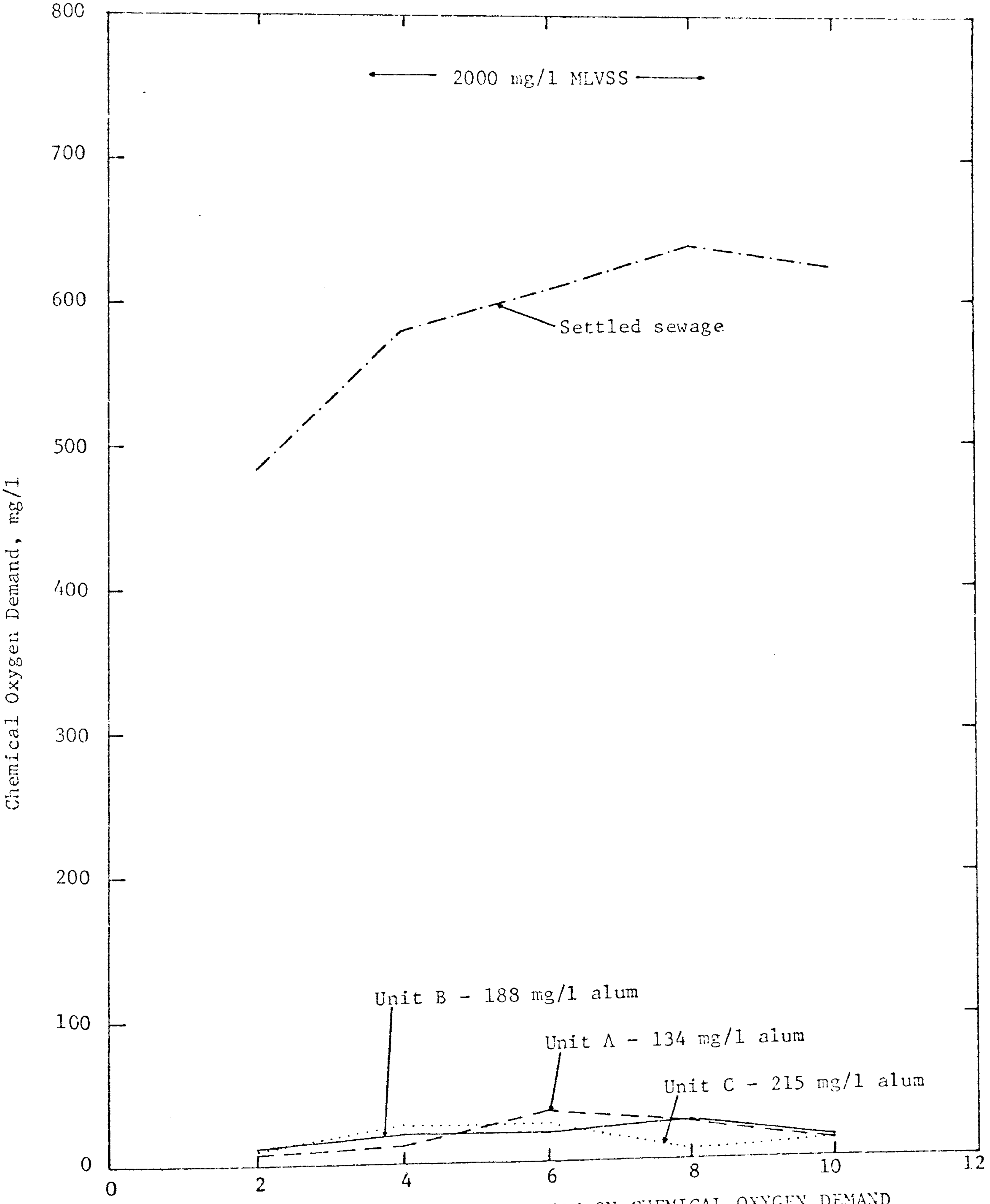

Figure 9. EFFECT OF ALUM CONCENTRATION ON CHEMICAL OXYGEN DEMAND REMOVAL

under different conditions of pH, aluminum to phosphorus ratio, and suspended solids content. Settled domestic sewage and a mixture of sewage and activated sludge, both acclimated and unacclimated, were used. The same sewage was used in all tests and had a pH of 7.3 and total phosphorus content of 12.9 mg/l P. The acclimated activated sludge was obtained from a two week composite of the MLSS wasted from the units during the latter part of the second run and had a 58 percent MLVSS content, while the unacclimated sludge was obtained from the stock fill and draw unit and had a 70 percent MLVSS content. An attempt was made to hold as many variables as possible constant during the various experiments. The results of the jar studies are presented in Table VI and Figure 10.

