THE FATE OF PHOSPHORUS IN WASTE TREATMENT PROCESSES: THE ENHANCED REMOVAL OF PHOSPHATE BY ACTIVATED SLUDGE

by

Arnold B. Menar[1] and David Jenkins[2]

For Presentation At The
24th Purdue Industrial Waste Conference
Purdue University, Lafayette, Indiana
May 6-8, 1969

[1] Doctoral Candidate, Department of Civil Engineering, University of California, Berkeley.

[2] Assistant Professor, Department of Civil Engineering, University of California, Berkeley, and Chief Chemist, Sanitary Engineering Research Laboratory, University of California, Berkeley.

I. Introduction

In the considerable body of literature concerning the fate of phosphate in the activated sludge process, there appear to be two distinct schools of thought. The first viewpoint, represented in papers by Sawyer [1], Sekikawa et al. [2], Hall and Engelbrecht [3], and Jenkins and Menar [4], can be summarized as follows: (i) The volatile mass of activated sludge contains between 2% – 3% by weight of biologically incorporated phosphorus; (ii) the amount of phosphate incorporated biologically into activated sludge is not affected by the growth rate of the sludge, or by process operating parameters such as organic loading, mixed liquor suspended solids concentration (MLSS), aeration rate, or mixed liquor dissolved oxygen (DO) concentration; (iii) phosphate removal is proportional to the net sludge growth.

With activated sludge P contents of 2% – 3%, domestic sewage P contents of 10 mg P/ℓ, and substrate removal rates in the standard-rate range (0.4 – 1.0 lb COD removed/lb MLVSS-day), biological removal of phosphate can only account for a maximum of 20% – 30% of the influent phosphate or about 2 – 3 mg P/ℓ of an influent 10 mg P/ℓ.

The second point of view, expounded in papers by Levin and Shapiro [5], Borchardt and Azad [6], and Connell and Vacker [7], embodies the idea that under certain conditions activated sludge is capable of removing more than the 2% – 3% phosphate-P that it requires for growth. The biological uptake of excess phosphate has been termed "luxury uptake." According to these authors phosphate removal by this mechanism is enhanced by high DO concentrations and, conversely, phosphate that has been incorporated into sludges by the luxury uptake mechanism can be released easily under anoxic conditions and conditions of low pH, such as those that might be encountered in the sludge blanket at the bottom of a secondary clarifier or in an anaerobic digestor. Further, luxury uptake of phosphate leads to sludges with phosphate contents 2 – 3 times greater than "normal" sludges and consequently, treatment of domestic sewage at standard organic loading rates can lead to phosphate removals of 60% – 90% of an influent 10 mg·P/ℓ.

A mechanism for the enhanced removal of phosphate must be consistent with these observations and in addition must provide satisfactory interpretation of the following observations made at the Rilling Road Plant, San Antonio, Texas – a plant that has experienced phosphate removals as high as 90%:

(i) At a point about 3/4 of the way along the 300 ft long aeration basin where the DO concentration increases from about 1.2 mg/ℓ to about 5 mg/ℓ there is a sharp drop in soluble orthophosphate concentration.

(ii) "Reversed tapered aeration," in which higher aeration rates are used at the tail end of the aeration basin than the head end of the basin, enhanced the removal of phosphate.

(iii) During aeration at the Rilling Road Plant, the pH of the sewage increased from 7.3 to 7.9.

(iv) Activated sludge with a high phosphate content had a very low (approximately 70%) volatile matter fraction.

II. Postulated Mechanism of Enhanced Phosphate Removal

Phosphate removal in excess of that predicted by biological growth requirements (to produce an activated sludge with a 2% – 3% P content and a P removal of 20% – 30% of the typical 10 mg P/ℓ in a domestic sewage) is caused by chemical precipitation. Following precipitation, the phosphate precipitate becomes physically entrapped in the matrix of the activated sludge floc and is removed with the waste-activated sludge.

In hard water sewages, such as at San Antonio, Texas, a significant part of the removal of phosphate by chemical precipitation is caused by calcium phosphate precipitation.

If it is postulated that the solubility of calcium phosphate in sewage is a function of the pH of the sewage, then it is possible to rationally explain the observations made at San Antonio [7] and by other workers [5,6] using a precipitation hypothesis.

In the metabolism of organic matter activated sludge consumes oxygen and produces CO_2. It is this CO_2, in any particular sewage, that controls the pH of the mixed liquor. To substantiate this contention, measurements of the CO_2 content of the diffused air issuing from a pilot activated sludge plant at SERL have been made by Weddle [8]. Concentrations of CO_2 were on the order of 0.5% by volume, compared with typical atmospheric CO_2 contents of 0.03% by volume.

