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THE FATE OF PHOSPHORUS IN SEWAGE TREATMENT PROCESSES

Part III

Post-Aeration, Anaerobic Digestion, and Preliminary Clean Solution Precipitation Experiments

by

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I. INTRODUCTION

SCOPE OF REPORT

This report will cover three aspects of the general topic of phosphorus removal in wastewater treatment processes. The report will summarize experimental work conducted between August 1968 and December 1969 under a Soap and Detergent Association Donation in support of research entitled "The Fate of Phosphorus in Sewage Treatment Processes." This work involved investigations into three major areas:

1. Phosphate precipitation from activated sludge effluent by a post-aeration scheme. This research was undertaken to determine whether it would be possible to take advantage of chemical precipitation phenomena observed in the enhanced removal of phosphate by activated sludge treatment in the design of a tertiary waste treatment scheme for phosphate removal.

2. The fate of phosphate in digesters with special reference to the fate of phosphate introduced into the digesters as waste activated sludge from processes achieving enhanced phosphorus removal (coprecipitation of calcium phosphate in activated sludge) or employing a post-aeration process for phosphate removal. This research effort resulted from the observation that significant releases of phosphate typically take place from the solid to the liquid phase in anaerobic digesters. Consequently, recycle of a significant fraction of the phosphate that enters the digesters takes place when the digester supernatant is returned to the head end of the treatment plant. The effectiveness of enhanced phosphate removal in an activated sludge aeration basin would be reduced if the digester supernatant returns a large part of the "already removed" phosphate to the plant in the digester supernatant stream.

3. Preliminary investigations on the influence of inorganic wastewater constituents on the rate and extent of calcium phosphate precipitation in model systems representative of typical wastewaters. This work was of a preliminary nature and since further work by one of the authors of this report and by others appears to have significantly advanced the knowledge of this area of research, these data (which in themselves do not present an adequate description of the phenomena encountered) will be discussed in the light of these more recent experimental data.

ACKNOWLEDGMENTS

The investigation was conducted at the Sanitary Engineering Research Laboratory, University of California and was supported in a donation from the Soap and Detergent Association. Mr. Arnold B. Menar was Project Manager. Professor David Jenkins was Project Director and Faculty Investigator.

The authors express their appreciation to Mr. Franklin Loo for his technical assistance.

II. POST-AERATION EXPERIMENTS

OBJECTIVES

The objective of the post-aeration experiments was to determine whether it would be possible to take advantage of a calcium phosphate precipitation mechanism that had been suggested in studies of the enhanced removal of phosphorus by activated sludge (Menar and Jenkins[1]) in the design of a chemical precipitation process for phosphate removal. The basis for the design rested in two observations made during the testing of the calcium phosphate precipitation mechanism for enhanced phosphorus removal by activated sludge. These were:

1. That increased activated sludge aeration rates caused increases in pH because of reduction of mixed liquor CO_2 concentrations by CO_2 stripping in the higher air flows, and
2. that removal of the precipitated calcium phosphate was made possible by its association with the flocculent activated sludge matrix.

It was postulated that a post-aeration process, in which secondary effluent was aerated, in which chemicals could be dosed if necessary to precipitate calcium phosphate, and in which a small amount of return activated sludge was fed to aid in the flocculation of the precipitate, would provide a more suitable environment for calcium phosphate precipitation and precipitate removal than would a typical activated sludge aeration basin. This is because in such a basin the CO_2 concentration would be lower than in the aeration basin and because in the sludge settled from such a basin the microorganism concentration would be so low that CO_2 production and therefore pH reduction in the sludge blanket at the bottom of a clarification basin would not reach levels that would cause a significant release of phosphate from the underflow into the treated effluent.

EXPERIMENTAL FACILITIES

To meet these objectives a pilot-scale activated sludge plant with post-aeration followed by a sedimentation basin was constructed and operated on settled sewage from the Sanitary Engineering Research Laboratory primary sedimentation basin. The aeration, post-aeration, secondary sedimentation, and final sedimentation basins were constructed from plastic bins (see Figure 1). The aeration basin consisted of three 30-gal bins in series (with an effective aeration volume of 225ℓ) and the secondary sedimentation basin consisted of one 45-gal bin in which a conical concrete bottom had been poured.

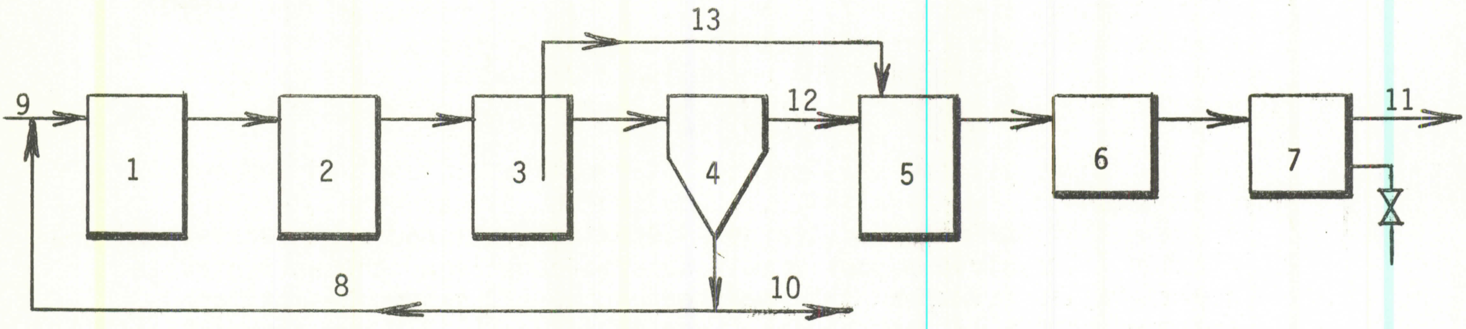

Figure 1. Schematic Diagram of Post-Aeration Activated Sludge Plant

1, 2, 3. Aeration basins.
4. Secondary sedimentation basin.
5. Post-aeration basin.
6, 7. Final sedimentation basins.
8. Return activated sludge.
9. Influent (SERL primary effluent).
10. Waste activated sludge.
11. Final effluent.
12. Activated sludge effluent.
13. Activated sludge to post-aeration for precipitate collection.

The effective volume of the secondary sedimentation basin was 90ℓ. The post-aeration basin consisted of one 30-gal bin with an effective volume of 75ℓ; and the final sedimentation basin was constructed from two plastic bins in series — the first was a 22ℓ bin (effective volume, 40ℓ). The term "final sedimentation" in this report will refer to the sedimentation basin that follows post-aeration.

Influent sewage, return, and waste activated sludge were pumped by peristaltic pumps; flows between the aeration basin compartments, the secondary sedimentation basin, and the final sedimentation basin were accomplished by gravity. The secondary effluent was pumped to the post-aeration basin using a submersible pump. Samples of influent, secondary effluent, and final effluent were taken every 15 min by a sampling pump operated on a cycle timer which pumped the samples directly into refrigerated containers. Air was supplied by a 1/3 hp compressor capable of delivering 5.9 cu ft/min at 0 psig. When a greater air rate was required it was possible to supplement this source with a house compressed air supply.

EXPERIMENTAL DESIGN

During each of the experiments the performance of the activated sludge process was characterized by organic loading (lb COD applied/lb MLVSS-day), hydraulic residence time (hr), mean cell residence time (days), substrate removal efficiency (%), and phosphorus removal efficiency (%). The performance of the post-aeration basin was characterized by phosphorus removal efficiency resulting from Ca(II) and OH^- or H^+ ion addition as liquid calcium chloride, sodium hydroxide, or hydrochloric acid, respectively.

Analyses of dissolved and total calcium, dissolved and total orthophosphate, pH, alkalinity, and dissolved oxygen were performed on samples of influent, activated sludge effluent, and post-aeration effluent. Dissolved magnesium was determined only on the activated sludge effluent and the post-aeration basin effluent. The activated sludge mixed liquor was characterized by analyses of MLSS and MLVSS. Analytical methods where not according to Standard Methods [2] are described in the Appendix.

The combined activated sludge, post-aeration basin units were operated at a given condition for at least 24 hr before any samples were taken. This was sufficient time to establish steady conditions since the activated sludge section was operated without disturbance and the only changes in operation that were made were in the post-aeration section of the treatment plant train. These changes usually took the form of alterations in chemical doses, changes in concentration of dosing solutions, and flow rates. Prior to the start of each set of operating conditions the post-aeration basin and final sedimentation basins were drained.

EXPERIMENTAL RESULTS

The mean operating data for the seven experimental runs are summarized in Table I. During each experimental run, dosing chemicals were added constantly at the indicated doses.

The activated sludge section of the plant behaved satisfactorily at all times with substrate removal rates varying from 0.24 to 1.15 lb COD/VSS-day and effluent dissolved COD concentrations ranging from 32 to 51 mg/ℓ. The effluent dissolved phosphate from the activated sludge section of the plant ranged from 0.2 to 0.37 mM. Since high removal of phosphate per se was not the major experimental objective, it was desired to determine what phosphate removals could be achieved at given chemical doses.

The nominal hydraulic residence time of the post-aeration basin was 2 hr (range 1.6 to 2.6 hr). Air was supplied to the basin at the rate of 4 cu ft/gal liquid treated and the temperature was maintained constant at 70°F. Various combinations of chemical additions were made with the objective of determining independently the effects of pH and the calcium concentration on phosphorus residuals.

TABLE I

MEAN OPERATING DATA FOR POST-AERATION SYSTEM

ACTIVATED SLUDGE SYSTEM		Experiment Number						
		1	2	3	4	5	6	7
Substrate Removal Rate	lb COD/lb MLVSS-day	0.56	0.38	0.56	1.15	0.26	0.22	0.26
Mean Cell Residence Time	days	4.5	10.7	3.8	3.7	7.1	7.2	19.0
Hydraulic Residence Time	hr	5.9	5.7	4.9	7.7	6.8	1.8	5.8
MLVSS	mg/ℓ	1210	1910	1620	336	1170	2670	2650
MLSS Volatile Fraction	%	84	84	86	87	83	79	81
Influent Total COD	mg/ℓ	208	217	249	184	126	177	193
Effluent Dissolved COD	mg/ℓ	41	40	51	47	45	38	32
Influent Total P	mM	0.38	0.38	0.42	0.34	0.23	0.41	0.38
Effluent Dissolved P	mM	0.34	0.33	0.38	0.30	0.20	0.37	0.34
Influent Total Ca	mM	0.68	0.63	0.61	0.66	0.81	0.80	0.75
Effluent Dissolved Ca	mM	0.65	0.6	0.65	0.69	0.82	0.80	0.71
Influent Total Mg	mM	--	--	--	--	--	--	--
Effluent Dissolved Mg	mM	1[a]	1[a]	0.74	0.8	1.24	1.13	1.11
Influent Total Alkalinity	mM	2.3	2.3	2.2	2.2	2.7	3.2	2.9
Effluent Dissolved Alkalinity	mM	1.4	1.2	1.4	1.8	1.6	1.3	1.3
Influent pH	--	6.8	6.8	7.0	7.1	7.7	7.7	7.6
Effluent pH	--	6.5	6.7	6.5	7.0	7.4	7.6	7.6

TABLE I (continued)

POST AERATION SYSTEM		Experiment Number						
		1	2	3	4	5	6	7
Hydraulic Residence Time	hr	2.0	1.9	1.6	2.6[b]	2.3	1.8	1.9
Aeration Rate	cu ft/gal	4	4	4	4	4	4	4
Temperature	°F	70	70	70	70	70	70	70
Ca added	mM	1.65	1.56	1.79	2.49	2.55	2.59	2.42
Ca dose (Ca added and Ca present)	mM	2.30	2.16	2.44	3.18	3.37	3.39	3.13
OH^- or H^+ * dose	mM	3.24	6.27	2.63	0.67	0.79	12.8	9.82
Effluent Dissolved Mg	mM	--	--	0.78	0.84	1.29	0.10	0.48
Effluent Dissolved P	mM	0.042	0.036	0.17	0.19	0.21	0.008	0.026
Effluent Dissolved Ca	mM	1.3	0.63	2.24	3.04	3.60	0.73	0.57
Effluent Dissolved Alkalinity	mM	1.7	1.7	1.5	1.8	0.47	1.1	2.2
Effluent pH	--	9.0	9.75	8.0	7.6	6.8	11.4	10.5
Sludge Solids	mg/ℓ	175	160	123	102	39	190	126
Sludge P	% as P	7.5	12.1	6.8	6.0	2.1	5.3	7.3
Sludge Ca	% as Ca	20.6	18.2	11.8	11.9	13.8	24.7	26.0
Sludge Ca/P mole ratio	--	2.2	1.2	1.3	1.5	5.1	3.6	2.8
Influent Ca/Mg mole ratio	--	0.6	0.6	0.9	0.9	0.7	0.7	0.6
Post Aeration Reactor Ca/Mg mole ratio		1.3	0.6	2.9	3.6	2.8	7.3	1.2

[a] Assume

[b] Evidence of some low pH precipitation at highest Ca/Mg ratio

DISCUSSION

A discussion of the post-aeration experimental data will be made from both the practical and theoretical points of view. With reference to the former aspect, it is evident that additions of lime (or chemical additions to simulate an addition of lime) to achieve a pH in the region of 11 (as is common practice in phosphate precipitation in tertiary treatment processes) is not necessary (in this particular sewage) to produce phosphorus residuals of <2 mg/ℓ (the figure often quoted as being the residual dictated by a treatment objective of "80% P removal"). In this instance it was possible to achieve P levels of <2 mg/ℓ at pH 9 and at a total calcium concentration of 230 mg/ℓ as $CaCO_3$ — a calcium concentration which included 65 mg/ℓ Ca as $CaCO_3$ already present in the sewage and therefore represented an additional dose requirement of only 165 mg $CaCO_3$/ℓ. If this calcium dose is compared to the calcium (or lime) dose required to reach pH 11 (which would be the dose used if a typical tertiary phosphorus precipitation process were to be employed), it can be deduced from the data of Buzzel and Sawyer [3] that a lime dose of approximately 270 mg $CaCO_3$/ℓ would be required to reach pH of about 11 at this alkalinity (approximately 1.4 mM/ℓ). Thus for meeting the objective of <2 mg P/ℓ (which can be achieved at a pH of about 9 instead of at pH 11) a saving in lime dose of approximately 100 mg $CaCO_3$/ℓ can be realized. Moreover, the effluent pH is in a range in which it could be possibly discharged without adjustment downward — a step that would almost certainly be required if the effluent pH were 11.

The post-aeration experiments on the SERL sewage did illustrate that P residuals of much lower than 2 mg/ℓ could be achieved by increasing pH values to above 9. Indeed it appeared that phosphorus residuals (at the relatively constant calcium, alkalinity, and magnesium concentrations used in these experiments) were largely controlled by pH (Figure 2).

The use of a small amount of waste activated sludge (approximately 1% of the return activated sludge flow) or approximately 70 mg/ℓ on the basis of volatile suspended solids (VSS) concentration in the post-aeration basin as a precipitate collector for the precipitate from the post-aeration basin, was successful. A sludge with excellent settling characteristics was obtained at all pH values. Throughout the post-aeration experiments the final effluent suspended solids concentration averaged 55 mg/ℓ. There was no detectable release of soluble phosphorus from the post-aeration basin sludge into the final effluent following clarification of the post-aeration basin effluent. This indicates that pH decreases (if any) caused by CO_2 production from the activated sludge (precipitate collector) in the post-aeration basin sludge were not significant enough to produce any dissolution of calcium phosphate.