Tests 1 and 2 were conducted to determine the optimum pH for the removal of phosphorus in the Rolla sewage by precipitation. The initial pH of the sewage was adjusted with sulfuric acid or sodium hydroxide, as appropriate, to obtain a range from 4 to 9 in each test and sodium aluminate or alum was added to give a one to one aluminum to phosphorus molar ratio. The final rather than the initial pH was most significant in this study because this value could be compared to the pH in the aeration chamber in the continuous flow studies and, therefore, provide an indication of the optimum pH for phosphorus precipitation in the activated sludge process. Optimum precipitation of phosphorus with sodium aluminate and alum occurred at the pH ranges of 6.4 to 7.5 and 5.8 to 7.2, respectively. The pH in the aeration chamber of the continuous flow activated sludge units was generally outside these ranges but close to their upper limits. The lower phosphorus residual obtained with sodium aluminate at the pH of 8.9 was probably due in part to the formation of calcium phosphate, as described by Bogan (36).

## TABLE VI

## REMOVAL OF PHOSPHORUS BY CHEMICAL PRECIPITATION IN JAR STUDIES

| System Studied | Precipitant | | Al/P Ratio | Sludge Solids mg/1 | pH | | Total Phosphorus, mg/1 P | |
|---|---|---|---|---|---|---|---|---|
| | Type | mg/1 | | | Initial | Final | Initial | Final |
| Effect of pH | | | | | | | | |
| Settled Domestic Sewage | Sodium Aluminate | 45.5 | 1.0 | N/A | 4 | 5.4 | 12.9 | 8.8 |
| | | | | | 5 | 5.8 | | 5.9 |
| | | | | | 6 | 6.4 | | 4.3 |
| | | | | | 7 | 7.5 | | 4.3 |
| | | | | | 8 | 8.1 | | 4.7 |
| | | | | | 9 | 8.9 | | 4.0 |
| | Alum | 139 | | | 4 | 3.7 | | 8.5 |
| | | | | | 5 | 4.1 | | 8.4 |
| | | | | | 6 | 5.8 | | 2.8 |
| | | | | | 7 | 6.7 | | 2.8 |
| | | | | | 8 | 7.2 | | 2.4 |
| | | | | | 9 | 8.0 | | 3.8 |
| Effect of Al/P Ratio | | | | | | | | |
| Settled Domestic Sewage | Sodium Aluminate | 0 | N/A | N/A | 7.3* | 7.6 | 12.9 | 9.1 |
| | | 45.5 | 1.0 | | | 8.1 | | 5.2 |
| | | 56.9 | 1.25 | | | 8.1 | | 4.5 |
| | | 68.3 | 1.5 | | | 8.3 | | 2.8 |
| | | 79.6 | 1.75 | | | 8.3 | | 2.8 |
| | | 91.0 | 2.0 | | | 8.4 | | 2.0 |
| | Alum | 0 | N/A | | | 7.6 | | 9.1 |
| | | 139 | 1.0 | | | 7.1 | | 3.5 |
| | | 174 | 1.25 | | | 7.0 | | 2.0 |
| | | 208 | 1.5 | | | 6.9 | | 1.1 |
| | | 243 | 1.75 | | | 6.8 | | 0.6 |
| | | 278 | 2.0 | | | 6.8 | | 0.4 |

* No pH adjustment was made.

## TABLE VI (Continued)

## REMOVAL OF PHOSPHORUS BY CHEMICAL PRECIPITATION IN JAR STUDIES

| System Studied | Precipitant | | Al/P Ratio | Sludge Solids mg/1 | pH | | Total Phosphorus, mg/1 P | |
|---|---|---|---|---|---|---|---|---|
| | Type | mg/1 | | | Initial | Final | Initial | Final |
| Effect of Mixed Liquor Suspended Solids | | | | | | | | |
| Settled Domestic Sewage and Acclimated Activated Sludge Solids (Containing 52% VSS) | Sodium Aluminate | 45.5 | 1.44 | 1000 | 7.4* | 7.9 | 9.0 | 3.2 |
| | | | | 1500 | | 7.9 | | 3.3 |
| | | | | 2000 | | 7.8 | | 3.1 |
| | | | | 2500 | | 7.7 | | 3.1 |
| | | | | 3000 | | 7.7 | | 3.1 |
| | | | | 3500 | | 7.6 | | 2.9 |
| | Alum | 139 | | 1000 | | 7.0 | | 1.0 |
| | | | | 1500 | | 7.0 | | 1.3 |
| | | | | 2000 | | 7.0 | | 1.2 |
| | | | | 2500 | | 7.0 | | 1.2 |
| | | | | 3000 | | 7.0 | | 1.4 |
| | | | | 3500 | | 7.0 | | 1.3 |
| Settled Domestic Sewage and Unacclimated Activated Sludge Solids (Containing 70% VSS) | Sodium Aluminate | 45.5 | 1.84 | 1000 | 8.0* | 8.3 | 7.0 | 2.1 |
| | | | | 1500 | | 8.3 | | 2.2 |
| | | | | 2000 | | 8.3 | | 2.2 |
| | | | | 2500 | | 8.3 | | 2.4 |
| | | | | 3000 | | 8.3 | | 2.6 |
| | | | | 3500 | | 8.3 | | 2.7 |
| | Alum | 139 | | 1000 | | 7.1 | | 2.1 |
| | | | | 1500 | | 7.2 | | 2.8 |
| | | | | 2000 | | 7.2 | | 3.6 |
| | | | | 2500 | | 7.2 | | 4.2 |
| | | | | 3000 | | 7.3 | | 4.5 |
| | | | | 3500 | | 7.3 | | 4.8 |