In an activated sludge aeration basin the DO concentration is controlled by the rate of aeration and the rate at which the activated sludge consumes oxygen (for a constant rate of oxygen transfer). It can also be reasoned that, since O_2 is consumed and CO_2 is produced by activated sludge in the metabolism of its substrate, the rates of O_2 uptake and CO_2 production should parallel each other.

In a conventionally operated activated sludge basin, the return activated sludge and settled sewage enter at the head end of the basin. At this point the rates of CO_2 production and DO consumption are high. Consequently the DO concentration in the mixed liquor is low. The high CO_2 production rate leads to high CO_2 concentrations in the mixed liquor. This results in a low pH in the mixed liquor. As the mixed liquor proceeds down the aeration basin, the amount of degradable organic matter decreases and this decrease is reflected by both decreasing DO consumption and decreasing CO_2 production rates. At a constant air supply rate, decreasing DO consumption and CO_2 production rates lead to an increase in mixed liquor DO concentration and a lower dissolved CO_2 content. The lower CO_2 content allows the pH of the mixed liquor to rise to a value higher than that at the head end of the basin. Thus an increase in DO concentration should be accompanied by an increase in mixed liquor pH.

At some point along the length of the basin the pH will rise to a value at which calcium phosphate precipitation will take place.

This point will coincide <u>fortuitously</u> with the point at which the mixed liquor DO concentration increases, and <u>significantly</u> with the point at which a decreased CO_2 content in the mixed liquor has allowed the mixed liquor pH to rise to a point where calcium phosphate precipitation occurs.

In addition to these factors, if one assumes that the dissolved Ca^{+2} cation and the dissolved orthophosphate anion are the species involved in calcium phosphate precipitation then several other changes that take place during aeration may influence the precipitation of calcium phosphate.

In a settled sewage entering an activated sludge aeration basin the total calcium and total phosphate consist of several forms. For example, the total phosphate may be a combination of dissolved orthophosphate, some organic phosphate both in solution and suspension and some condensed phosphate. Calcium may be present as the free cation and also as particulate salts with fatty acid anions and particulate or dissolved complexes with condensed phosphate anions.

During aeration the microbiological action of the activated sludge results in the rapid hydrolysis of condensed phosphates to orthophosphate, producing dissolved orthophosphate and possibly releasing calcium from condensed phosphate complexes. Microbial degradation of fatty acid salts of calcium would also be expected to release Ca^{+2} ions and degradation of organic compounds containing phosphate might release further small amounts of phosphate. The net result of these processes is that both the dissolved orthophosphate and the dissolved calcium ion may be expected to increase as a result of the treatment of settled sewage in an activated sludge aeration basin. These changes would all tend to increase the amount of the postulated precipitating ions.

The observation that release of phosphate takes place from activated sludge when it is held under anoxic conditions can also be explained by a calcium phosphate precipitation mechanism.

When anoxic conditions develop in activated sludge, it is a sign that the DO consumption rate of the activated sludge has exceeded the rate of oxygen supply to the liquid and that all DO has been exhausted. It can be reasoned that this consumption of DO is accompanied by a production of CO_2 and hence anoxic conditions should be accompanied by a pH decrease. The decrease in pH as well as the anoxia should be more severe in the matrix of the activated sludge floc than in the liquid surrounding the floc, especially if the activated sludge is in a quiescent condition such as that found in the sludge blanket at the bottom of a secondary sedimentation basin.

The precipitation hypothesis envisages an intimate association of the colloidal calcium phosphate particles with the activated sludge matrix. Consequently, pH decreases associated with anoxic conditions will be especially felt by the enmeshed calcium phosphate particles. Since it is possible that locally acid conditions may exist in an anoxic floc interior, it is conceivable that the calcium phosphate would be dissolved and orthophosphate released into solution.

This mechanism is in perfect agreement with observed phenomena. Thus it is observed that phosphate is released when the DO concentration is below 0.3 mg/ℓ [5] and that the phosphate released from activated sludge under anoxic conditions is from the acid-soluble fraction [9].

In summary, it can be seen that a mechanism for enhanced phosphate removal involving the precipitation of calcium phosphate is entirely plausible in light of reported observations. The experimental work that follows will provide confirmatory evidence that precipitation of calcium phosphate is an important mechanism for enhanced phosphate removal at plants with hard sewages such as the Rilling Road Plant at San Antonio, Texas.