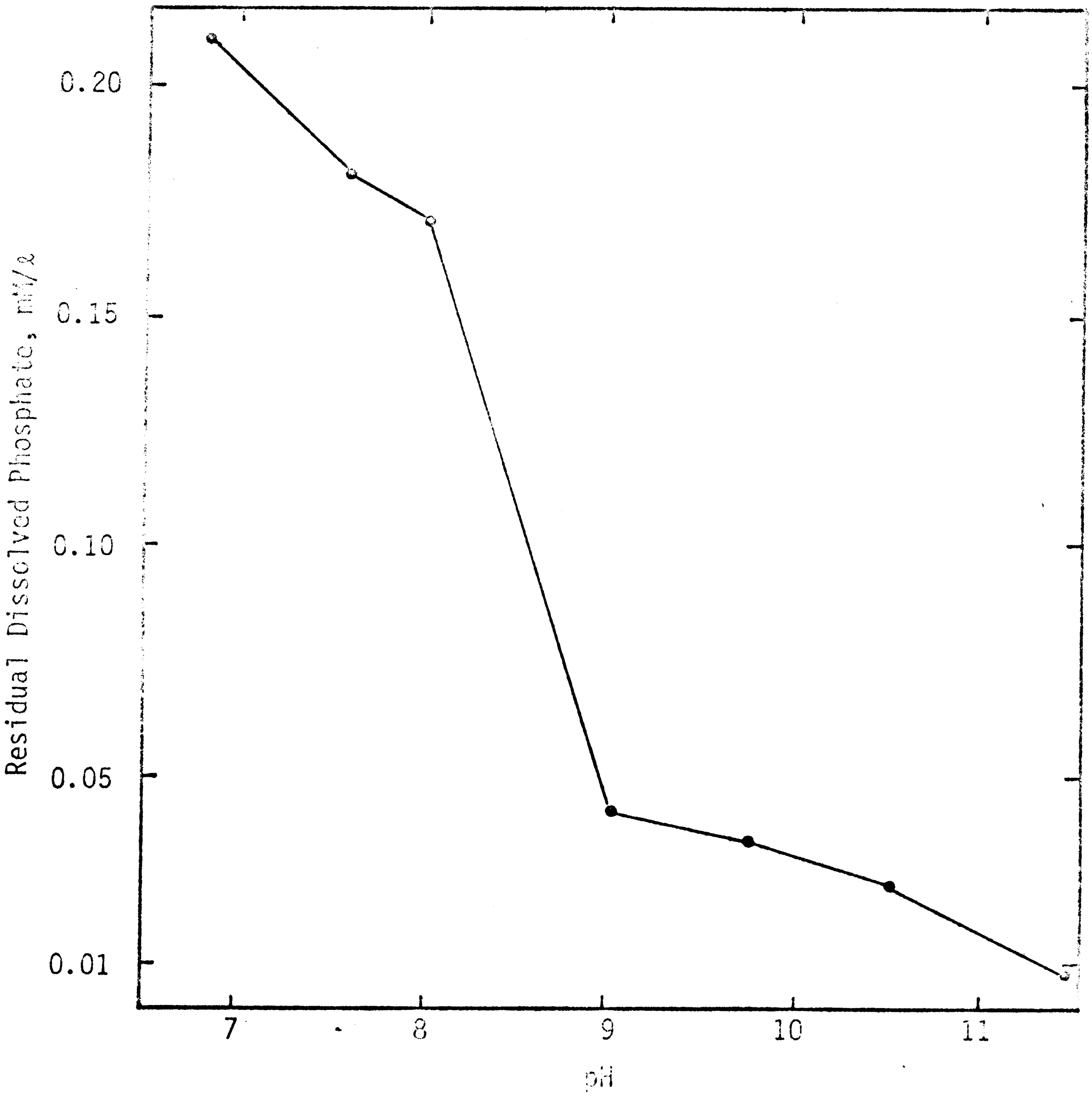

Figure 2. Effect of pH on Post Aeration Dissolved Phosphate.

In experiments 1, 2, 6, and 7 the computed experimental activity products indicate that $CaCO_3$ (calcite) precipitation is likely (Table II). The experimental data indicate that this indeed took place. Thus, in these experimental runs the sludge contained the highest percent calcium; these experiments showed the highest post-aeration basin solids content and effluent dissolved calcium concentrations from these four experiments were the four lowest of the seven experimental series.

It is not possible to indicate the nature of the precipitated phosphate phase. However, from activity product calculations (Table II) it can be seen that it is very unlikely that dicalcium phosphate (DCP) was the solid phase (at pH values >8) because in most of the experiments the liquid was undersaturated with respect to DCP. However, with respect to crystalline octacalcium phosphate (OCP) and hydroxylapatite (HAP) significant degrees of oversaturation exist. Lesser degrees of oversaturation exist with respect to tricalcium phosphate (TCP) in most of the experiments. It should be realized that while these figures indicate the possibility of precipitation of various calcium phosphate phases, they are based upon activity products derived from crystalline materials and it has been shown by numerous workers such as Ferguson _et al._ [4] and Leckie and Stumm [5] that calcium phosphate precipitation under conditions typified by these experiments results in amorphous or poorly crystalline solids phases and that the formation of crystalline solids is kinetically controlled.

Notwithstanding these observations, the data obtained by these experiments when plotted on the empirical correlation between $[Ca]P_T$* and pH (Figure 3) represent a perfect fit to the line derived from previous wastewater calcium phosphate precipitation experiments by Menar and Jenkins [1]. For data from the post-aeration experiments below pH 8, this empirical correlation appears to follow the line that would be predicted if DCP were the solid calcium phosphate phase controlling solution dissolved phosphate concentration. Interestingly, the activity product data also indicate oversaturation with respect to DCP below pH values of 8. It is suggested therefore that in this pH range DCP is the controlling calcium phosphate solid phase.

The chemical characteristics of the SERL sewage treated by post-aeration resemble those of the wastewater studied by Schmidt and McKinney [6] who used lime precipitation to achieve pH 9 to 10 in primary sedimentation basins without recycle of precipitated sludge. These authors reported that with low lime doses (approximately 150 mg $Ca(OH)_2/\ell$) and in the reported pH range, polyphosphates present in the raw wastewater inhibited $CaCO_3$ precipitation and redirected

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$*P_T = \sum [H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^\equiv]$

TABLE II

EXPERIMENTAL ACTIVITY PRODUCTS FOR POST-AERATION DATA

ACTIVITY PRODUCT						
Experiment No.	pH	Dicalcium Phosphate (DCP)	Tricalcium Phosphate (TCP)	Octacalcium Phosphate (OCP)	Hydroxylapatite (HAP)	Calcite ($CaCO_3$)
1	9.00	7.3	24.0	43.6	42.5	6.1
2	9.75	7.8	24.0	44.1	41.9	5.9
3	8.00	6.5	23.3	43.0	42.7	7.5
4	7.60	6.8	24.7	43.4	44.8	7.7
5	6.80	6.7	26.8	39.0	48.7	8.0
6	11.40	11.8	33.2	59.3	56.1	3.3
7	10.50	8.2	24.3	45.0	41.9	6.3

Saturation Activity Products

DCP	6.9
TCP	26.0
OCP	57.8
HAP	46.9
$CaCO_3$	8.4

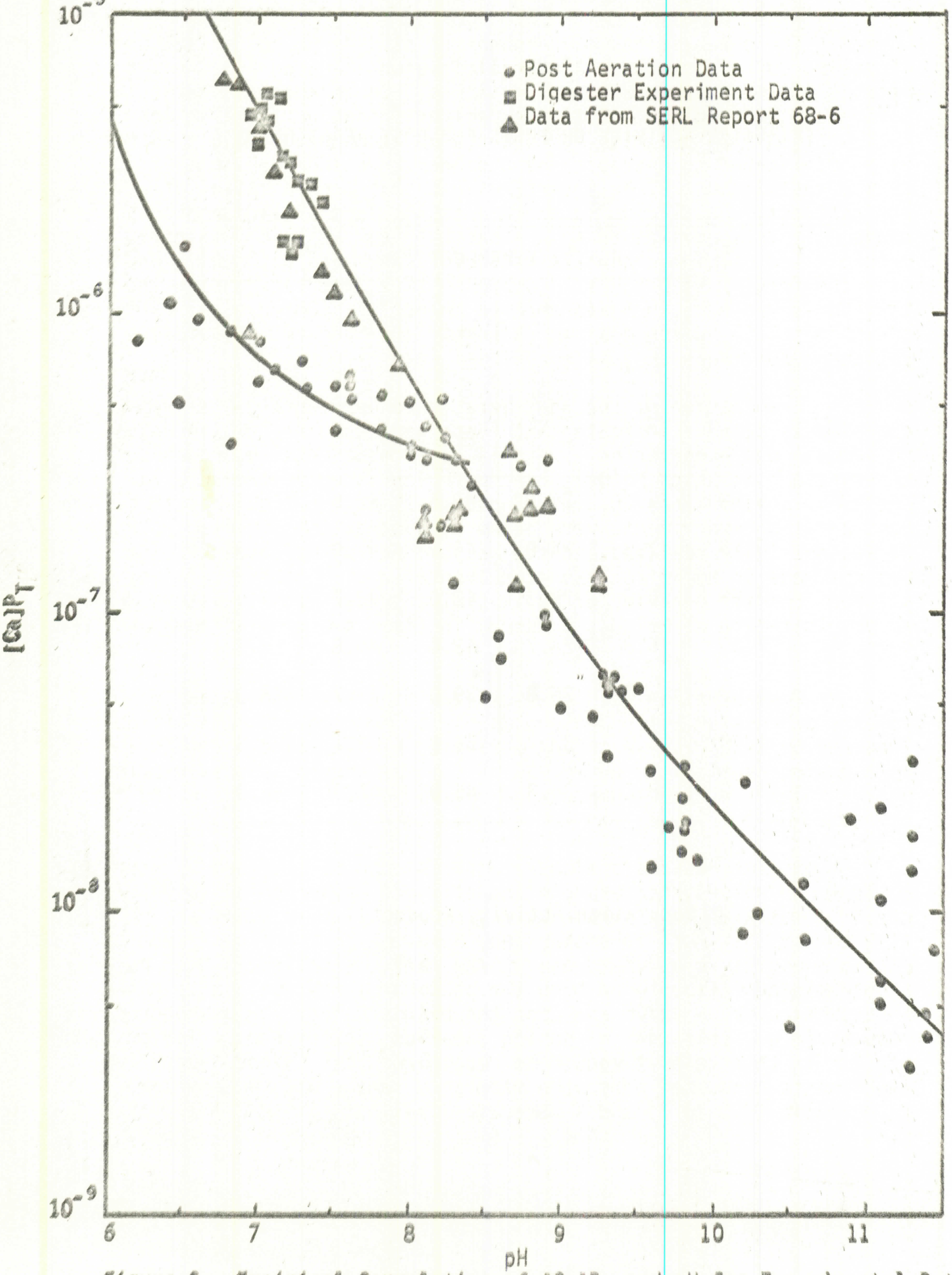


Figure 3. Empirical Correlation of $[Ca]P_T$ and pH for Experimental Data.

the calcium to calcium phosphate precipitation. Their hypothesis was supported by their experimental data which showed that the amount of $CaCO_3$ precipitation was far smaller than that predicted by equilibrium data and by previous wastewater treatment experiences.

The observations of Ferguson et al. [4] on the effect of magnesium on calcium phosphate precipitation are also pertinent to the results of the post-aeration experiments. These authors showed in laboratory batch clean solution experiments that waters with low Ca/Mg ratios (<2) and high Mg contents an increase of Mg concentration at pH 9.5 tended to decrease the phosphorus residual (Figure 4). It was postulated that Mg interferes with the precipitation of calcite and redirects the calcium to preferentially form a calcium phosphate phase. It is suggested that in a batch system at this pH, initially precipitated calcium phosphate will redissolve and $CaCO_3$ will precipitate over the first 1 to 2 hours. Combining this observation with the fact that Mg is known to increase calcite solubility (Chave et al. [7]) and to inhibit $CaCO_3$ phase changes (Bischoff and Fyfe [8]) provides a rationale for these phosphate residual results.

Examination of the post-aeration experimental data from experiments 6 and 7 indicate that these were the only two in which Mg removal was experienced — this is in accordance with previous observations in which $Mg(OH)_2$ precipitation is not detected until the pH is greater than 10.3. Unfortunately at the time that these post-aeration experiments were being conducted, the importance of Mg was not fully realized and the measurement of Mg concentration was not made in the first two experimental runs. However, it may be assumed from the behavior of Mg in similar experimental systems that no precipitation of $Mg(OH)_2$ occurred in these two runs at pH 9 and 9.75.

Post-aeration with chemical addition has been demonstrated to be a process by which phosphorus may be removed from the effluent produced by an already existing activated sludge plant. Using lime as a dosing chemical at pH values of 10.5 it should be possible to attain soluble effluent phosphorus residuals of 0.5 mg P/ℓ using this process.

Higher residuals (lower removals) can be obtained by operating at lower pH values; for example the effluent criterion of <2 mg P/ℓ could be met with this sewage by dosing with lime to achieve a pH of 9 to 9.5. It must be emphasized, however, that effluent chemical characteristics (e.g., hardness, Ca/Mg ratio, alkalinity) will have a determining influence on both the phosphorus residuals attainable at a particular pH value and upon the best strategy for phosphorus removal (e.g., selection of dosing location, dosing chemicals, pH, etc.). In this vein it should be recognized that the post-aeration experiments conducted here were made on a sewage with a very low Ca/Mg ratio (0.5 to 1) and a moderate alkalinity (1 to 2 mM).

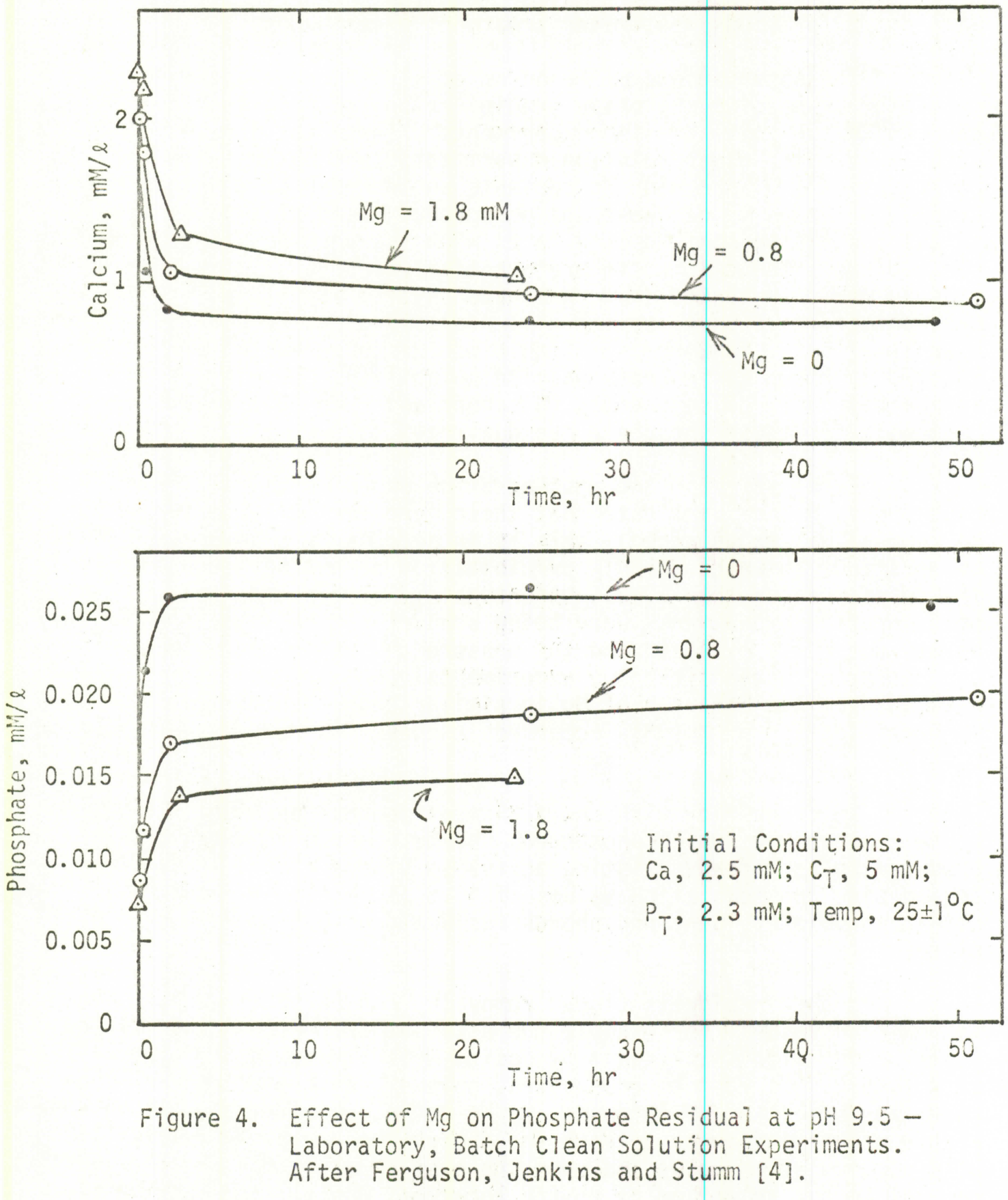


Figure 4. Effect of Mg on Phosphate Residual at pH 9.5 — Laboratory, Batch Clean Solution Experiments. After Ferguson, Jenkins and Stumm [4].