* No pH adjustment was made.

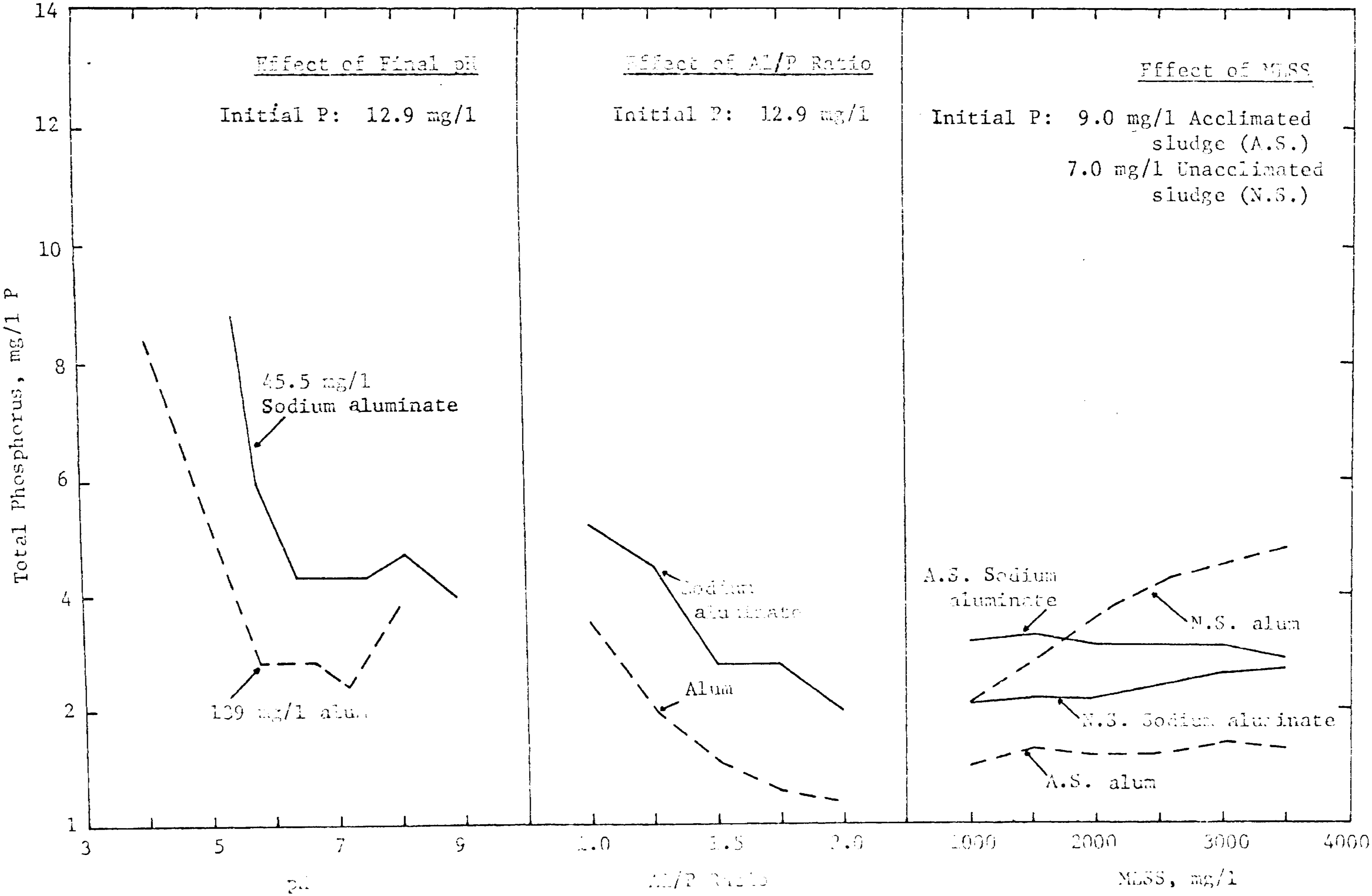

Figure 10. PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION IN JAR STUDIES