III. Experimental Results

1. Laboratory Experiments

Effect of aerating gas on calcium phosphate precipitation. Batches of activated sludge effluent from the Valley Community Services District (VCSD) Water Reclamation Plant, San Ramon, California [which has mineral characteristics similar to those of San Antonio Sewage (Table I)], were aerated with air, pure nitrogen, pure oxygen, and air + 5% CO_2. The results of this experiment, (Figure 1), show that the important function of the aerating gas is CO_2-stripping which subsequently causes an increase in the pH of the liquid.

DO concentration per se is unimportant in the removal of dissolved orthophosphate, since O_2 and N_2 were equally effective in causing calcium phosphate precipitation. These two gases raised the pH of the activated sludge effluent to an identical value and at an identical rate while the DO in the effluent aerated with O_2 reached 34.4 mg/ℓ, the DO in the sample bubbled with N_2 fell from 7.2 mg/ℓ to 1.7 mg/ℓ.

Air was not as effective as either N_2 or O_2 in causing the precipitation of orthophosphate because air, containing approximately 0.03% CO_2, is not as efficient a CO_2-stripper as pure N_2 or O_2. This is reflected by the pH changes caused by bubbling air, in comparison to those caused by N_2 and O_2. The final pH in the N_2- and O_2-bubbled activated sludge effluents was 9.20, whereas the final pH of the effluent bubbled with

TABLE I

COMPARISON OF MINERAL CHARACTERISTICS OF WATER FROM SAN ANTONIO, TEXAS, AND SEWAGE FROM SAN RAMON, CALIFORNIA

Constituent	San Antonio, Texas, mg/ℓ	San Ramon,[c] California, mg/ℓ
PO_4 as P	9 [b]	16
Ca	64 [a]	66
Mg	17 [a]	44
Total Hardness as $CaCO_3$	230 [a]	346
Alkalinity as $CaCO_3$	225 [b]	405
pH	7.3 [b]	7.7

[a] Data for water supply from C. N. Durfor, and E. Becker, USGS Survey Paper 1812, 1964.

[b] Data from San Antonio Sewage Treatment Plant operating records for 1965.

[c] Mean of analytical data collected during this study.