When considering phosphorus removal strategy one must work within three major constraints: 1) the present treatment capability, 2) the future effluent requirements, and 3) the water chemistry. One can conceive of two possible situations where post-aeration with chemical addition might be considered as a process alternative for phosphorus removal.

1. Existing primary-secondary treatment plant with anaerobic digestion on which an additional effluent requirement of 2 mg P/ℓ is imposed.

   While post-aeration might be considered for this treatment situation, it would probably not compete well with a scheme in which phosphorus precipitants were added directly to the treatment units because P residuals of this magnitude can be met in this fashion without construction of additional basins as would be necessary for a post aeration scheme. If this is the case, then lime and/or other chemicals designed to form a calcium phosphate precipitate would not be the chemicals of choice because of the release of phosphate from calcium phosphates that takes place in the secondary clarifier sludge blanket and during anaerobic digestion. Alum or ferrous or ferric salts added to the aeration basin would yield the best results.

2. Existing primary-secondary treatment plant with anaerobic digestion on which an additional effluent requirement of 0.5 mg P/ℓ is imposed.

   Here the use of chemical addition to primary or secondary treatment units cannot be relied upon to produce the desired effluent phosphorus residual. Moreover, the attainment of such a low phosphate residual by chemical precipitation in the secondary treatment unit would raise the danger that phosphate starvation conditions might result in the biological treatment reactor. For this case a tertiary precipitation/flocculation/sedimentation process must be considered and a post-aeration basin might offer a convenient reactor in which to conduct the precipitation flocculation steps. While the choice of precipitant and operating pH will be largely dictated by the chemical composition of the wastewater and by local chemical prices, the post-aeration basin offers the capability for using the phosphate precipitants already present in the wastewater, i.e., the calcium hardness. For example, if the wastewater were of the same composition as that at San Antonio, Texas where Ferguson [9] has suggested that the low pH precipitation (pH 7.7 to 8.5) of phosphate to dissolved residuals of <1 mg P/ℓ takes place in the aeration basin by the formation of a carbonate apatite, it should be possible to devise a post-aeration scheme that will remove phosphate to these low levels without the danger of release from sludge in the secondary clarifier. In such a scheme the activated sludge system would be operated to produce complete oxidation of ammonia. The production of NO_3^- (a strong acid) from NH_3 (a weak base) would result in the titration of some alkalinity and therefore an alkalinity reduction during secondary treatment. Precipitation of calcium phosphate could be avoided in the aeration basin by keeping aeration rates low enough to maintain pH levels below 7.5 In the post-aeration basin the pH would be raised to 7.8 to 8.0 by aeration and the precipitated calcium phosphate would be removed by enmeshment in a small amount of waste activated sludge fed into the post-aeration basin. The substitution of carbonate into the precipitated carbonate apatite would be reduced since a significant reduction in alkalinity will have been achieved during secondary treatment. In this case, phosphate removal would be achieved without chemical addition but with only a judicious adjustment of pH because sufficient calcium was present in the wastewater. However, in soft, low Mg, low alkalinity wastewater the addition of Ca may be necessary to reach low phosphate residuals. Post-aeration with Ca addition (as $CaCl_2$, not as lime) and pH control to approximately pH 8 would be an ideal process of phosphate removal in this type of situation. The use of post-aeration in conjunction with chemical additives other than those designed to produce calcium phosphate precipitation should be considered. For example, it is conceivable that post-aeration would offer an ideal physical arrangement for the homogenous generation of Fe(III) from Fe(II) as proposed for phosphate precipitation by the Dow Process (Wukasch [10]) and demonstrated by Singer and Stumm [11] to provide a more efficient scavenger system for phosphate than does the direct addition of Fe(III).

III. ANAEROBIC DIGESTION EXPERIMENTS

OBJECTIVES

The general objective of these experiments was to determine the fate of phosphorus during anaerobic digestion. Special attention was paid to the behavior of precipitated calcium phosphate introduced into the digester in the sludge from a post-aeration precipitation basin. Experiments were also conducted to determine whether recycle of phosphate in the supernatant from a digester treating a mixture of raw sludge, activated sludge, and post-aeration sludge could be reduced by supernatant aeration followed by sedimentation for solids separation prior to its return to the headworks of the plant. Preliminary data were obtained on the effect of dissolved calcium concentrations on the dissolved phosphate content of anaerobic digester liquors. Confirmation of the empirical relationship between $[Ca]P_T$ and pH found previously by Menar and Jenkins [1] for anaerobic, high CO_2 environments was sought.

EXPERIMENTAL RATIONALE

In a traditional primary-secondary sewage treatment flow scheme, the anaerobic digester is the receptacle for sludge streams from the primary and secondary treatment sections of the plant. In an activated sludge plant, these streams comprise the underflow of the primary clarifier (raw sludge) and the waste activated sludge stream. Two liquid streams emanate from the anaerobic digester – the digested sludge and the supernatant. The latter stream is generally returned to the headworks of the plant and recycled through the treatment process. Recycling of the supernatant stream leads to recycling of phosphate that has already been "removed" by incorporation into the primary and activated sludges. The magnitude of this recycling has been estimated by Jenkins et al. [12] to be 80 lb/day for a typical primary-secondary (activated sludge) anaerobic digestion combination which receives 1000 lb P/day (Figure 5). In comparison with wastewater, anaerobic digestor supernatant is a concentrated waste stream – several workers have reported that its phosphorus content appears to be in the neighborhood of 50 to 200 mg P/ℓ (Table III).

If phosphate removal schemes are superimposed upon, or appended to, typical primary-secondary sewage treatment processes and the anaerobic digester remains as a receptacle for sludge streams, then even more phosphorus will be channelled to the anaerobic digester. Table IV illustrates the estimates of Jenkins et al. [12] on the magnitude of this increase in phosphorus load to the anaerobic digester when calcium phosphate precipitation occurs in the activated sludge process. These

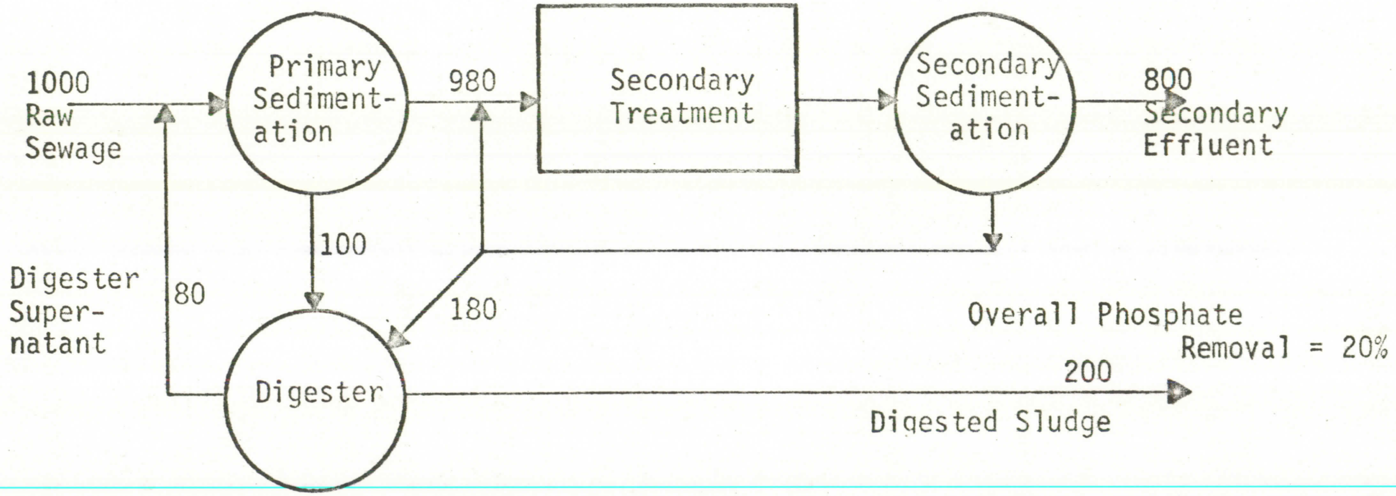


Figure 5. Distribution of Phosphorus in Secondary Treatment Flows. (Figures in lb/day)

TABLE III

DIGESTER SUPERNATANT PHOSPHATE CONCENTRATIONS

Reference	Total P mg/ℓ	Ortho P mg/ℓ
Johnson *et al.* [13]	225	42
Wukasch, [10]	100-200	--
Barth *et al*, [14]	170	--
Barth and Ettinger. [15]	50-100	--
Anon. (1969) FMC Corporation, [16]	15-120 (mean, 40)	--

TABLE IV

CHARACTERISTICS OF SLUDGES FROM CONVENTIONAL AND COMBINED CHEMICAL - BIOLOGICAL PHOSPHATE REMOVAL SCHEMES

Process	Phosphorus		Total #/MG	Process Solid				
	Influent mg/ℓ	Effluent mg/ℓ		Precipitate #/MG	Organic Volatile #/MG	P #/MG	Conc. %	Volume 1000 gal/MG
Conventional Primary	13	12	1250	--	875	8	5	3
Primary + Act. Sludge								
a) Conventional	12	10	700	--	500	17	1.5	5.6
b) High Rate	12	9	850	--	650	25	1.5	6.8
c) Enhanced* Phosphate Removal	12	1.2	1200	500	500	90	1.5	17.6

*Removal mechanism assumed to be calcium phosphate precipitation.

authors indicate an increase from about 20 lb P/MG waste treated to about 90 lb P/MG waste treated when phosphorus removal is increased from that expected from a typical primary-secondary waste treatment process train to that achieved by calcium phosphate precipitation in the activated sludge process to produce a phosphorus residual of about 1.2 mg/ℓ (such as that encountered at San Antonio, Texas).

It was the intent of this research to determine whether it would be possible to conduct phosphorus removal by chemical precipitation in a scheme such as that described in the post-aeration experiments earlier in this report, and still retain the anaerobic digester as a sludge treatment unit. To accomplish this, the anaerobic digester was operated on mixtures of activated sludge, primary sludge, and post-aeration sludge that would typically originate from a primary-secondary (activated sludge)-post-aeration waste treatment scheme. The levels of phosphorus and calcium in the sludge and supernatant were followed over a 7-month period. When it became evident that significant phosphorus was being carried into the supernatant (and would hence be subject to recycle through the treatment processes) effort was devoted toward devising techniques for supernatant treatment to decrease this phosphorus recycling.

MATERIALS AND METHODS

The anaerobic digestion experiments were conducted in a 10-liter laboratory fermenter which had an effective volume of 8 liters (Figure 6). The digester was located in a constant temperature room at 37°C. The digester was mixed by a centrifugal pump that operated for 2 1/2 min every 10 min. The entire digester and its appurtanences were mounted on a balance so that rapid determination of the sludge mass could be made. The digester was fed through an opening in its top; sampling and digested sludge withdrawal was conducted through a valve at the bottom of the unit. The gas produced during digestion was collected above 25% H_2SO_4 in a gas holder located outside the constant temperature room and kept under a slight positive pressure.

The digester was fed at an organic loading rate of 0.02 lb volatile matter (V_m)/cu ft-day with a mixture of raw sludge, activated sludge and post-aeration sludge that would be typical of the mixtures encountered in a primary-secondary treatment plant followed by post-aeration for phosphate removal. The digester was fed three times per week. Before each feeding the digester was mixed well. Feeding and digested sludge withdrawal were accomplished simultaneously, and after feeding and sampling the valves were closed, and the digester was mixed for a further 2 to 3 min. The performance of the anaerobic digester was characterized by organic loading (lb V_m/cu ft-day), hydraulic residence time (days), V_m destruction rate (lb V_m removed/cu ft-day), gas production rate (cu ft gas produced/lb V_m destroyed), pH, alkalinity, and materials balances

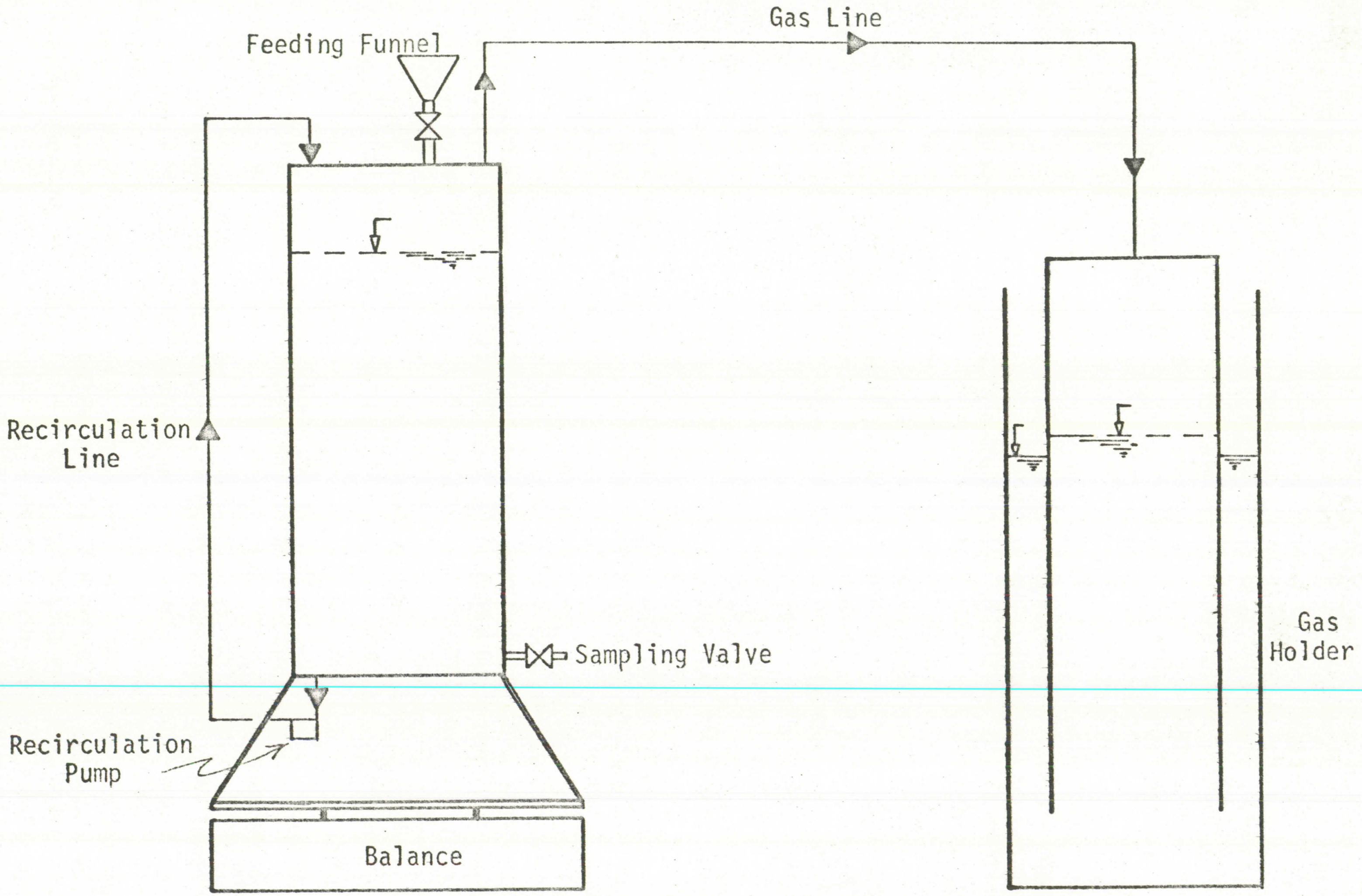


Figure 6. Schematic Diagram of Laboratory Anaerobic Digester.

on calcium and phosphate. Gas analyses were conducted once per month. Analyses of total volatile solids, total calcium, and total phosphate were conducted on all feedings and withdrawals from the digester. Alkalinity and pH measurements were made on supernatant samples obtained by settling the sludge withdrawn from the digester and settled for 48 hr at 4°C. When it was desired to conduct analyses of dissolved orthophosphate and dissolved calcium, digester supernatant samples were filtered through 0.45μ membrane filters (Millipore HA) prior to analysis.