Sodium aluminate and alum were added at varying concentrations to settled sewage in tests 3 and 4 in order to determine the effect of the aluminum to phosphorus ratio on phosphorus removal. Ratios in the range of 1.0 to 2.0 were used and a control was employed in each test. No pH adjustments were made because the initial pH of the sewage (7.3) was either in or very near the optimum range determined in the previous tests. The removal of phosphorus increased with the aluminum to phosphorus ratio. It is also interesting to note that pH increased at higher sodium aluminate concentrations but decreased at higher alum doses. This was probably caused by the release of hydroxide ions by sodium aluminate and the release of hydrogen ions by alum.

In tests 5 and 6 the removal of phosphorus by sodium aluminate and alum in the presence of varying concentrations of MLSS acclimated to aluminum was investigated. The initial phosphorus content of the sewage-activated sludge mixture was less than that of the sewage because of the lower phosphorus concentration in the activated sludge portion of the sample. An aluminum to phosphorus ratio of 1.44 to 1 was employed. Increasing the MLSS level from 1000 to 3500 mg/1 had little noticeable effect on the phosphorus removal. This was in agreement with the results of the continuous flow study where MLSS concentrations in the range of 3000 to 5000 mg/1 were found to effect only a minor improvement on the removal of phosphorus.

Finally, the effect of varying concentrations of unacclimated activated sludge solids was investigated in tests 7 and 8. The aluminum to phosphorus ratio in this case was 1.84 to 1. The presence of MLSS at concentrations ranging from 1000 to 3500 mg/1 had little effect on the removal of phosphorus by sodium aluminate; however, a pronounced increase in the concentration of total phosphorus remaining at the end of the coagulation-sedimentation period was noted when alum was employed. Contrary to the findings in the previous tests, alum was relatively ineffective in removing phosphorus at the greater MLSS concentrations.

# V. DISCUSSION

The primary objective of this investigation was to study the removal of phosphorus by chemical precipitation with sodium aluminate and alum in the activated sludge aeration chamber; this was accomplished in continuous flow bench-scale units and in jar tests using settled domestic sewage as the substrate and source of phosphorus. The effect of the aluminum to phosphorus ratio, the mixed liquor suspended solids (MLSS) concentration, and pH on total phosphorus removal, and the effect of the chemical precipitants on the performance of the activated sludge system, as evidenced by the effluent chemical oxygen demand (COD), were investigated.

The major findings of the activated sludge studies are summarized in Table VII in which the average COD and total phosphorus removal data are presented according to the aluminum to phosphorus ratio present in the units. Without the addition of chemicals, total phosphorus was reduced by an average of 30.8 percent, from an influent concentration of 11.7 mg/1 P to an effluent concentration of 8.1 mg/1 P. This removal is in agreement with the 14 to 50 percent range reported by Vacker, et al. (43) in conventional activated sludge treatment plants. With the addition of chemicals, the efficiency of the activated sludge units in removing phosphorus was improved considerably. Approximately 63 to 90 and 86 to 90 percent of the total phosphorus was removed by sodium aluminate and alum at aluminum to phosphorus ratios ranging from 0.45 to 1.9 and 0.8 to 1.75, respectively. The percent removal, however, also depended upon the influent phosphorus content, as indicated by the fact that a reduction of almost 94 percent was effected by alum at an aluminum to phosphorus ratio of 1.3 when the influent concentration was 15.3 mg/1 P, the highest observed in the studies.