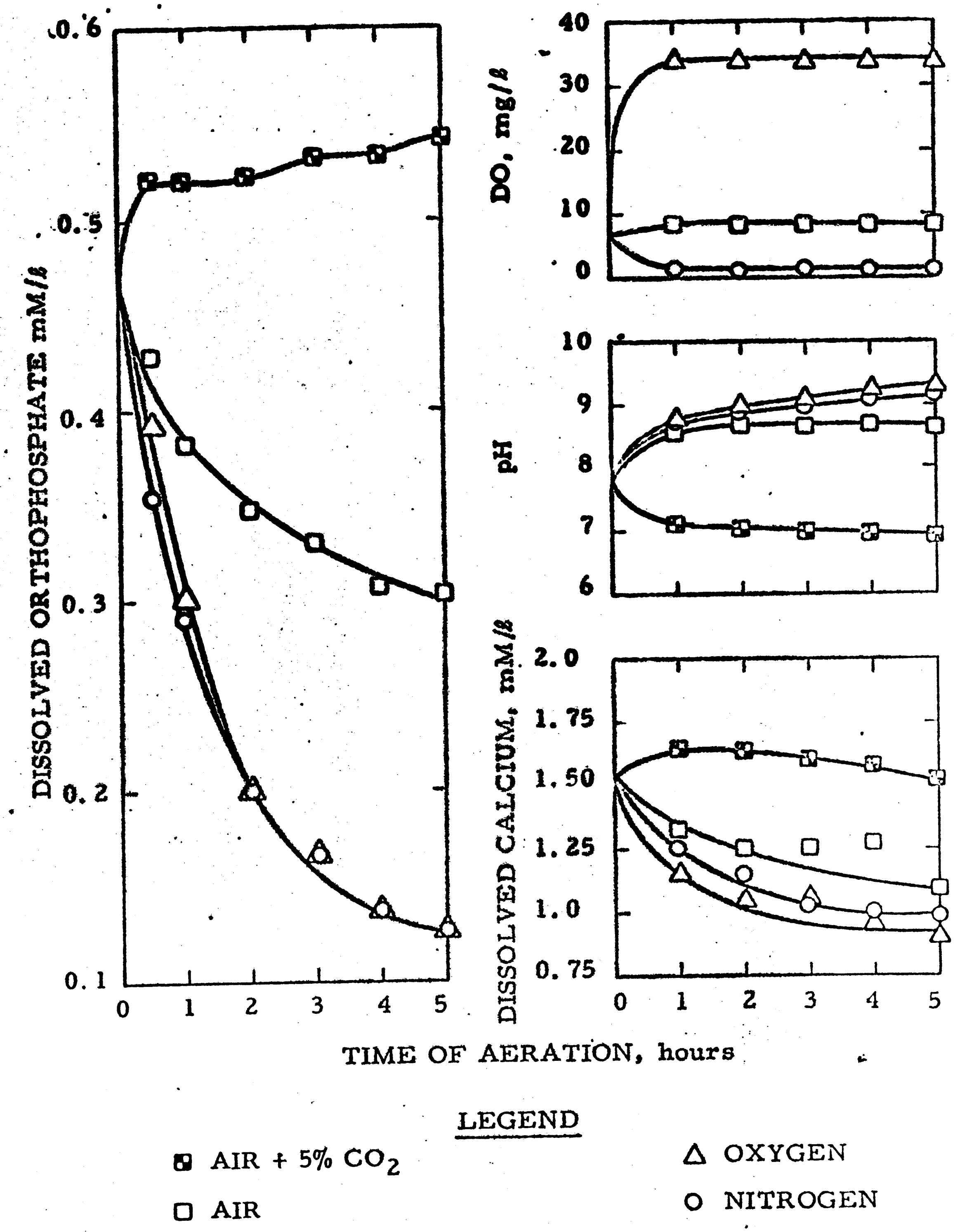

FIGURE I. BATCH AERATION OF ACTIVATED SLUDGE EFFLUENT WITH AIR, AIR + 5% CO_2, O_2, AND N_2

air was 8.65. Similarly, dissolved orthophosphate and calcium levels fell more rapidly and to lower values in the N_2- and O_2-aerated samples than in the effluent bubbled with air.

Aeration with air + 5% CO_2 caused a fall in pH from 7.75 to 6.95 since the aerating gas mixture contained a higher CO_2 content than that to which the activated sludge effluent had been equilibrated. A small increase in dissolved orthophosphate and calcium took place indicating that the sludge contained some calcium and orthophosphate that could be solubilized at a pH below 7.75.

Comparison of the results of aeration with air and with air + 5% CO_2 provides further indication of the unimportance of DO concentration in orthophosphate precipitation. While the DO concentration in both samples was identical at all times during the experiment, the dissolved orthophosphate concentration fell from 14.6 mg P/ℓ to 9.4 mg P/ℓ in the air-bubbled sample and rose from 14.6 mg P/ℓ to 16.9 mg P/ℓ in the sample aerated with air + 5% CO_2.

Release of calcium phosphate from activated sludge. Aliquots of activated sludge mixed liquor from a pilot plant that was being operated to produce a high phosphate sludge (5.2% P on a VSS basis) were aerated with air, air + 0.5% CO_2 and air + 5% CO_2. Initially and after 3 hours of aeration the DO, pH, dissolved orthophosphate, and dissolved calcium concentrations were determined. The DO concentration in all three aliquots increased from 5.8 mg/ℓ to 8.4 mg/ℓ (Table II). In the sample aerated with air the pH increased from 8.17 to 8.43 and the dissolved calcium and orthophosphate decreased by 0.13 and 0.08 mM/ℓ, respectively. In the activated sludges aerated with air + 0.5% CO_2 and with air + 5% CO_2, the pH fell from 8.17 to 7.60 and 6.85, respectively. In both of these samples, dissolved calcium and orthophosphate were released (Table II), the releases being greater for the sample aerated with air + 5% CO_2 (and having the lower pH).

2. Pilot Plant Experiments

A four-compartment, 300-ℓ aeration-capacity activated sludge pilot plant was located at the VCSD Water Reclamation Plant, San Ramon, California. The pilot plant was fed with primary effluent from the VCSD primary sedimentation basins. The plant was equipped with composite samplers that sampled the influent and effluent flows every 15 minutes and pumped these samples into refrigerated containers.

During each of the experiments the pilot plant performance (and where applicable the performance of the VCSD plant) was characterized by organic loading, hydraulic residence time, mean cell residence time, and substrate removal efficiency.