RESULTS

The anaerobic digester was operated for a period of seven months — between July 1968 and February 1969 at an organic loading of 0.02 lb V_m/cu ft-day and a hydraulic retention time of 67 days. During this period, two series of experiments were conducted: between July 1968 and January 1969 the digester was operated at steady state on a feed that consisted of primary, secondary, and post-aeration sludges in the mixture described in Table V; from January 1969 to February 1969 the digester was fed with post-aeration basin sludge rich in calcium carbonate so that the effect of changes in pH and alkalinity on the distribution of phosphate in the digester supernatant could be studied. Throughout the entire experimental period the digester performed satisfactorily. Table VI illustrates the performance parameters and shows that satisfactory materials balances for phosphate and calcium were obtained. The efficiency of volatile matter destruction averaged 70.7%. Gas production was 10.9 cu ft/lb V_m destroyed and gas analysis indicated a gas composition of 60% CH_4 and 30% CO_2. Alkalinity averaged 3080 mg as $CaCO_3/\ell$ for the first part of the experimental period when the digester was being fed a mixture of primary, secondary, and post-aeration sludges. During the latter part of the experiment the use of solely post-aeration sludge as a feed produced a significant increase in the alkalinity of the digester contents. These latter data are excluded from the computation of this mean alkalinity value. During the first part of the experiment the pH of the digester contents varied between 6.9 and 7.4 and averaged 7.1.

SUPERNATANT PHOSPHATE CONCENTRATION

As indicated previously, the digester contents were well mixed so that separate supernatant and digested sludge streams could not be withdrawn from the digester. Consequently an arbitrary definition of supernatant was made. The mixed digested sludge stream withdrawn from the digester was allowed to settle for 48 hr at 4°C and the liquid withdrawn from the surface of the settled mixture was defined as supernatant. Because of the extreme opacity of the mixture it was not possible to obtain an accurate estimate of the volume of supernatant and digested sludge fractions. Therefore in later computations it is assumed that the digested sludge represents 30% of the digested

TABLE V

ANALYSIS OF FEED TO LABORATORY DIGESTER

Constituent	Volumetric Fraction,%	Total Solids, %	Total P, mg/ℓ	Total Ca, mg/ℓ
Raw Sludge	56	6.0	180	230
Activated Sludge	8	1.0	225	320
Post-Aeration Sludge	8	32.4	1040	12900
Distilled Water	28	0	0	0
Mixture	100	6.0	200	1150

TABLE VI

AVERAGE DIGESTER PERFORMANCE

Organic loading lbV_m/cu ft/day		0.02
V_m destroyed, per cent		70.70
Hydraulic residence time, days		67
Gas production, cu ft/lb V_m destroyed		10.93
Gas production, lb gas/lb V_m destroyed		0.77
Gas analyses	CH_4, %	60.00
	CO_2, %	30.00
	Air $+H_2$, %	10.00
Alkalinity, mg $CaCO_3$/ℓ		3080[a]
pH		7.1
Phosphate Balance		
(initial + added) g P		5.28
(removed + remaining) g P		4.59
balance, % of completion[b]		86.93
Calcium Balance		
(initial + added) g $CaCO_3$		74.88
(removed + remaining) g $CaCO_3$		71.30
balance, % of completion[b]		95.23

[a] Excluding period of $CaCO_3$ - rich sludge addition.

[b] $$\text{P balance, \%} = \frac{\text{P removed + P remaining}}{\text{P initial + P added}} \times 100$$

$$\text{Ca balance, \%} = \frac{\text{Ca removed + Ca remaining}}{\text{Ca initial + Ca added}} \times 100$$

sludge stream and supernatant represents 70% of this volume. This assumption is based on data from well-operated anaerobic digestion units where volume reductions from incoming to digested sludge of approximately 70% are commonly experienced.

Using the experimental definition of supernatant, it was found that feeding post-aeration sludge to the anaerobic digester produced significant increases in the phosphorus content of the supernatant. The digested sludge supernatant phosphorus increased from approximately 20 mg P/ℓ to an average value of 68 mg P/ℓ for that period of the experiment when the digester had reached steady state conditions with respect to phosphorus concentration. This represents almost a 3.5-fold increase in supernatant phosphorus concentration over digested sludge not containing the phosphorus-rich post-aeration sludge. Reference to Figure 7 clearly shows the increase of supernatant phosphorus during the first residence time during which the digester was fed post-aeration phosphorus-rich sludge. It appears that the calcium content of the supernatant remains fairly constant throughout the experiment — averaging approximately 450 mg $CaCO_3/\ell$ (4.5 mM) throughout the experimental period.

These data demonstrate that feeding post-aeration sludge rich in phosphorus to a digester will result in the dissolution of some of the calcium phosphate — a conclusion that is somewhat expected since a reduction in pH values from those experienced in the post-aeration basin (approximately 9 and greater) to the pH of approximately 7 encountered in the anaerobic digestion process can be expected to increase the solubility of calcium phosphate.

Based on the experimental data and the assumed volumes of supernatant and digester sludge, it is possible to construct a materials balance for phosphorus circulation through a typical plant in which primary-secondary (activated sludge) post-aeration for phosphorus removal and digestion with recycle of the supernatant to the primary portion of the plant are included (Figure 8). From this flowsheet it is evident that the digester supernatant would almost double the phosphorus input to the treatment plant for the case considered (that of a post-aeration process in conjunction with an activated sludge plant that together effect an overall 80% phosphorus removal). If it is assumed that primary sedimentation will remove approximately the same fraction of phosphorus from supernatant that it does from raw sewage (i.e., 10%) then Figure 8 shows that the flow of phosphorus through the secondary treatment plant and to the post-aeration unit is almost doubled. This imposes a great load on the post-aeration unit which without supernatant recycle (for this particular example) would be called on to remove ~600 lb P/day while with supernatant recycle the removal of >1400 lb P/day is required.

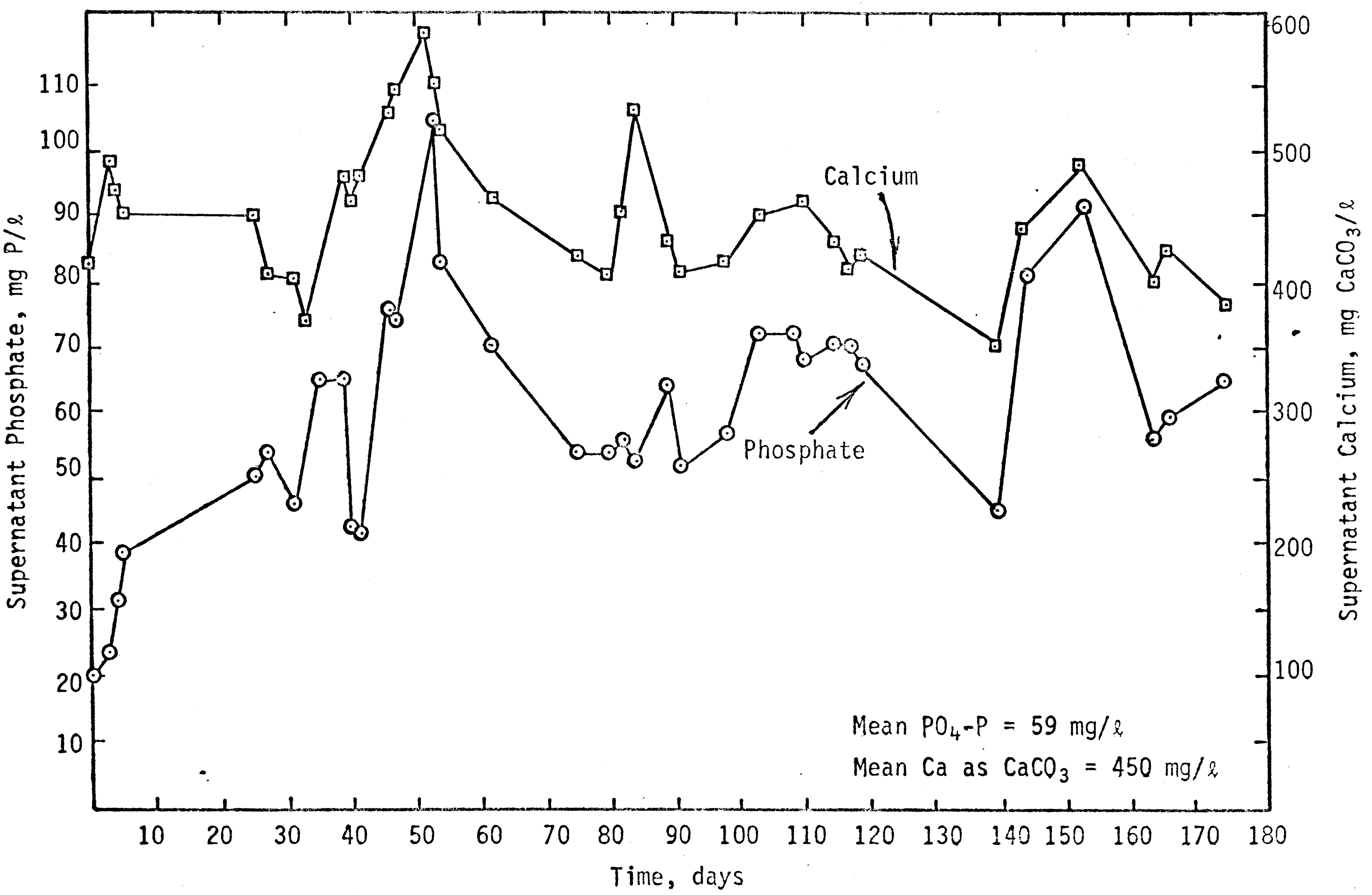
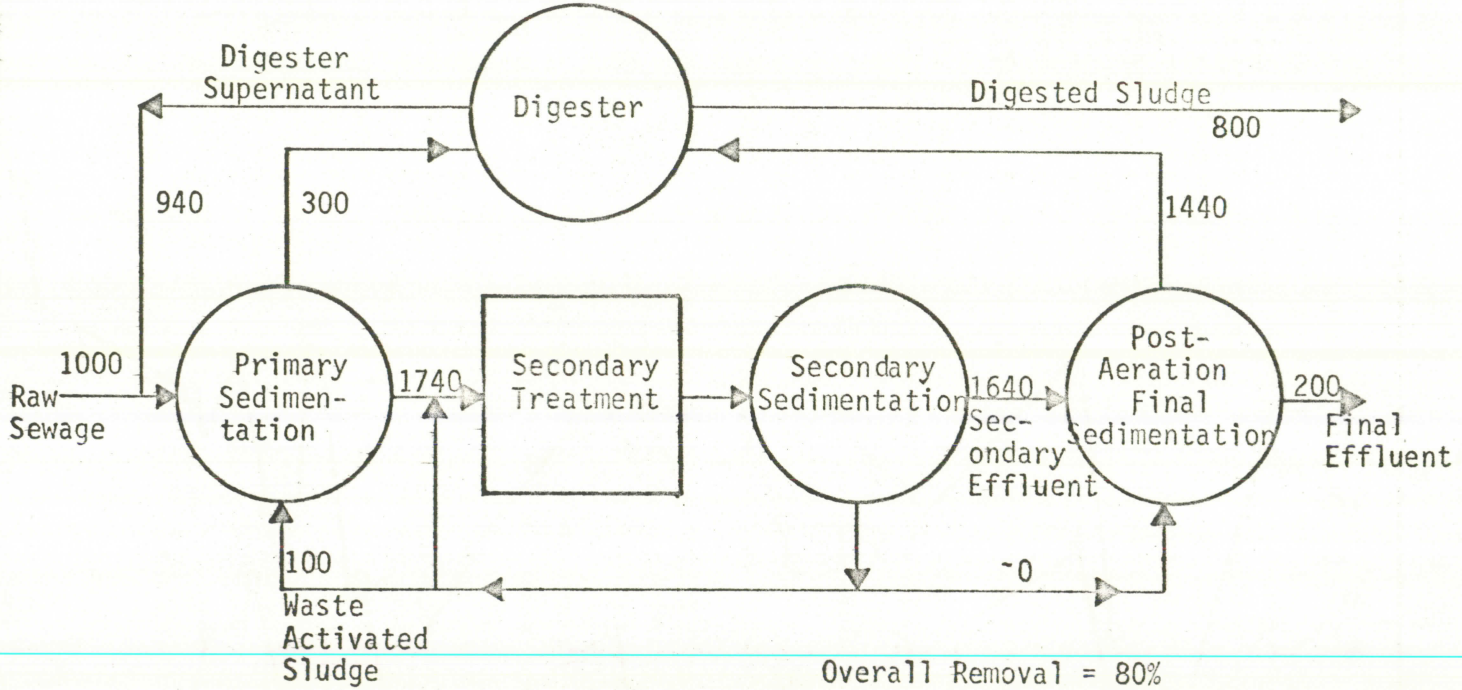


Figure 7. Supernatant Phosphate and Calcium Concentrations.



Overall Removal = 80%

Figure 8. Phosphorus Flowsheet for Post-Aeration and Anaerobic Digestion with Supernatant Recycle. (Figures in lb/day)

TREATMENT OF DIGESTER SUPERNATANT

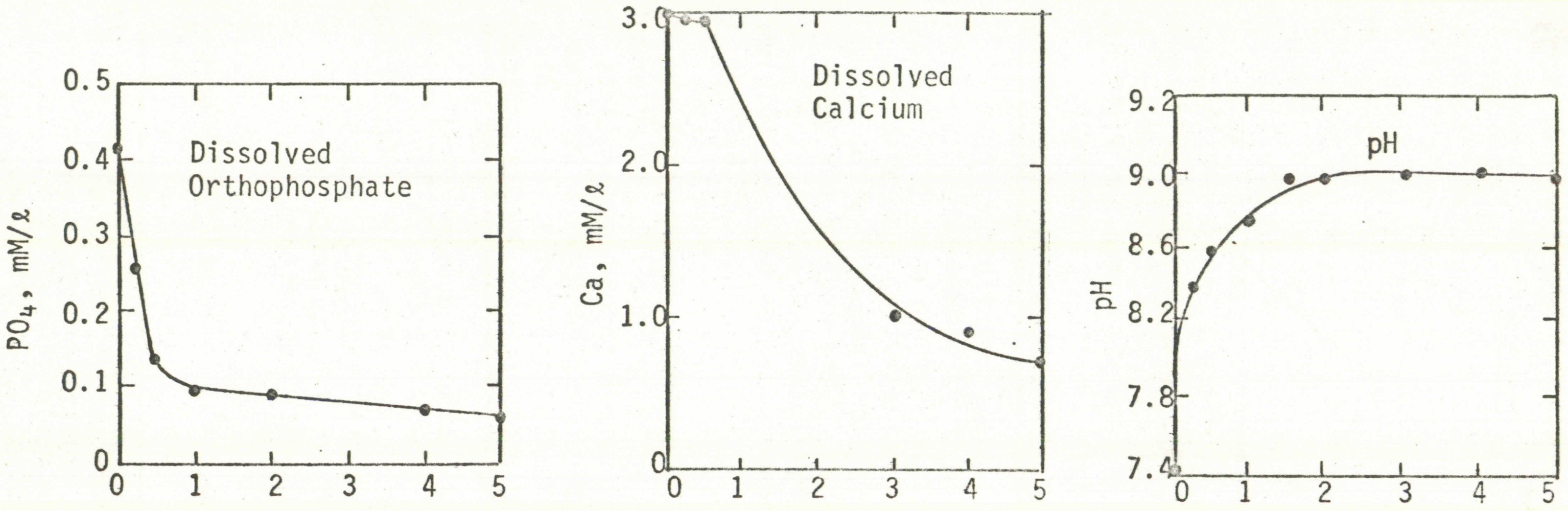
Since a considerable release of phosphorus to the supernatant stream was observed during digestion, the possibility of treating this stream for phosphorus removal was investigated. Aeration was selected as the method of treatment. It was reasoned that aeration of the supernatant would be a simple technique for raising the pH of this stream since it would provide a method of removing CO_2, which in a typical digester atmosphere is approximately 1000 times greater than its concentration in air. Also, preliminary experiments with batch aeration of two supernatants from local wastewater treatment plants had shown that aeration caused rapid (within 1 to 2 hr) decreases in soluble orthophosphate, soluble calcium, and increases in pH (Figure 9). Thus, within 2 hr of aeration, decreases of 77% and 55% in soluble orthophosphate concentrations were obtained for the Stege and Richmond, Calif. sewage treatment plant digester supernatants, respectively.