### TABLE VII

### REMOVAL OF PHOSPHORUS BY CHEMICAL PRECIPITATION IN THE ACTIVATED SLUDGE AERATION CHAMBER#

| Length of Run | Precipitant | | Mixed Liquor Solids | | COD | | | Total Phosphorus | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Added | Al/P | Total | Volatile | Influent | Effluent | Removal | Influent | Effluent | | Filtered Effluent | |
| days | mg/l | ratio | mg/l | mg/l | mg/l | mg/l | % | mg/l | mg/l | Removal % | mg/l | Removal % |
| Control | | | | | | | | | | | | |
| 39 | N/A | N/A | 2260* | 1800* | 350 | 30.9 | 91.2 | 11.7 | 8.1 | 30.8 | -- | -- |
| Sodium Aluminate | | | | | | | | | | | | |
| 15 | 17.6 | 0.44 | 3000 | -- | 339 | 24.7 | 92.7 | 11.4 | 4.17 | 63.4 | -- | -- |
| 13 | 35.2 | 0.69 | 3000 | -- | 359 | 29.0 | 91.9 | 14.4 | 2.96 | 79.4 | -- | -- |
| 12 | 35.2 | 0.76 | 3000** | 1800** | 415 | 30.4 | 92.7 | 13.1 | 3.55 | 72.9 | -- | -- |
| 8 | 52.7 | 1.05 | -- | 1800 | 440 | 35.5 | 91.9 | 14.3 | 2.85 | 80.1 | -- | -- |
| 12 | 52.7 | 1.40 | -- | 1800 | 296 | 15.3 | 94.8 | 10.7 | 1.62 | 84.9 | -- | -- |
| 10 | 52.7 | 1.43 | 3000 | -- | 475 | 22.6 | 95.2 | 10.5 | 1.82 | 82.7 | -- | -- |
| 10 | 52.7 | 1.43 | 4000 | -- | 475 | 23.0 | 95.2 | 10.5 | 1.52 | 85.5 | -- | -- |
| 10 | 52.7 | 1.43 | 5000 | -- | 475 | 23.2 | 95.1 | 10.5 | 1.40 | 86.7 | -- | -- |
| 10 | 70.2 | 1.89 | -- | 1800 | 299 | 14.4 | 95.2 | 10.6 | 1.08 | 89.8 | -- | -- |
| Alum | | | | | | | | | | | | |
| 10 | 134 | 0.82 | -- | 2000 | 587 | 18.8 | 96.8 | 15.3 | 2.14 | 86.0 | 1.78 | 88.4 |
| 10 | 188 | 1.14 | -- | 2000 | 587 | 18.2 | 96.9 | 15.3 | 1.34 | 91.2 | 1.05 | 93.1 |
| 10 | 215 | 1.31 | -- | 2000 | 587 | 17.8 | 97.0 | 15.3 | 0.98 | 93.6 | 0.69 | 95.5 |
| 12 | 161 | 1.75 | 3000 | -- | 376 | 25.5 | 93.2 | 8.6 | 0.98 | 88.6 | -- | -- |
| 12 | 161 | 1.75 | 4000 | -- | 376 | 25.8 | 93.1 | 8.6 | 0.93 | 89.2 | -- | -- |
| 12 | 161 | 1.75 | 5000 | -- | 376 | 20.5 | 94.5 | 8.6 | 0.87 | 89.9 | -- | -- |

\# Average values are given.

* MLSS were controlled during the first 19 days of the run and MLVSS were controlled thereafter.

** MLSS were controlled during the first 4 days of the run and MLVSS were controlled thereafter.

Theoretically, one mole of aluminum will react with one mole of phosphorus to form aluminum phosphate; this is shown by the following equation proposed by Tenney and Stumm (17):

$$Al^{+3} + H_nPO_4^{-(3-n)} = AlPO_4 + nH^+$$

According to these investigators this ratio applies not only to orthophosphate but to pyrosphosphate, metaphosphate, and tripolyphosphate as well. Barth and Ettinger (19) have also reported that excellent phosphorus removal (a residual of less than 1.0 mg/l P) resulted by the addition of sodium aluminate at an aluminum to phosphorus ratio of one to one (see Table II, p. 16). Ratios of 1.3 and 1.9 for alum and sodium aluminate were, however, required in the present investigation in order to obtain effluent phosphorus concentrations of approximately 1.0 mg/l P. The fact that a significant portion of the phosphorus present in the sewage employed by Barth and Ettinger was added in the form of sodium tripolyphosphate may account for the greater efficiency observed by these investigators, and it is possible that a lower efficiency may have resulted in unfortified domestic sewage. This is substantiated by the findings of subsequent full-scale plant studies by the Federal Water Pollution Control Administration (44) which indicated that a 1.8 aluminum to phosphorus ratio was required in order for sodium aluminate to remove 85 to 90 percent of the influent phosphorus. Eberhardt and Nesbitt (18) have also found aluminum to phosphorus ratios of 1.5 or greater necessary when using alum as the precipitant in various activated sludge treatment systems (see Table I, p. 14). The need for aluminum concentrations higher than the theoretical may be explained on the basis of competing demands for aluminum, such as the formation of aluminum hydroxide and the reaction of aluminum with the ionogenic groups on the surface of the activated sludge cells (17).