For each experimental period the daily measurements of process performance were graphically summarized, and periods of steady operation were determined by inspection. The criterion for steady state operation of the pilot activated sludge plant

TABLE II

RELEASE OF ORTHOPHOSPHATE FROM ACTIVATED SLUDGE

Analysis	Initial Concentration	After 3-hr Aeration With:		
		Air	Air + 0.5% CO_2	Air + 5% CO_2
DO, mg/ℓ	5.8	8.4	8.4	8.4
pH	8.17	8.43	7.60	6.85
Dissolved Orthophosphate, mM/ℓ	0.33	0.25	0.51	1.04
Dissolved Calcium, mM/ℓ	1.49	1.36	1.72	2.45
Mole Ratio of Released Calcium and Orthophosphate: Ca:P	-	-	1.28	1.35

was ± 30% deviation of daily values of MLVSS and substrate removal rate from the mean value and a ± 15% deviation of daily sludge Ca and P values from the mean value. The data during periods of steady state operation were then screened for conformance to a phosphate materials balance. The criterion for conformance to the phosphate materials balance was ± 10% from completion. Only data that conformed to steady state and phosphate materials balance criteria were used.

"San Antonio" conditions. The pilot plant was operated to conform to the parameters reported to be important for enhanced phosphate removal by Connell and Vacker [7] in their studies at the San Antonio, Rilling Road Plant. The pilot plant aeration basin configuration with four 75-ℓ CSTR's* in series and with settled sewage and return activated sludge entering at the first reactor, closely resembled the 2-pass aeration basin of the Rilling Road Treatment Plant. The results of the six-week experiment (Table III) show that enhanced phosphate removal was not obtained in the pilot plant when the Rilling Road conditions were matched almost identically. Thus, under conditions of identical MLSS, BOD loading, effluent NO_3-N, and at mixed liquor DO concentrations that consistently exceeded the specified minimum of 1.5 mg/ℓ, the pilot plant reduced the phosphate concentration from 15.2 to 12.2 mg P/ℓ – a removal of phosphate that could be accounted for entirely by incorporation into activated sludge cell material, i.e.,

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*Continuously stirred tank reactors.

TABLE III

COMPARISON OF AVERAGE OPERATING CONDITIONS AND PHOSPHATE REMOVAL AT SAN ANTONIO RILLING ROAD PLANT AND AT PILOT PLANT OPERATED UNDER SAN ANTONIO CONDITIONS

Parameter	Rilling Road[a] Plant	Pilot Plant
MLSS, mg/ℓ	1130	1130
BOD Loading, lb BOD/lb MLSS-day	0.5	0.5
Mean Cell Residence Time, days (Sludge Age)	3.2	2.2
Mixed Liquor DO, mg/ℓ	3.0	2.8
Effluent NO_3-N, mg N/ℓ	1.0	1.5
Influent pH	7.3	7.7
Effluent pH	7.9	7.8
Influent Total Phosphate, mg P/ℓ	10.5	15.2
Effluent Dissolved Phosphate, mg P/ℓ	0.9	12.2
Phosphate Removed, mg P/ℓ	9.6	3.0

[a] Data from Connell and Vacker [7].

biological removal for growth. Indeed, during the entire period of operation under San Antonio conditions, the activated sludge P content in the pilot plant never exceeded 2.9% on a volatile matter basis and averaged 2.3% P — a figure which is in excellent agreement with that (2.6% P) obtained in previous work (Jenkins and Menar [4]).

It was concluded that the conditions of MLSS, BOD loading, effluent NO_3-N and mixed liquor DO reported by Connell and Vacker [7] were of no direct significance in the enhanced phosphate removal by activated sludge in this study.

<u>Preaeration experiment</u>. The purpose of this experiment was to determine whether the pH of the incoming sewage could be raised by preaeration to such a degree that phosphate precipitation would take place in the activated sludge aeration basins.

The pilot plant was divided into two sections of approximately equal volume, the first two reactors serving as preaeration basins and the latter two as the activated sludge aeration basins. Both the preaeration and aeration sections were further baffled to prevent short-circuiting by dividing each reactor into four compartments.

The operating conditions and the results of the 3-week long preaeration experiment are summarized in Table IV.

With average preaeration and aeration times of 4.3 and 4.4 hours respectively, the pH of the influent settled sewage