In the laboratory, digested sludge samples were withdrawn from the digester and split into two aliquots. The first aliquot was aerated with diffused air for 2 hr and then allowed to settle for 48 hr at 4°C. The second aliquot was settled for 48 hr at 4°C without prior aeration. After settling, the supernatants from both aliquots were analyzed for total phosphate and total calcium. The data, presented in Figure 10, show that pH values of the supernatant were increased from approximately pH 7 to approximately pH 9. For the period when steady operation had been achieved (after 67 days) calcium concentrations decreased from an average of 405 to 265 mg as $CaCO_3/\ell$ and phosphorus concentrations decreased on the average from 68 to 37 mg P/ℓ. These decreases represent a reduction in supernatant phosphate of approximately 46% — a lower decrease than that experienced in the batch aeration experiments on Stege and Richmond supernatants since these data represent reductions experienced in total phosphorus residual while the Stege and Richmond aeration experiments refer only to dissolved calcium and phosphate concentrations. These data indicate that significant recycling of phosphorus would still result even if digester supernatant aeration followed by sludge separation prior to recycle were practiced (Figure 11). Thus, the post-aeration treatment system would be required to remove approximately 1100 lb P/day compared with the 600 lb P/day removal necessary without digester supernatant recycle. Thus even with aeration and sedimentation of digester supernatant prior to recycle the phosphate removal load on the post-aeration system would be almost doubled.

HIGH $CaCO_3$ FEEDING STUDY

During the latter part of the anaerobic digestion experiments (for a period of 42 days) an attempt was made to determine the effects of variations in calcium and pH on the dissolved phosphorus concentration in the digester. The purpose of these experiments was to determine whether previous observations on the relationship between $[Ca]P_T$ and

Stege Sanitary District Supernatant



Richmond Sanitary District Supernatant

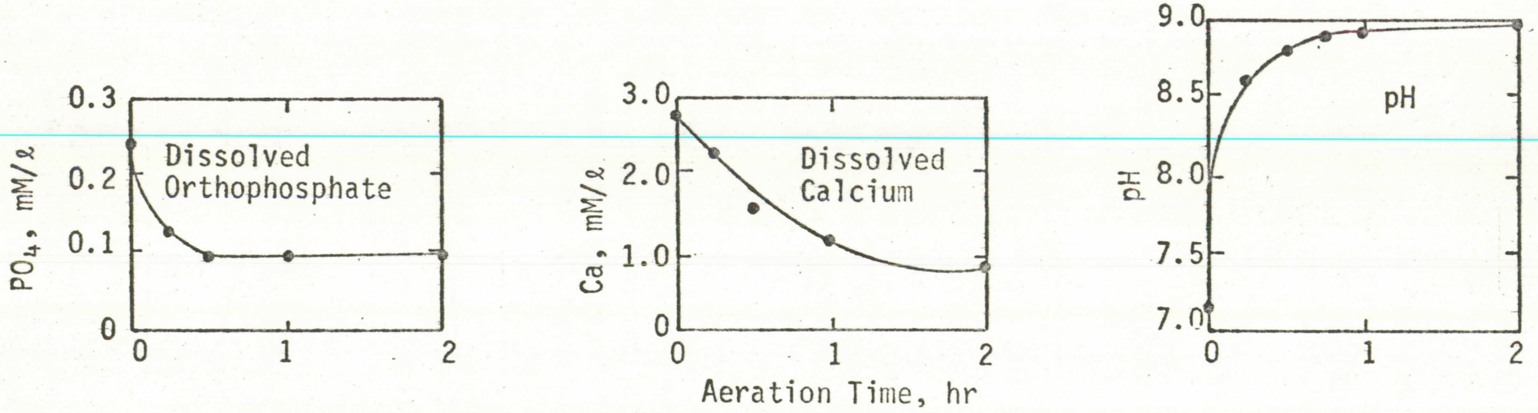


Figure 9. Effect of Batch Aeration on Composition of Digester Supernatants.

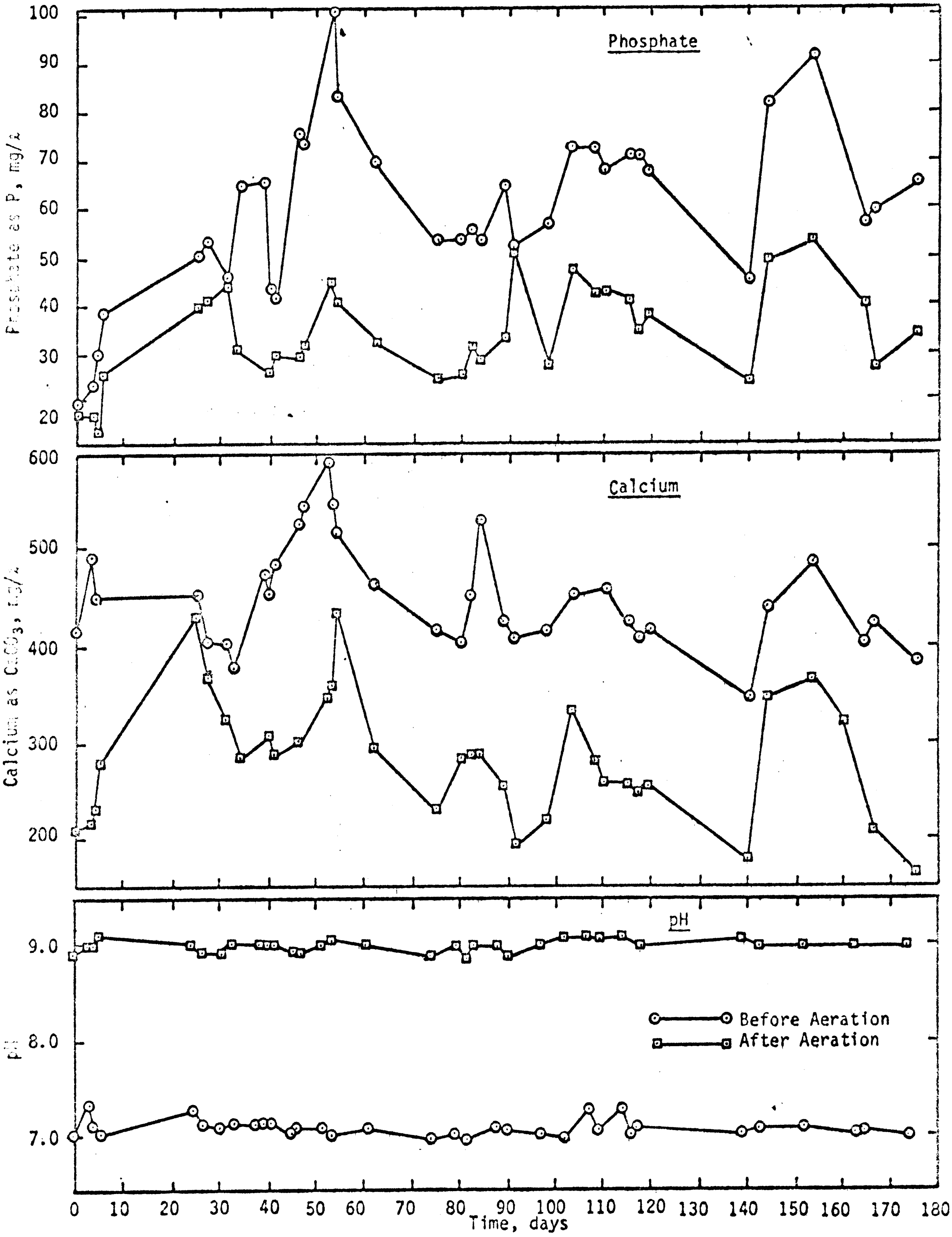


Figure 10. Effect of Aeration on Supernatant pH, Phosphate, and Calcium Concentrations.

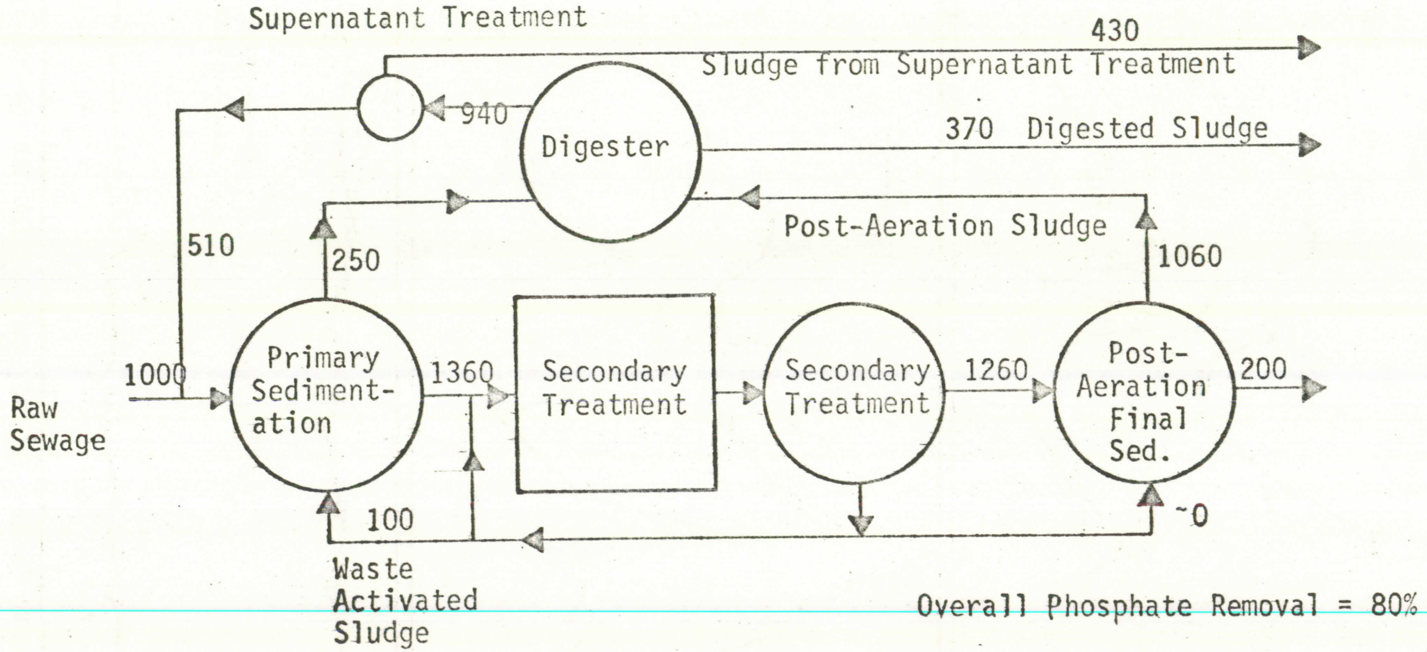


Figure 11. Phosphorus Flow Sheet for Post-Aeration and Anaerobic Digestion with Recycle of Aerated and Settled Supernatant. (Figures in lb/day)

pH could be substantiated and to determine the possible effect on dissolved phosphate that might be caused by practices such as liming a digester.

To avoid disturbing the digester by wide and sudden pH changes that could be caused by the addition of strong acid or strong base, the pH, alkalinity, and calcium concentrations in the digester were adjusted simultaneously by the addition of $CaCO_3$, added in the form of post-aeration basin sludge rich in $CaCO_3$. This sludge was identical in composition to that described in the previous section. Since the interest in these experiments was in dissolved phosphorus and calcium concentrations, it was necessary to separate the solids from the samples withdrawn from the digester, prior to analysis. To accomplish this the samples of digested sludge were immediately centrifuged at 15,000 rpm for 5 min and then filtered through 0.45μ membrane filters (Millipore HA). During this operation an upward pH change occurred (due to the equilibration of the liquid from the digester CO_2 concentration toward the atmospheric CO_2 concentration) especially during filtration when a partial vacuum was applied to the sample. Because of the pH change, two measurements of pH were made — one immediately on sampling and a second after centrifugation and filtration. The former pH value was used in assessing the effects of pH on dissolved phosphorus concentrations in the sludge digester because previous experiments on the batch aeration of supernatant from Stege and Richmond sewage treatment plant digesters (Figure 9) had shown that rapid pH changes took place prior to any changes in soluble phosphorus and calcium concentrations. The centrifugation and filtration operation took a maximum of only 10 min and reference to Figure 9 shows that during this time period no significant changes in soluble phosphorus and calcium took place although the pH changes were rapid.

The digester performed excellently during the six-week experimental period, producing 11 cu ft gas/lb V_m destroyed at an organic loading of 0.03 lb V_m/cu ft-day.

During the 42-day experimental period the addition of $CaCO_3$ rich post-aeration sludge affected the composition of the digester contents producing a steady rise in alkalinity (from about 1 mM/ℓ to approximately 14 mM/ℓ) and in pH from 7 to 7.3. Over the first 20 days of the experiment there was a three-fold increase in dissolved calcium (from 3 mM/ℓ to 9 mM/ℓ) and this increase was accompanied by a decrease in dissolved phosphorus concentration from approximately 1.7 mM/ℓ to 0.3 mM/ℓ (Figure 12). The data in Figure 12 combined with materials balance data for total and dissolved Ca and P (Table VII) make it plain that during the first 20 days of the experiment calcium phosphate precipitation was taking place. In the latter part of the experiment it appears that considerable $CaCO_3$ precipitation began to occur in conjunction with the calcium phosphate precipitation. Mole ratios of Ca/P in the solid increased from 1.5 to 1.8 in the first 20 days and from 1.8 to 5.5 during the final 20 days of the experiment.

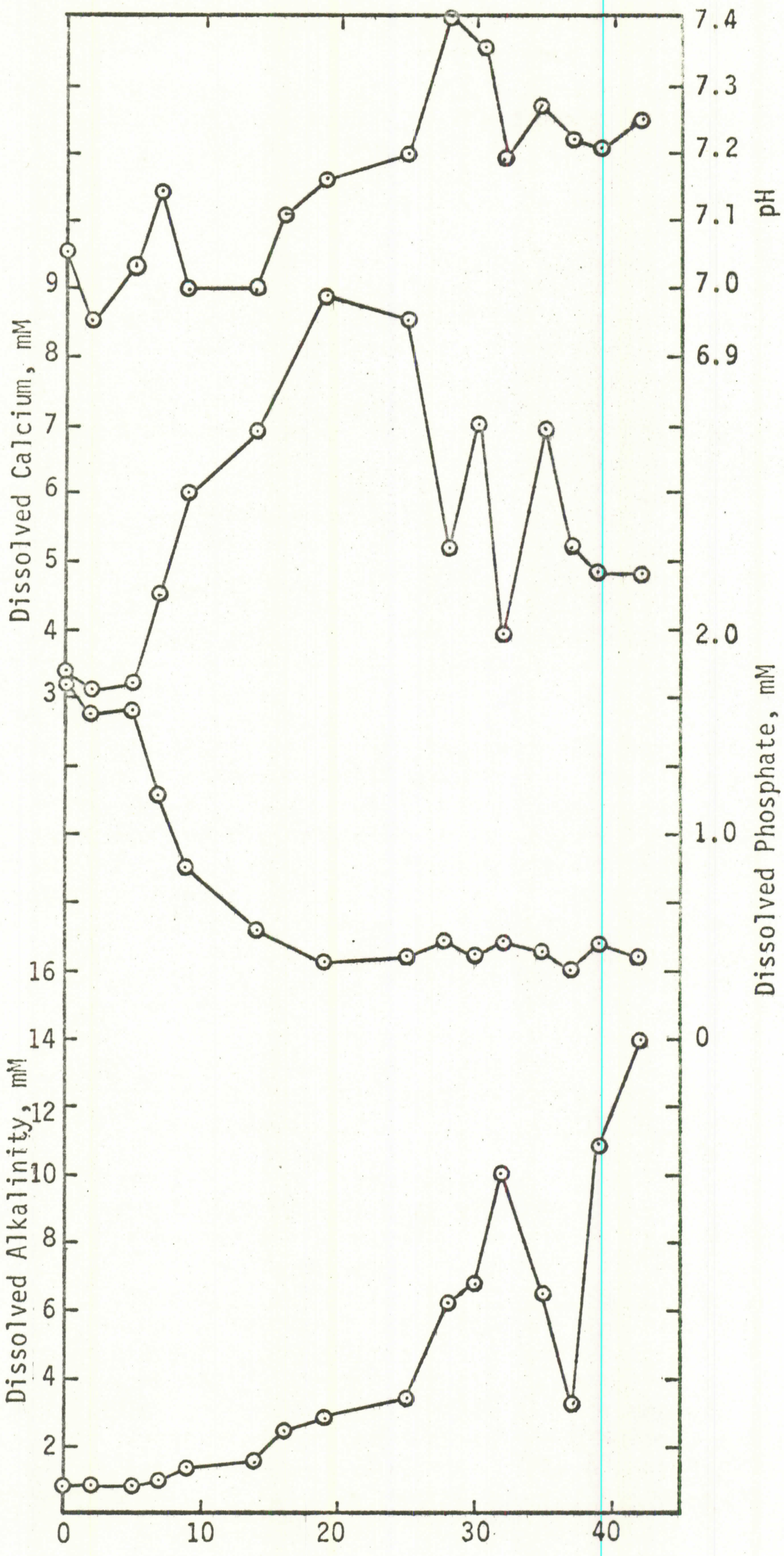


Figure 12. Effect of Ca, pH and Alkalinity on Dissolved Phosphate Content of Anaerobic Digester.