Increasing doses of the precipitants removed progressively less additional quantities of phosphorus. This is emphasized by the decreasing slope of the curves in Figure 11 where the residual phosphorus is plotted against the aluminum to phosphorus ratio. The minimum residual phosphorus concentrations which were obtained with alum and sodium aluminate were 0.9 and 1.1 mg/l P and required aluminum to phosphorus ratios of at least 1.3 and 1.9, respectively. For all practical purposes, higher concentrations of alum did not produce a lower phosphorus residual in the effluent and it would seem that the same would have been true for higher concentrations of sodium aluminate. Therefore, it is apparent that on a per milligram per liter of phosphorus removed basis, the precipitants were considerably more efficient when higher residuals remained in the effluent. The allowable phosphorus concentration in the effluent from a sewage treatment plant must be determined on the basis of the requirements for eutrophication control and would depend on the available dilution, the concentration of phosphorus already present in the receiving water, and the maximum allowable phosphorus concentration in the water to prevent algal blooms. Prolific algal growth has been reported to occur at phosphorus concentrations as low as 0.01 to 0.1 mg/l P (8, 12); however, much work still remains to be done on this important aspect of eutrophication control.

On an available aluminum basis, alum was more effective than sodium aluminate. This is shown in Figure 11 for the activated sludge studies and in Figure 10 (p. 55) for the jar studies. The reason for the difference in the phosphorus removal efficiency of sodium aluminate and alum can not be explained on the basis of the findings of this