TABLE IV

OPERATING CONDITIONS AND RESULTS OF PILOT-PLANT PREAERATION EXPERIMENT

	Influent	Preaeration	Overall (Preaeration + Activated Sludge)
<u>Operating Conditions</u>			
Substrate Removal Rate, lb COD removed/lb MLVSS-day	-	2.4	0.8
Mean Cell Residence Time, days	-	0.18	2.3
Hydraulic Residence Time, hours	-	4.3	8.7
Air Supply Rate, cu ft/gal waste treated	-	14.0	28.0
MLSS, mg/ℓ	-	443	770
MLSS, volatile fraction, %	-	81.1	76.5
<u>Results of Operation</u>			
Influent Total COD, mg/ℓ	217		
Effluent Dissolved COD, mg/ℓ		78	41
COD Removal Efficiency, %		64	81
Influent Total P, mg P/ℓ	15.3		
Effluent Dissolved P, mg P/ℓ		11.0	10.1
MLVSS, P Content, %		3.2	4.5
Influent Total Ca, mg Ca/ℓ	64.4		
Effluent Dissolved Ca, mg Ca/ℓ		62.0	58.8
Influent pH	7.7		
Effluent pH		8.3	8.3
Effluent DO, mg/ℓ	1.5	5.4	6.2

was raised from 7.7 to 8.3 during preaeration, a pH that was maintained in the mixed liquor aeration basins.

The phosphate concentration was reduced by 4.3 mg P/ℓ (total influent P − dissolved effluent P) during preaeration and further reduced by 0.9 mg P/ℓ by the activated sludge section of the plant. The overall reduction of 5.2 mg P/ℓ is far greater than the approximately 2 − 3 mg P/ℓ reduction that would be predicted by biological removal alone at a substrate removal rate of 0.8 lb COD/lb VSS-day (Jenkins and Menar [4]). The activated sludge in the aeration basin contained 4.5% P on a VSS basis, a figure which is significantly greater than the average 2.6% found by Jenkins and Menar [4] for activated sludge. Calcium concentrations were reduced by 2.4 mg Ca/ℓ (total influent − dissolved effluent) by preaeration and by 5.6 mg Ca/ℓ after aeration.

From these data it could be reasoned that as the pH rises and as calcium and orthophosphate are released during preaeration, precipitation of a colloidal calcium phosphate takes place. On contact with the mixed liquor in the aeration basin, the colloidal calcium phosphate particles agglomerate with activated sludge and are removed.

<u>Comparative study with VCSD plant</u>. The objective of the comparative study was to show that the phosphate removal of two activated sludge plants, operated with identical flow patterns and organic loadings and treating the same sewage,

could be regulated by the pH of the mixed liquor. The pilot plant was operated identically to the VCSD treatment facility, i.e., as a sludge reaeration plant with 25% of the aeration basin used for sludge reaeration. The only operating variable that differed between the two plants was the rate of aeration, which was 3 cu ft/gal in the VCSD plant and approximately 97 cu ft/gal in the pilot plant.

Mean operating conditions and results of the 11-week comparative study (Table V) show that the pilot plant and VCSD plant operating parameters were identical with the exception that the hydraulic residence time in the pilot plant was 7.8 hr compared with 9.1 hr in the VCSD plant.

In the VCSD plant the pH of the sewage fell from 7.7 to 7.2 during activated sludge treatment, while the increased rates of aeration in the pilot plant caused a pH <u>increase</u> of from 7.7 to 8.3 during treatment. The VCSD activated sludge plant removed 2.7 mg P/ℓ to produce an activated sludge with 2.1% P (VSS basis) – figures entirely predictable on the basis of phosphorus requirements for biological growth (Jenkins and Menar [4]). The pilot plant, however, effected a removal of 4.8 mg P/ℓ and produced an activated sludge containing 4.0% P (VSS basis) – values far in excess of those predictable from sludge growth requirements.

The pilot plant activated sludge was significantly lower in volatile matter content than the VCSD sludge (79% compared with 85%), indicating that it contained a higher

TABLE V

OPERATING CONDITIONS AND RESULTS FOR COMPARATIVE STUDY

	Pilot Plant	VCSD Plant
Operating Conditions		
Substrate Removal Rate, lb COD removed/lb MLVSS-day	0.25	0.20
Mean Cell Residence Time, days	12.6	12.9
Hydraulic Residence Time, hours	7.8	9.1
Air Supply Rate, cu ft/gal waste treated	97	3.0
MLSS, mg/ℓ	2,780	2,935
MLSS, volatile fraction, %	79.1	85.2
Mixed Liquor Temperature, °F	68.4	67.5
Results of Operation		
Influent Total COD, mg/ℓ	267	264
Effluent Dissolved COD, mg/ℓ	30	23
COD Removal Efficiency, %	88.8	91.3
Influent Total P, mg P/ℓ	16.6	16.8
Effluent Dissolved P, mg P/ℓ	11.8	14.1
MLVSS, P Content, %	4.0	2.1
Influent Total Ca, mg Ca/ℓ	69.6	68.0
Effluent Dissolved Ca, mg Ca/ℓ	56.0	58.0
MLVSS, Ca Content, %	4.4	1.4
Influent pH	7.7	7.7
Effluent pH	8.3	7.2
Effluent DO, mg/ℓ	8.4	4.2

content of inorganic material. The calcium content of the pilot plant activated sludge was 4.4% Ca (VSS basis) compared with 1.4% Ca (VSS basis) in the VCSD activated sludge. The calcium removal effected by the VCSD plant was 10 mg Ca/ℓ, whereas in the pilot plant 13.6 mg Ca/ℓ was removed.