TABLE VII

MASS BALANCE ON TOTAL AND DISSOLVED Ca AND P FOR HIGH $CaCO_3$ SLUDGE FEEDING EXPERIMENT

DATE	DIGESTER P CONTENT				DIGESTER Ca CONTENT				Ca/P, mole Ratio in Solid
	Total	Dissolved	Solid		Total	Dissolved	Solid		
1969	mg	mg	mg	mM	mg	mg	mg	mM	
22 Jan	2301	522	1779	58	11878	3228	8650	86	1.5
24	2305	469	1836	59	11955	3043	8910	89	1.5
27	2280	476	1804	58	11835	3185	8650	86	1.5
29	2309	363	1846	60	14669	4484	10200	102	1.4
31	2302	250	2152	69	16536	6019	10500	105	1.5
5 Feb	2341	162	2179	70	19010	6913	12100	121	1.7
7	2391	326	2065	66	20813	8490	12300	123	1.8
10	2445	114	2331	75	22502	8954	13500	135	1.8
14	2415	119	2296	74	23529	8515	15000	150	2.0
17	2419	143	2276	74	28779	5103	23700	237	3.2
19	2431	120	2311	75	33428	6981	26400	264	3.5
21	2444	138	2306	74	37125	3900	33200	332	4.5
24	2443	125	2318	75	40397	6900	33500	335	4.5
26	2446	98	2348	76	43452	5143	38300	383	5.0
28	2482	138	2344	76	46452	4759	41700	417	5.5
3 Mar	2581	112	2402	78	46655	4817	41800	418	5.4

Activity product data for each of the 16 experimental points are presented in Table VIII. On the basis of these data it appears that digester liquid is highly supersaturated with respect to calcite and one would therefore expect that this solid would form. Of the calcium phosphate phases enumerated, only supersaturation with respect to apatite appears to exist.

Unfortunately, magnesium data were not taken during these experiments because at that time the importance of this cation in phosphate precipitation was not fully comprehended. The absence of absolute values for magnesium and the conduct of the experiment over a somewhat limited pH range makes comparisons with other workers difficult. If one makes the reasonable assumption that the Ca/Mg mole ratio was 5, then this digester appears to be representative of the model of Ferguson [9] in which the probable solids forming would be poorly crystalline hydroxylapatite (pA 52) and calcite (pA 8.3).

The digester data fall perfectly on the correlation curve of $[Ca]P_T$ vs. pH (Figure 3) that was derived from previous work by Menar and Jenkins [1] and are in excellent agreement with previous data from anaerobic and high CO_2 environments.

CONCLUSIONS

The general conclusion from these experiments is that calcium phosphate precipitates formed in a post-aeration basin (and indeed in any primary, secondary, or tertiary precipitation scheme) tend to redissolve at the lower pH values encountered in anaerobic digestion and are released into the supernatant stream. This conclusion is an extension of the observation of Menar and Jenkins [1] that even in the slightly lower pH (higher CO_2) environment of a secondary clarifier activated sludge blanket, a redissolution of calcium phosphates takes place. Also, release of phosphate has generally been observed from all activated sludges claimed to be showing "luxury uptake," when the sludges were exposed to anaerobic conditions and a lowering of pH. This conclusion makes it plain that the anaerobic digester is not a good unit for the treatment of high phosphorus activated sludge or post-aeration sludge if digester supernatant recycle is contemplated and if high phosphorus removals are desired from the wastewater stream. Aeration of the digester supernatant caused precipitation of phosphate by stripping CO_2 and raising its pH, but significant amounts of phosphate would still be recycled even if perfect separation of precipitated phosphate from the aerated supernatant were achieved.

These experiments have also shown that an increase in calcium concentration in an anaerobic digester leads to a decrease in dissolved phosphate concentration. The exploration of this technique of phosphorus removal from digester supernatant was not pursued to a degree that would allow the conclusion that it offered a satisfactory phosphorus removal

TABLE VIII

EXPERIMENTAL ACTIVITY PRODUCTS FOR DIGESTION EXPERIMENT DATA

pH	Experimental Activity Product[a]				
	DCP	TCP	OCP	HAP	Calcite
7.05	7.0	28.4	47.7	51.3	3.7
7.00	7.1	28.9	48.3	52.3	3.8
7.03	7.0	28.5	47.9	51.6	3.7
7.14	6.9	27.8	47.0	50.4	3.5
7.00	7.2	28.9	48.4	52.2	3.2
7.00	7.4	29.2	49.0	52.7	3.4
7.16	7.3	28.5	49.1	51.4	3.0
7.20	7.7	29.5	49.5	53.0	3.1
7.40	7.3	28.2	37.8	50.7	2.9
7.35	7.4	28.4	39.0	42.0	3.0
7.27	7.4	28.7	48.4	51.7	2.9
7.22	7.5	28.9	48.7	51.9	3.2
7.20	7.9	30.1	50.3	54.1	2.9
7.25	7.9	30.2	50.5	54.3	2.8

[a] For data points in Figure 12.

Saturation Activity Products

DCP	6.9
TCP	26.0
OCP	57.8
HAP	46.9
Calcite	8.4

technique. Ferguson [1], however, in more extensive work on the fate of phosphorus in digesters, is of the opinion that phosphate removal by the treatment of digester supernatant with calcium is a feasible process. Indeed, he states that it is possible that the high concentrations of phosphate in this waste stream may make chemical treatment relatively efficient and inexpensive. One such scheme suggested by Ferguson [1] for the precipitation of phosphate from digester supernatant involves adjusting the Ca/P mole ratio to 2.5 (using calcium chloride) and adjusting the pH to 8 (by aeration to drive off CO_2). After precipitation (with solids recycle to minimize the detention time for crystal growth) the solids would be separated by vacuum filtration. Another scheme suggested for the removal of phosphate (and ammonia) from digester supernatants involves the addition of approximately 4 g/ℓ $Ca(OH)_2$ to precipitate calcium phosphate (probably a poorly crystalline carbonate apatite) and to raise the pH to 11.5 to enable ammonia removal by air stripping [16].

IV. PURE SYSTEM EXPERIMENTS

OBJECTIVES

The objective of these preliminary experiments on calcium phosphate precipitation in distilled water solutions was to provide some information on the effect of such common wastewater constituents as H^+, C_T*, Mg, and CO_2 on the extent of calcium phosphate precipitation at concentrations and Ca/P mole ratios typical of wastewater treatment situations.

EXPERIMENTAL PROCEDURE

Batch precipitation experiments were conducted at 30°C using a 250-mℓ initial liquid volume contained in 300-mℓ BOD bottles as reactors. The contents of the bottles were mixed by water-driven magnetic stirrers. In experiments where the liquid was aeration with various gases, these gases were introduced through glass diffusers immersed in the liquid so that they allowed a small clearance above the magnetic stirring bar.

The reagents for an experiment were pre-mixed in a 400-mℓ beaker which had been flushed out with nitrogen gas. Deionized water was used for all dilutions and reagent preparation. One molar stock solution of $CaCl_2$, $MgCl_2$, Na_2HPO_4, and $NaHCO_3$ were prepared using analytical grade reagents. Working solutions of the following concentrations were prepared by diluting the stock solutions with deionized water just prior to their use in an experiment to: $CaCl_2$, 0.1 M/ℓ; $MgCl_2$, 0.1 M/ℓ; Na_2HPO_4, 0.096 M/ℓ; $NaHCO_3$, 0.05 M/ℓ.

The order of reagent addition was identical in all experiments: $CaCl_2$ solution was always added first to vigorously stirred deionized water; when magnesium was used, the $MgCl_2$ solution was added next, then the $NaHCO_3$ solution, and finally the Na_2HPO_4 solution. The mixture was stirred for 1 min and then the "initial pH' was measured and recorded. After pH measurement the mixture was transferred into the BOD-bottle reactor, which was then placed in a constant-temperature bath where mixing was continued. If aeration was being employed, the diffuser was immersed at this time and aeration started. Aeration was by cylinder gases of either air, air + 0.5% CO_2, or air + 5% CO_2. The reactor contents were sampled by withdrawing liquid with a 50-mℓ

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*$C_T = [H_2CO_3] + [HCO_3] + [CO_3^=]$

pipette. The sample was filtered immediately through 0.45μ membrane filters (Millipore HA) and pH, orthophosphate, and calcium were determined immediately on the filtrate. Samples for analyses were taken after 1.5 hr, after 48 hr, and after 96 hr.

RESULTS

The results of these experiments were of a preliminary nature and were designed to screen out significant effects on calcium phosphate precipitation of some of the common wastewater constituents singly and in combination. These results will be discussed in the context of later work in this area by one of the authors and others (Ferguson *et al.* [4]; Jenkins *et al.* [12]).

The current experimental results are somewhat confounded by the inability to control pH closely during a precipitation experiment. The buffering components of the mixture were often the reactants in the precipitation and therefore as these buffers were removed the mixture became subject to pH changes. However, if one surveys Table IX and Figure 13 it is possible to make a significant observation from the 96-hr dissolved phosphate residual values. In the Ca - P_T - C_T - H^+ - H_2O - (Mg) system the only samples with extremely low phosphorus residuals (<0.05 mM/ℓ) are those in which Mg is absent. In only one instance does the presence of Mg appear to decrease the phosphorus residual. This was in experiment 13 which when compared to experiment 20 only differed in the presence of 0.8 mM/ℓ Mg in the former. In both of these experiments the initial composition (4 mM/ℓ Ca, 0.5 mM/ℓ P_T, 5 mM/ℓ C_T), the aerating gas (air + 5% CO_2), and the pH profile (pH 8.0 initially and pH 7.1 to 7.2 finally) were all the same. However, the P residual in experiment 13 after 96 hr was 0.31 mM/ℓ and in the Mg-containing experiment 20 the P residual was 0.08 mM/ℓ.

Extremely high carbonate concentrations (30 mM/ℓ) appear to suppress calcium phosphate precipitation (independently of affecting the pH during precipitation). For example, comparison of experiment 23 with experiment 21 shows that the phosphorus residuals in experiment 23 (with an initial composition of 4 mM/ℓ Ca, 0.5 mM/ℓ P_T, 30 mM/ℓ C_T, 4 mM/ℓ Mg, and an initial pH of 8.4) was 0.38 mM/ℓ while in experiment 21, in which the only difference in initial conditions was the pH of 8 and C_T of 5 mM/ℓ there was a P residual of 0.18 mM/ℓ. The pA value for $CaCO_3$ of 5.9 and the residual calcium concentration of 1.4 mM/ℓ indicate the occurrence of $CaCO_3$ precipitation in experiment 23 but not in experiment 21 (residual Ca = 3.6 mM/ℓ).

A similar pair of experiments (experiment 24 and experiment 22) in which initial Mg was 8 mM and initial Ca/Mg mole ratio was 1/2 does not confirm this behavior. In this instance it is possible that the very low Ca/Mg mole ratio was sufficient to almost completely inhibit calcium phosphate precipitation but to allow $CaCO_3$ precipitation to take place in the case of experiment 24 with the high initial C_T concentration

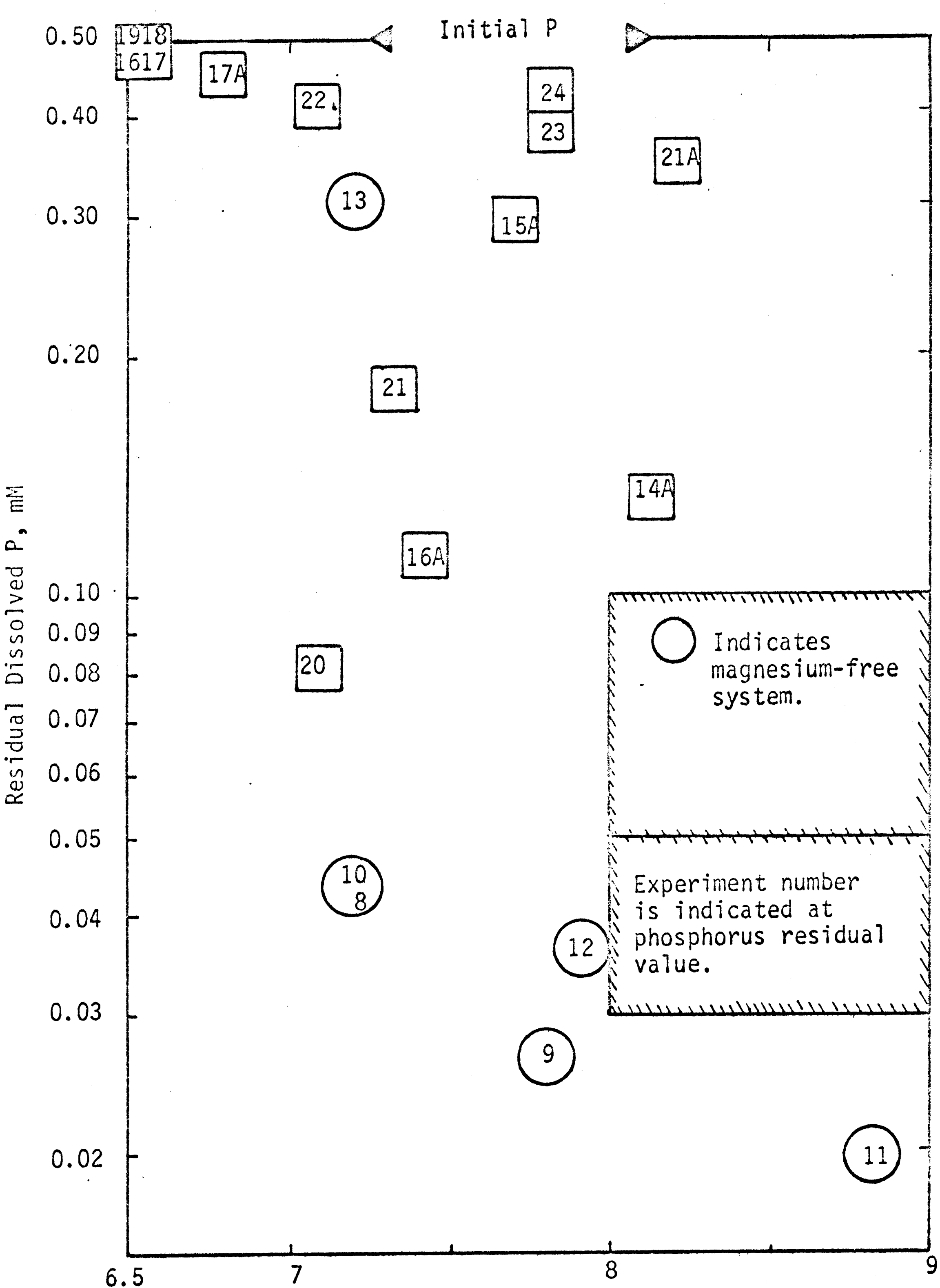

Figure 13. Residual Dissolved Phosphate in the $Ca - P_T - C_T - H^+ - H_2O - (Mg)$ Systems vs. pH (98-hr values).