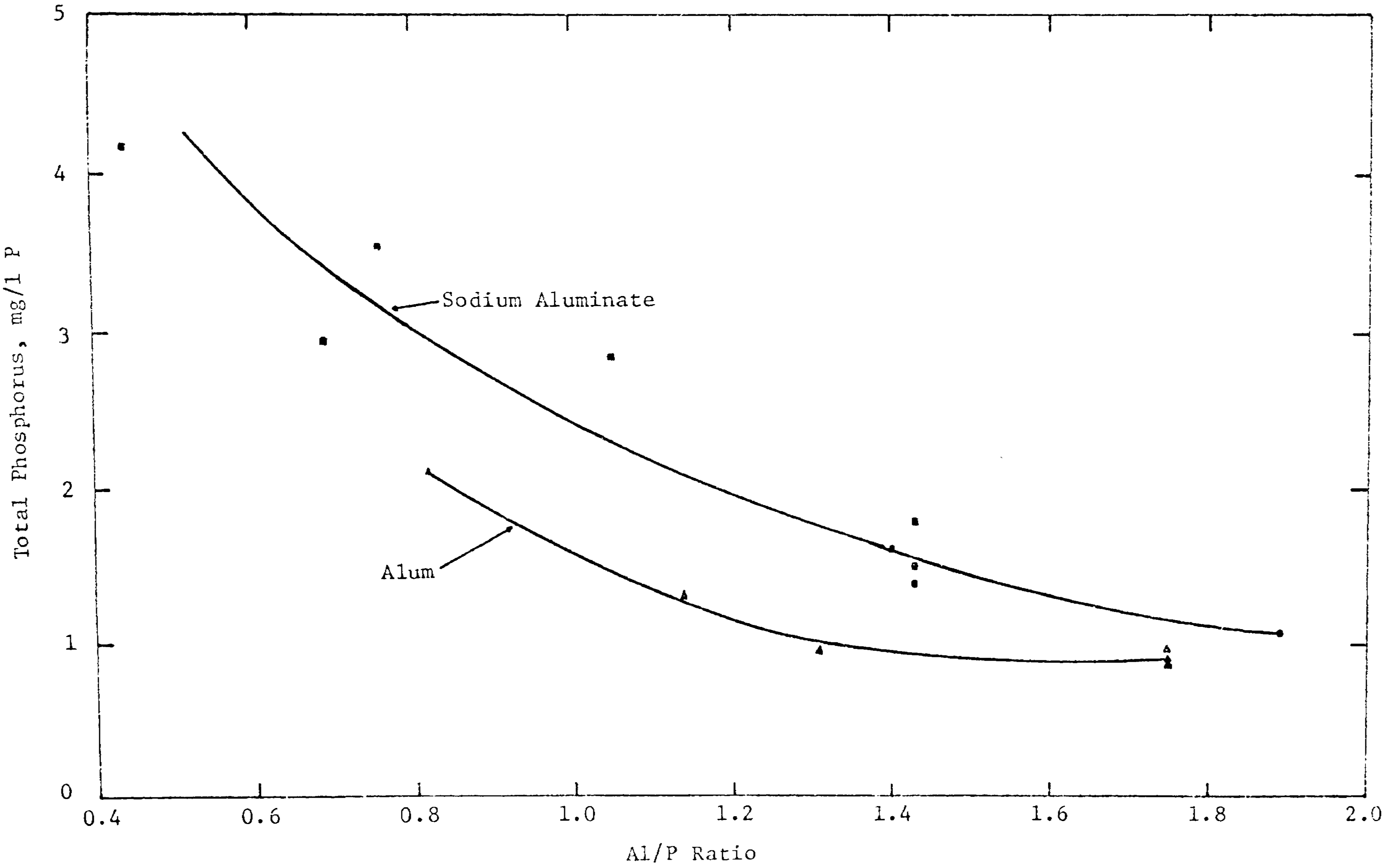

Figure 11. EFFECT OF ALUMINUM TO PHOSPHORUS RATIO ON TOTAL PHOSPHORUS RESIDUAL IN EFFLUENT FROM ACTIVATED SLUDGE TREATMENT

investigation. An exception to the higher removal efficiency of alum was noted in jar tests 7 and 8 in which a mixture of unacclimated sludge solids and settled domestic sewage was treated with the two precipitants (see Table VI, p. 53).

In spite of the higher efficiency of alum on an available aluminum basis, sodium aluminate is the more economical precipitant when the molecular weight and cost of the chemicals are considered. As has been previously stated, aluminum to phosphorus ratios of 1.3 for alum and 1.9 for sodium aluminate were required to produce an effluent phosphorus concentration of 1.0 mg/l P. On this basis, and taking into account the molecular weights of the commercially available (50, p. 918) alum $[Al_2(SO_4)_3 \cdot 14H_2O]$ and sodium aluminate $(Na_2O \cdot Al_2O_3)$ which are 594.4 and 163.9, respectively, 100 pounds of alum would be equivalent to 40.3* pounds of sodium aluminate. Therefore, considering an approximate cost of $42.00 per ton of alum and $2.70 per 100 pounds of sodium aluminate (51), the corresponding cost of alum and sodium aluminate will be $2.10 and $1.09 or an approximate dollar ratio of 2 to 1.

The removal of phosphorus increased slightly as the MLSS concentration in the aeration chamber increased (Table VII). At 3000, 4000, and 5000 mg/l MLSS, 82.7, 85.5, and 86.7 percent of influent phosphorus was removed with sodium aluminate, and 88.6, 89.2, and 89.9 percent was removed with alum. The larger separation in percent removal observed when sodium aluminate was used was the result of an abrupt increase of 4 mg/l P in the influent phosphorus concentration on the 7th and 8th days of the sodium aluminate study; however, a similar increase in influent

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* $100 \times \frac{163.9}{594.4} \times \frac{1.9}{1.3} = 40.3$ pounds.

phosphorus during the last six days of the alum study had little effect (see Figure 6, p. 45). Because the MLVSS which are a measure of the biologically active portion of the MLSS constituted essentially the same fraction of the total solids, it could not be determined whether the higher removal efficiency observed at higher MLSS concentrations was the result of increased biological uptake or greater adsorption by the activated sludge mass. The presence of a higher suspended solids concentration adversely affected the removal of phosphorus in the jar studies when sludge which had not previously been exposed to aluminum was used (see Figure 10, p.55 ). It is possible that a portion of the aluminum was adsorbed by the unacclimated microbial cells and, consequently, was not available to precipitate phosphorus; however, this does not explain the greater effect of suspended solids on the removal efficiency of alum as compared to sodium aluminate.

The addition of alum and sodium aluminate significantly decreased the volatile fraction in the MLSS to a level of approximately 50 percent, as compared to 80 percent in the control unit. The settling characteristics of the activated sludge remained good throughout most of the studies as indicated by sludge volume index (SVI) values of 50 to 180 which are within the limits considered normal for activated sludge. The SVI was found to depend upon the available organic food supply and generally increased as the COD increased.

The visual appearance of the effluent from the various units exposed to the two chemicals was excellent. Filtration of the effluent in the alum study indicated that the majority (73 to 83 percent) of the phosphorus present in the effluent was in a soluble form (see Table V, p. 48 ). This is contrary to the findings by Eberhardt and Nesbitt (see Table I, p. 14) who reported that when alum was added directly to the activated sludge aeration chamber, highly turbid effluents resulted and were accompanied by low phosphorus removals of 50.5, 42.1, and 15.3 percent at aluminum to phosphorus ratios of 1.88, 2.37, and 2.09, respectively. When the effluent was filtered, however, the removal in all systems was found to be greater than 99 percent. Turbid effluents were never a problem in this investigation.