Further experiments. Two additional pilot plant experiments, the first conducted at an average substrate removal rate of 0.2 lb COD/lb VSS/day and MLSS of 4950 mg/ℓ and the second at an average substrate removal rate of 0.59 lb COD/lb VSS/day and MLSS of 1850 mg/ℓ demonstrated that all the conditions associated with enhanced phosphate removal in the previous pilot scale experiments were effective in low-rate, high-solids units and in standard rate activated sludge units (Table VI and VII).

Parallel between Ca and P removal. During the comparative study a cold spell caused the performance of the relatively exposed pilot plant to deteriorate; especially with regard to phosphate removal. Figure 2 shows that the phosphate and calcium removals and the sludge phosphate and calcium contents fell simultaneously at the onset of the cold weather and recovered in perfect step following the return of normal temperatures. The parallel behavior of calcium and phosphate removals and sludge calcium and phosphate contents is strong evidence for a precipitation mechanism being involved in the enhanced phosphate removal by the pilot plant.

TABLE VI

OPERATING CONDITIONS AND RESULTS FOR LOW LOADING – HIGH SOLIDS STUDY

Operating Conditions	
Substrate Removal Rate, lb COD removed/lb MLVSS-day	0.2
Mean Cell Residence Time, days	14.5
Hydraulic Residence Time, hours	6.7
Air Supply Rate, cu ft/gal waste treated	83
MLSS, mg/ℓ	4950
MLSS, volatile fraction, %	66.1
Mixed Liquor Temperature, °F	77.6
Results of Operation	
Influent Total COD, mg/ℓ	273
Effluent Dissolved COD, mg/ℓ	33
COD Removal Efficiency, %	87.7
Influent Total P, mg P/ℓ	17.7
Effluent Dissolved P, mg P/ℓ	11.1
MLVSS, P Content, %	6.8
Influent Total Ca, mg Ca/ℓ	64.3
Effluent Dissolved Ca, mg Ca/ℓ	55.5
MLVSS, Ca Content, %	10.0
Influent pH	7.5
Effluent pH	8.1
Effluent DO, mg/ℓ	6.0

TABLE VII

OPERATING CONDITIONS AND RESULTS FOR STANDARD-RATE ACTIVATED SLUDGE STUDY

Operating Conditions

Substrate Removal Rate, lb COD removed/lb MLVSS-day	0.59
Mean Cell Residence Time, days	4.0
Hydraulic Residence Time, hours	6.0
Air Supply Rate, cu ft/gal waste treated	75
MLSS, mg/ℓ	1850
MLSS, volatile fraction, %	72.6
Mixed Liquor Temperature, °F	75.9

Results of Operation

Influent Total COD, mg/ℓ	232
Effluent Dissolved COD, mg/ℓ	36
COD Removal Efficiency, %	84.3
Influent Total P, mg P/ℓ	15.8
Effluent Dissolved P, mg P/ℓ	10.4
MLVSS, P Content, %	6.0
Influent Total Ca, mg Ca/ℓ	62.8
Effluent Dissolved Ca, mg Ca/ℓ	56.0
MLVSS, Ca Content, %	8.3
Influent pH	7.7
Effluent pH	8.1
Effluent DO, mg/ℓ	6.2