TABLE IX

BATCH DISTILLED WATER PRECIPITATION EXPERIMENTS — INITIAL CONDITIONS

Expt. No.	Initial Conditions[a]					
	Ca	P	C_T	Mg	pH	Gas
1	4.0	0.5	0	0	7.4	NONE
2	4.0	0.5	0	0	7.5	NONE
3	4.0	0.5	0	0	8.0	NONE
4	4.0	0.5	0	0	8.1	NONE
5	4.0	0.5	0	0	8.1	NONE
6	4.0	0.5	0	0	7.5	AIR + 0.5% CO_2
7	4.0	0.5	0	0	7.4	AIR + 5% CO_2
8	4.0	0.5	1.0	0	8.2	NONE
9	4.0	0.5	5.0	0	8.0	NONE
10	4.0	0.5	1.0	0	8.2	AIR + 5% CO_2
11	4.0	0.5	5.0	0	8.8	AIR
12	4.0	0.5	5.0	0	7.9	AIR + 0.5% CO_2
13	4.0	0.5	5.0	0	8.0	AIR + 5% CO_2
14A	4.0	0.5	5.0	4.0	8.0	AIR + 0.5% CO_2
14	4.0	0.5	0	4.0	7.6	NONE
15A	4.0	0.5	1.0	4.0	7.8	NONE
15	4.0	0.5	0	4.0	7.6	AIR + 0.5% CO_2
16A	4.0	0.5	1.0	4.0	7.8	AIR + 0.5% CO_2
16	4.0	0.5	1.0	0.8	7.6	AIR + 5% CO_2
17A	4.0	0.5	1.0	4.0	7.7	AIR + 5% CO_2
17	4.0	0.5	1.0	2.0	7.7	AIR + 5% CO_2
18	4.0	0.5	1.0	2.0	7.7	AIR + 5% CO_2
19	4.0	0.5	1.0	2.0	8.0	AIR + 5% CO_2
20	4.0	0.5	5.0	0.8	8.0	AIR + 5% CO_2
21A	4.0	0.5	5.0	4.0	8.0	NONE
21	4.0	0.5	5.0	4.0	8.0	AIR + 5% CO_2
22	4.0	0.5	5.0	8.0	8.1	AIR + 5% CO_2
23	4.0	0.5	30.0	4.0	8.4	AIR + 5% CO_2
24	4.0	0.5	30.0	8.0	8.3	AIR + 5% CO_2

[a] All concentrations are mM.

TABLE X

BATCH DISTILLED WATER PRECIPITATION DATA [a]

	After 15 hr			After 48 hr			After 96 hr		
Expt No.	Ca	P	pH	Ca	P	pH	Ca	P	pH
1	3.7	0.31	6.6	3.6	0.27	5.9	3.6	0.27	5.9
2	3.6	0.31	6.8	3.5	0.26	6.0	3.6	0.27	5.9
3	3.6	0.18	7.8	3.5	0.17	7.8	3.4	0.17	5.7
4	3.3	0.14	7.9	3.2	0.094	6.2	3.2	0.090	6.2
5	3.3	0.13	7.7	3.2	0.097	6.2	3.2	0.10	6.2
6	3.6	0.44	6.6	3.8	0.38	6.5	3.9	0.39	6.4
7	3.9	0.48	5.9	3.9	0.49	5.8	4.0	0.49	6.0
8	3.7	0.33	7.6	3.1	0.074	7.2	3.1	0.042	7.2
9	3.1	0.16	8.1	2.8	0.026	7.9	2.5	0.026	7.8
10	3.2	0.20	7.1	3.2	0.055	7.3	3.3	0.042	7.2
11	2.8	0.04	8.7	1.2	0.036	8.9	1.7	0.019	8.8
12	3.1	0.18	7.9	2.7	0.019	8.1	1.0	0.036	7.9
13	3.95	0.49	7.3	3.8	0.37	7.2	3.7	0.31	7.2
14A	3.5	0.19	8.0	3.3	0.15	8.2	3.4	0.13	8.1
14	3.9	0.46	7.5	3.6	0.45	7.5	3.9	0.44	7.4
15A	3.8	0.35	7.8	3.7	0.32	7.7	3.6	0.29	7.7
15	4.0	0.49	6.7	4.0	0.50	6.5	4.1	0.49	6.5
16A	3.8	0.33	7.8	3.5	0.21	7.5	3.4	0.11	7.4
16	-	-	-	4.1	0.49	6.5	4.1	0.47	6.5
17A	-	-	-	3.9	0.48	6.7	3.8	0.46	6.8
17	-	-	-	4.0	0.48	6.6	4.3	0.48	6.5
18	3.7	0.46	6.5	4.1	0.50	6.7	-	-	-
19	1.6	0.49	6.4	1.6	0.49	6.5	1.8	0.50	6.6
20	-	-	-	3.5	0.12	7.1	3.5	0.08	7.1
21A	3.4	0.39	8.1	4.0	0.38	8.1	4.6	0.35	8.2
21	-	-	-	3.8	0.36	7.3	3.6	0.18	7.3
22	-	-	-	3.9	0.46	7.2	4.0	0.41	7.1
23	-	-	-	1.5	0.38	7.9	1.4	0.38	7.8
24	-	-	-	1.8	0.39	7.8	1.9	0.43	7.8

[a] All concentrations are mM

DISCUSSION

The results obtained in these preliminary experiments are suggestive of data obtained recently by Ferguson et al. [4] in a study of calcium phosphate precipitation in batch systems with chemical compositions similar to those studied in the preliminary experiments and encountered in many wastewaters. In these experiments it was found that the effect of pH in the Ca - P_T - C_T - H^+ - H_2O system was complex (Figure 14). While the general effect of increasing pH was to decrease residual soluble phosphate, induction periods were long at low pH values (pH 7.6 and pH 8). These induction periods could be eliminated if previously precipitated calcium phosphate solids were present (Figure 15) and were therefore most probably due to the nucleation of poorly soluble phases followed by subsequent rapid crystal growth. At pH 10 and 11 there was a very rapid precipitation of most of the phosphate, then the soluble phosphate concentration increased to a value that after about 1 hr remained virtually constant. Electron micrograph data indicate that this kinetic pattern was caused by an instantaneous precipitation of a calcium phosphate followed by a slower conversion to calcite which is accompanied by the re-solution of some of the initially precipitated calcium phosphate — presumably a poorly crystalline carbonate-apatite.

The effect of carbonate concentration on calcium phosphate precipitation appeared to be exerted both kinetically and on the value of the long term residual soluble phosphate (Figure 16). As carbonate concentration is increased through the range commonly found in wastewaters, slower phosphate removal occurs and significantly higher phosphate residuals are present at high carbonate levels even after several hundred hours.

While the effect of carbonate on phosphate solubility is not fully understood, it is believed that the occurrence of calcium carbonate precipitation above pH 9 and the substitution of carbonate in apatite (increasing its solubility with respect to phosphate) are involved.

This work indicated that the effect of magnesium on the precipitation of calcium phosphate was exerted through its influence on the nature of the calcium-containing solids but not through the formation of magnesium carbonate or phosphate precipitates. At pH 8, Mg retarded the rate of phosphate precipitation and resulted in much higher phosphate residuals in samples that contained high Mg concentration (Figure 17). This behavior is indicated in experiments conducted in the preliminary study reported herein and may be due to the inhibition of nucleation and crystal growth — an interpretation that has been suggested for similar inhibitory effects of Mg in $CaCO_3$ phase changes. Magnesium may also cause a change in the nature of the calcium phosphate solid. For example, Ferguson [9] has proposed that in the presence of Mg, β-tricalcium phosphate can be precipitated in systems that otherwise would precipitate hydroxylapatite. The

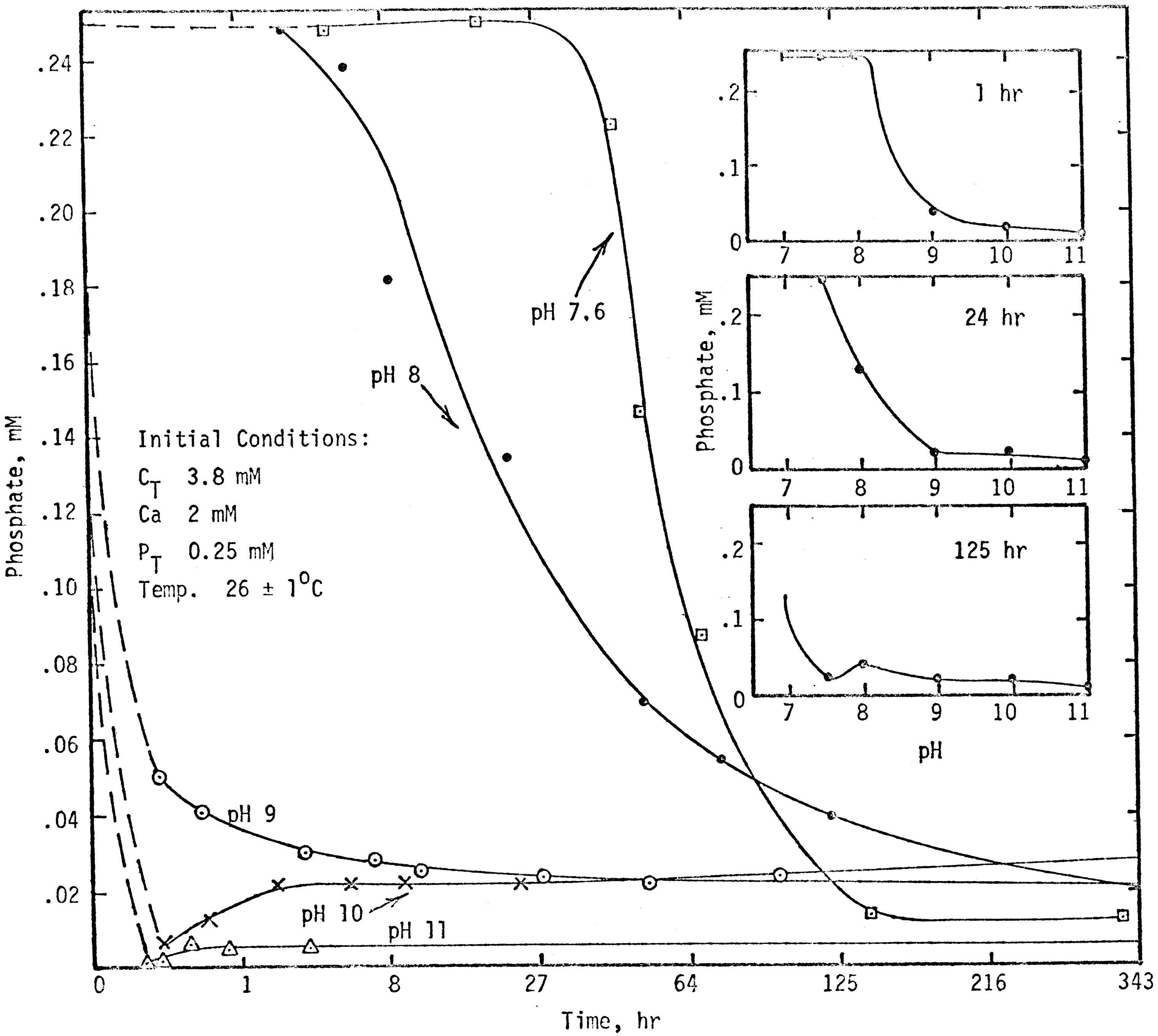

Figure 14. The Effect of pH and Time on Phosphate Removal.

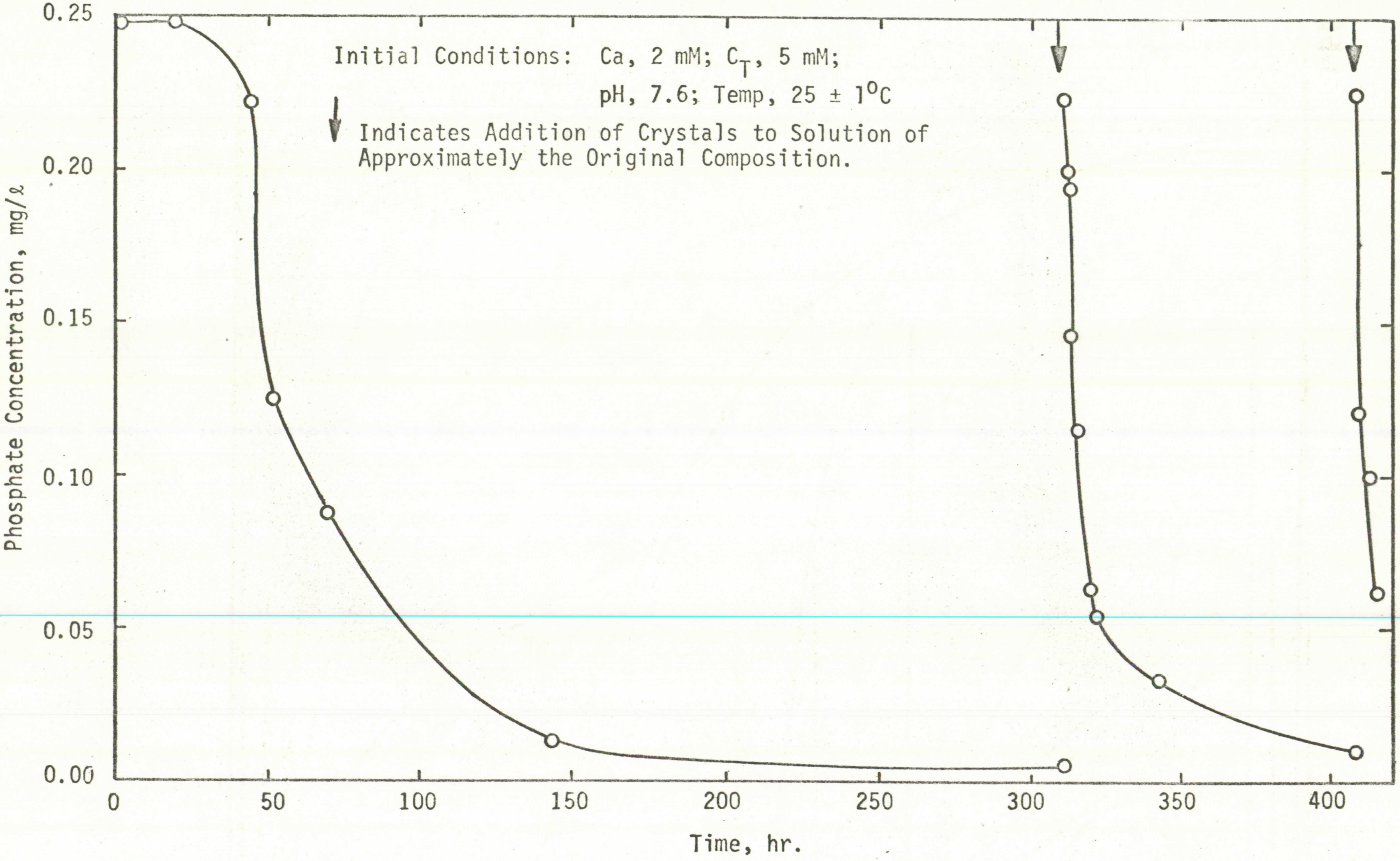

Figure 15. Effect of Crystal Seeding on Rate of Calcium Phosphate Precipitation.