The performance of the activated sludge units from the standpoint of their ability to reduce the pollutional organic matter present in the influent sewage remained excellent throughout the studies as shown by the resulting COD removals which averaged well in excess of 90 percent (Table VII). It is significant that these COD removals were accomplished in spite of the fact that high influent COD values were present on several occasions. The high COD values observed in a number of the settled domestic sewage samples were probably caused by digester supernatant return. Although it was attempted to collect sewage when supernatant was not being returned, this was not always feasible. The addition of alum and sodium aluminate did not adversely affect the removal of COD in the units, in fact it may even have slightly increased it; this is illustrated in Figure 5 (p. 40) where COD data from both a control and two units which received sodium aluminate were plotted. Previous investigators (18, 19) have also reported that the addition of aluminum precipitants had no noticeable effect on COD removal; however, the test and control units were not maintained in parallel in those studies as was the case in the early part of the present investigation.

No attempt was made to regulate the pH in the activated sludge aeration chamber but the pH of the mixed liquor was recorded to determine if the addition of sodium aluminate or alum had a significant effect. The pH values remained in the range of 7.3 to 8.2 throughout all studies and little variation was noted between the control, sodium aluminate, and alum units. This range was higher than the optimum pH of 5 to 6 for the formation of aluminum phosphate reported by Tenney and Stumm (17); however, jar studies conducted as part of this investigation indicated that the optimum pH for phosphorus precipitation in the Rolla sewage ranged from 6.4 to 7.5 for sodium aluminate and from 5.8 to 7.2 for alum. The pH in the aeration chamber was within or near the upper limits of these ranges, indicating that pH did not greatly influence the phosphorus removal efficiency of the precipitants employed.

# VI. CONCLUSIONS

On the basis of the results obtained in this investigation, the following conclusions were drawn:

1. Sodium aluminate and alum added directly to the activated sludge aeration chamber were capable of precipitating phosphorus and effecting a sizeable reduction in the phosphorus content of the influent sewage. The degree of phosphorus removal depended primarily upon the type of precipitant and the aluminum to phosphorus ratio employed, and the influent phosphorus concentration.
2. Aluminum to phosphorus ratios in excess of the stoichiometric one to one requirement for the formation of aluminum phosphate were needed in order to obtain a low residual total phosphorus concentration in the effluent. Ratios of 1.3 and 1.9 were required with alum and sodium aluminate to produce a minimum residual phosphorus concentration in the range of 1.0 mg/l P.
3. On an available aluminum basis, alum was more effective in removing phosphorus than sodium aluminate, but sodium aluminate was more economical than alum when molecular weight and cost were taken into account. The chemical cost for equivalent phosphorus removals would be approximately one-half as much with sodium aluminate as with alum.
4. The mixed liquor suspended solids concentration in the activated sludge aeration chamber had very little effect on the removal of total phosphorus. An increase in the MLSS concentration from 3000 to 5000 mg/l resulted in an increase in phosphorus removal from 83 to 87 percent when sodium aluminate was used and from 89 to 90 percent when alum was employed.

5. The addition of sodium aluminate and alum significantly decreased the volatile fraction in the MLSS to a level of approximately 50 percent, as compared to 80 percent which was maintained in a control unit.
6. The presence of sodium aluminate or alum did not adversely affect the chemical oxygen demand removal efficiency of the activated sludge system but may, in fact, have increased it slightly; while the average influent COD values varied from 300 to 600 mg/l, the resulting COD removals averaged in excess of 90 percent.
7. The pH of the mixed liquor in the activated sludge aeration chamber was not significantly changed by the addition of sodium aluminate or alum but remained in the 7.3 to 8.2 range which was essentially the same as that observed in a control unit. On the basis of jar studies, the optimum pH for phosphorus precipitation in the Rolla sewage with sodium aluminate and alum ranged from 6.4 to 7.5 and from 5.8 to 7.2, respectively.
8. The addition of aluminum to the aeration chamber was an effective method which could be readily integrated into the activated sludge process and required little additional equipment.

# VII. RECOMMENDATIONS FOR FUTURE RESEARCH

This investigation has established, on the basis of continuous flow bench-scale studies, that the addition of alum or sodium aluminate to the activated sludge aeration chamber was an effective means of reducing the phosphorus concentration in the waste. In the course of the investigation it became apparent that the research areas outlined below required further study.

1. The actual phosphorus removal mechanism should be ascertained and the relationship between the precipitant, microbial floc, and precipitate and their effect on the phosphorus removal process should be determined.
2. Phosphorus removal by chemical precipitation in the activated sludge process should be further evaluated in plant-scale studies and emphasis should be placed on methods for sludge treatment and disposal.
3. Further investigations are necessary to determine to what extent and at what concentration phosphorus is limiting to algal blooms. Knowledge of the minimum allowable phosphorus concentration is necessary in determining an acceptable phosphorus residual in sewage.

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