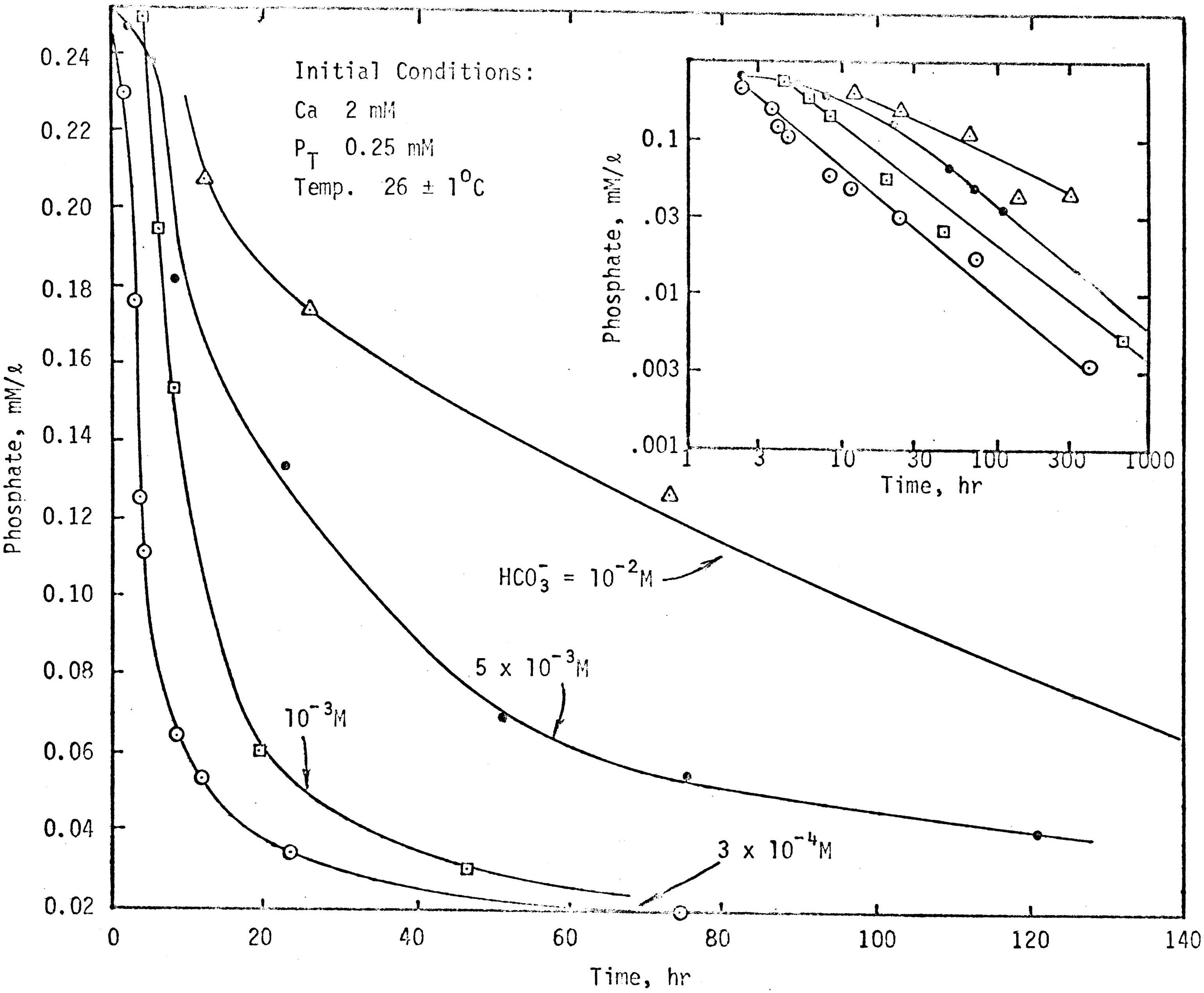

Figure 16. The Effect of Carbonate Concentration on Phosphate Removal at pH 8.

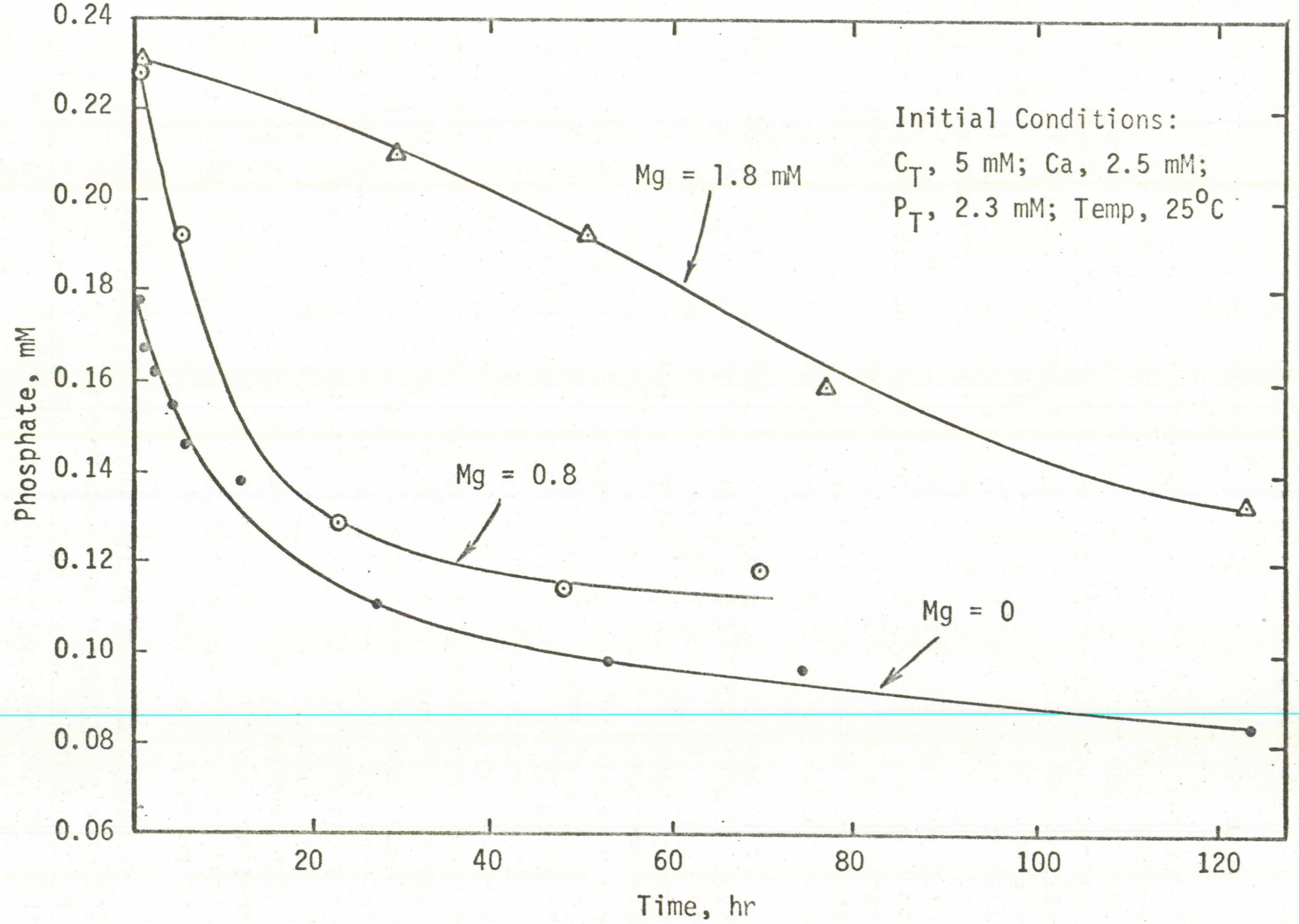

Figure 17. The Effect of Magnesium on Phosphate Removal at pH 8.0.

former solid is slightly more soluble with respect to phosphate and calcium than the latter and would therefore result in higher phosphate residuals in the presence of magnesium.

At pH values where calcium carbonate precipitation takes place in the Ca - P_T - C_T - H^+ - H_2O - Mg system, magnesium exerts a rather different effect than that observed at pH 8 (Figure 4). In the experiments of Ferguson et al. [4] at pH 9.5, phosphate residuals increased rapidly from a very low initial value to a concentration that appeared to be dependent on the Mg concentration. These results were interpreted to indicate that calcium phosphate and calcium carbonate both precipitated initially. Then the initially precipitated calcium phosphate redissolved and calcium carbonate precipitated over the first 1 to 2 hr. Since it is known that Mg increases the solubility of calcite and inhibits calcium carbonate phase changes, the presence of Mg in a system in which calcium phosphate and calcium carbonate both precipitate would tend to produce lower P residuals than a system in which Mg was absent (and in which phases change between calcium phosphate and calcium carbonate proceeded uninhibited).

It is possible to discuss the existing and proposed phosphate precipitation practices in the context of the research conducted by Ferguson et al. [4]. Phosphate precipitation by the addition of lime is practiced almost exclusively at pH values in excess of 10.5. Phosphate residuals of less than 0.5 mg P/ℓ are common, but chemical doses are directly related to wastewater alkalinity and generally exceed 400 mg/ℓ of lime. The work of Ferguson et al. indicates that where P residuals of less than 0.3 mg P/ℓ are desired this high pH precipitation process would probably operate most efficiently at short contact times (<0.5 hr) and with rapid solids separation devices such as centrifugation followed by filtration. Since calcium carbonate precipitation will take place at these high pH values a large fraction of the sludge from such processes will be calcium carbonate and the economic feasibility of recalcining for lime recovery should be considered on a case by case basis. The high pH lime addition process would be a serious candidate to obtain low P residuals in wastewaters with a high carbonate content (300 mg as $CaCO_3$/ℓ) and a high Mg concentration (>24 mg/ℓ) since, at pH values in excess of 11, the deleterious effects of these components on calcium phosphate precipitation appear to be relatively small.

Schmidt and McKinney [6] have recently suggested that phosphate precipitation can be conducted in primary sedimentation basins by the addition of lime to achieve a pH value of 9 to 10. The results of the work of Ferguson et al. [4] suggest that precipitation at this pH would be a preferred process where Ca/Mg ratios are high (Ca/Mg <2) i.e., typically in an area with hard water and high Mg. This process would also be applicable where recycle of precipitated solids was impractical. At these pH values calcium carbonate precipitation will take place and where high wastewater carbonate concentrations exist excessive calcium carbonate precipitation may interfere with calcium phosphate precipitation. Solids separation in such a process should be rapid at these pH values because phosphate release from precipitated solids occurs during the first few minutes after chemical addition. It would appear that solids recycle which seems to be an integral part of the PEP process (Albertson and Sherwood [17]) may be desirable for flocculation but is probably not optimum for phosphate precipitation at pH values of 9 to 10.

The research of Ferguson et al. further helps to define the conditions that were necessary for calcium phosphate precipitation at pH values consistent with the activated sludge process. The suggestion that enhanced phosphate removal by activated sludge at San Antonio, Texas is caused by calcium phosphate precipitation (Menar and Jenkins [1]) has been reinforced. The long nucleation times observed for calcium phosphate precipitation at low pH values may account for the absence of phosphate removal at many locations, while the recycle of precipitated solids with return activated sludge (eliminating the nucleation lag time) may explain the effectiveness of the process where it does occur. The hindering effects of Ca and Mg on calcium phosphate precipitation at low pH values may account for some of the differences in phosphate removal observed at different locations; for example, the high concentrations of these two components have been suggested by Ferguson [9] to be the reason why it was impossible for Menar and Jenkins [1] to obtain very low soluble phosphate residuals in their activated sludge experiments at San Ramon, Calif. [1]. This is very possibly the same reason that it was impossible to obtain extremely low phosphate residuals in the SERL post-aeration experiments discussed earlier in this report. Ferguson et al. [4] suggest that phosphate precipitation at pH values of 7.5 to 8.5 is most readily applicable in soft water areas, and in such areas it can be used in combination with activated sludge treatment or in a post-aeration system. In a typical low-hardness wastewater (e.g., Ca, 0.8 mM/ℓ; Mg, 0.4 mM/ℓ; alkalinity, 150 mg as $CaCO_3$/ℓ; bicarbonate 3 mM/ℓ; and phosphate, 0.3 mM/ℓ) the addition of 1 to 2 mM/ℓ Ca and 0.3 to 1 mM/ℓ strong base would raise the pH to slightly above pH 8 and the calcium concentration to about 2 mM/ℓ. Under these conditions, nucleation should take place rapidly (within hours) and recycle of solids should result in rapid crystal growth and effective phosphate removal to low residuals (approximately 0.3 mM/ℓ). Sludge production should be small since calcium phosphate precipitation should take place in the absence of calcium carbonate formation.

V. SUMMARY AND CONCLUSIONS

The following conclusions can be reached as a result of the research conducted here and later work discussed in conjunction with the currently reported work:

1. It has been demonstrated that post-aeration with the use of a small amount of waste activated sludge as a precipitate collector in the post-aeration basin is a viable process for phosphate removal following the activated sludge process.

2. It has been demonstrated that the anaerobic digester would cause a significant recycle of phosphorus when used in conjunction with activated sludge and a post-aeration process for phosphorus removal.

3. It has been demonstrated that anaerobic digester supernatant aeration causes rapid precipitation of phosphate but that separation of the precipitated material is difficult and significant phosphorus recycle will still result even if supernatant aeration and separation of precipitated solids is conducted.

4. It has been demonstrated that dosing of the digester supernatant with lime will cause decreases in the recycling of phosphorus but a significant amount of recycling will still occur. In view of these findings it is recommended that the anaerobic digester not be considered as a sludge treatment device if it is desirable to produce low (<2 mg P/ℓ) phosphorus residuals and if it is impossible to eliminate digester supernatant recycle.

5. Preliminary experiments on clean solutions have indicated that pH, carbonate, and magnesium have complex effects on the rate and extent of calcium phosphate precipitation at wastewater treatment concentrations. These data have been discussed in the light of later work by Ferguson _et al_. [4] and lead to the suggestion of new techniques for the removal of phosphate from wastewater by calcium phosphate precipitation as well as contributing information that helps to explain previously observed results from such phosphate removal processes.

APPENDIX

ANALYTICAL TECHNIQUES

Soluble Calcium. Soluble calcium was determined by EDTA titration using hydroxynaphthol blue as indicator [18].

Total Calcium (sludge samples). Total calcium was determined on a sample after ashing. A suitable sample volume (usually 20 mℓ) was evaporated to dryness on a steam table. The dried sample was ashed at 800°C for 30 minutes. The residue was heated on a steam table with 10 mℓ of 2N HCl for 10 minutes and then transferred to a 250-mℓ beaker using deionized water. The sample was neutralized to a pH of 7.0 with 0.1N NaOH and titrated with EDTA using hydroxynaphthol blue as indicator.

Chemical Oxygen Demand. COD was determined by the method given in Standard Methods 12th Edition [19] using a silver sulfate catalyst.

Magnesium. Magnesium was determined by the difference between the total hardness and the calcium concentrations.

pH. The pH measurements were made using a Beckman Expandomatic pH meter.

Sludge Volume Index (SVI). SVI of the mixed liquor was determined using the method given in Standard Methods 12th Edition [19].

Suspended Solids (sewage samples). Suspended solids were determined by the membrane (Millipore) filter technique of Winneberger et al. [20].

Suspended Solids in Activated Sludge. Suspended solids in activated sludge were determined by filtration through a Whatman GF/C glass filter followed by drying at 105°C and weighing of the residue (Jenkins [21]).

Total Solids in Raw Sludge. Total solids were determined gravimetrically on raw sludge following blending of the sludge in a Waring blender.

Total Phosphate. Total phosphate was determined on a sample after alkaline ashing. A suitable sample volume (usually 10 mℓ) was treated with 1 mℓ of 5% $MgCl_2 \cdot 6H_2O$ solution and evaporated to dryness on a steam table. The dried sample was ashed at 800°C for 1 hr. The residue was heated on a steam table for 30 min with 3 mℓ strong acid molybdate solution and after cooling was transferred to a 100-mℓ volumetric flask. Aminonaphthol sulfonic acid (4 mℓ) was added and the volume made up to 100 mℓ. The absorbence of the molybdenum blue was read at 630 mμ after 6 min using a 1-in cell in a Bausch and Lomb Spectronic 20. The concentrations of all reagents were as given in Standard Methods 10th Edition [22].

Soluble Phosphate. Soluble phosphate was determined by filtering the sample through washed 0.45-μ membrane filters and then proceeding as for the total phosphate.

Orthophosphate. Orthophosphate was determined using the aminonaphthol sulfonic acid (ANS) method outlined in Standard Methods 10th Edition [22] with the following modifications:

1. Absorbence was read at 630 mμ instead of 690 mμ.
2. Three mℓ of strong-acid molybdate was used instead of 4 mℓ.
3. Six minute reaction time was used instead of 10 min. The two latter modificationswere made to reduce the possibility of polyphosphate hydrolysis during the orthophosphate analysis.

Ortho + Hydrolyzable Phosphate. The sample was placed in a 250-mℓ beaker, 8 mℓ of 8N H_2SO_4 were added and the mixture diluted to 40 mℓ with distilled water. Two Hengar selenized granules were added, the beaker covered with a watch glass, and the mixture boiled gently for 40 min. After cooling, the sample was neutralized with 8 N NaOH to the phenolphthalein end point. A few drops of 4.5N H_2SO_4 were added until the pink color disappeared. The sample was then transferred to a 100-mℓ volumetric flask and 3 mℓ strong acid molybdate solution was added and mixed by swirling. ANS reducing agent (4 mℓ) was added and mixed and then the mixture diluted to 100 mℓ with distilled water. The absorbence was read after 6 min on a Bausch and Lomb Spectronic 20 at 630 mμ using a 1-in cell. Reagent concentrations were as described in Standard Methods, 10th Edition [22].

Total Hardness. Total hardness was determined by EDTA titration using eriochrome black T as indicator [23].

Volatile Suspended Solids in Activated Sludge. Volatile suspended solids in activated sludge were determined by combustion of the solids retained by a Whatman GF/C glass filter at 500°C for 30 min [21].

Digester Gas Analysis. The amounts of CH_4 and CO_2 in the digester gas were determined by gas chromatography [24].

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