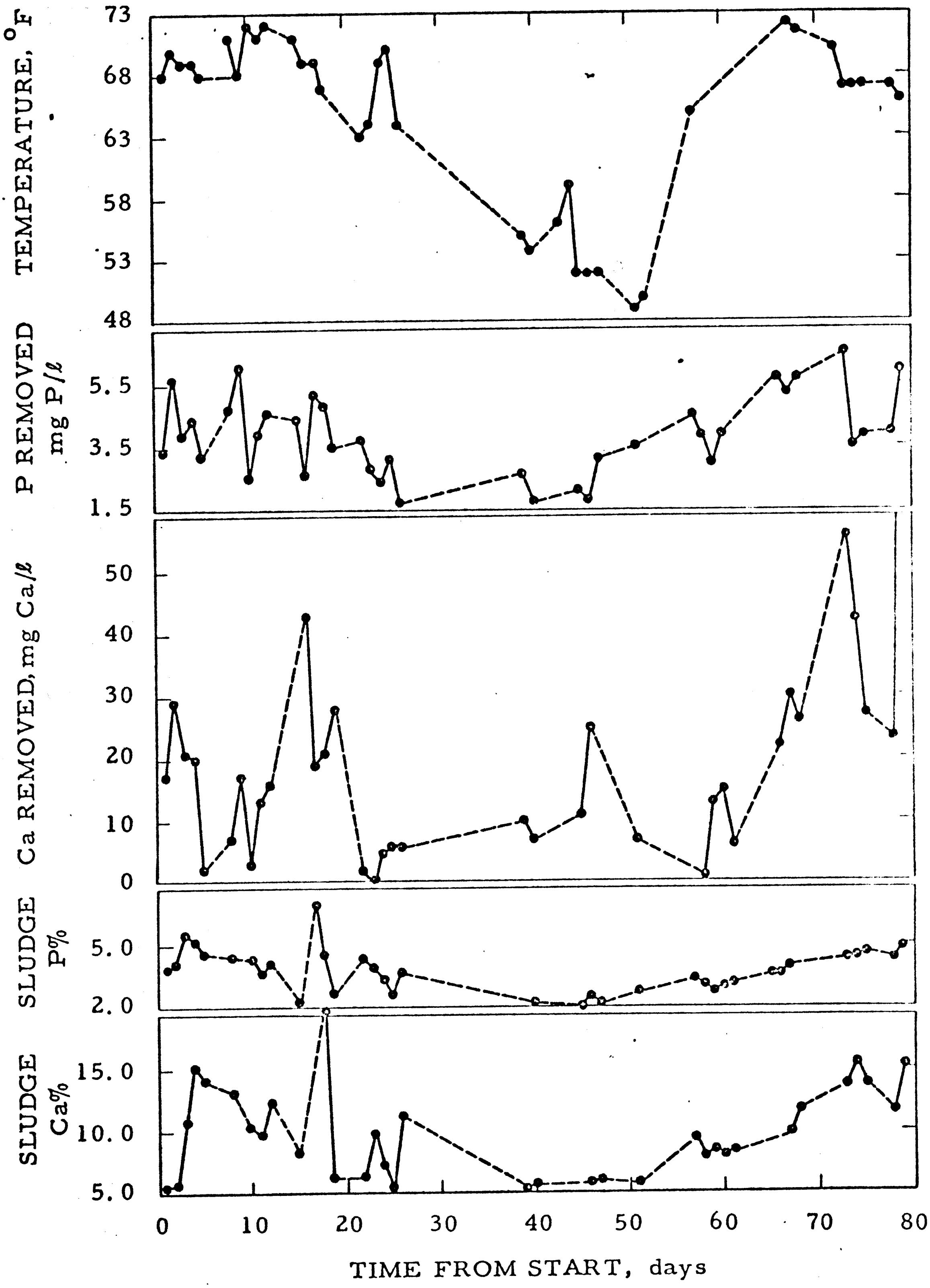

FIGURE 2. PARALLEL BETWEEN Ca AND P REMOVAL AND Ca AND P IN SLUDGE FOR PILOT PLANT

IV. Discussion

Laboratory and pilot plant experiments have shown that enhanced phosphate removal by activated sludge can be rationally explained by calcium phosphate precipitation followed by trapping of the precipitate by the activated sludge floc. Laboratory experiments demonstrated the insignificance of DO as a parameter in calcium phosphate precipitation and showed that pH was of decisive significance. The pilot plant experiments show that aeration basin DO reflects the pH value of the mixed liquor (Figure 3) with high DO concentrations being associated with high pH values for a given set of operating conditions.

Pilot plant activated sludge experiments have shown that decreases of dissolved phosphate were accompanied by decreases of dissolved calcium and that the activated sludge phosphate and calcium contents paralleled each other (Figure 4). Further evidence that increased activated sludge phosphate content was associated with an inorganic compound and not caused by a biological uptake was obtained from the relationship of activated sludge phosphate content to the volatile fraction of activated sludge (Figure 5). As the phosphate content of the activated sludge increases, its volatile fraction decreases. Data included in Figure 5 from the current pilot plant studies, from the San Antonio, Rilling Road Plant, and from prior studies by Jenkins and Menar [4] show that as phosphate incorporation into activated sludge increases a progressively more nonvolatile sludge is produced.

An examination of all laboratory and pilot plant data shows that there is a correlation between the apparent equilibrium ion

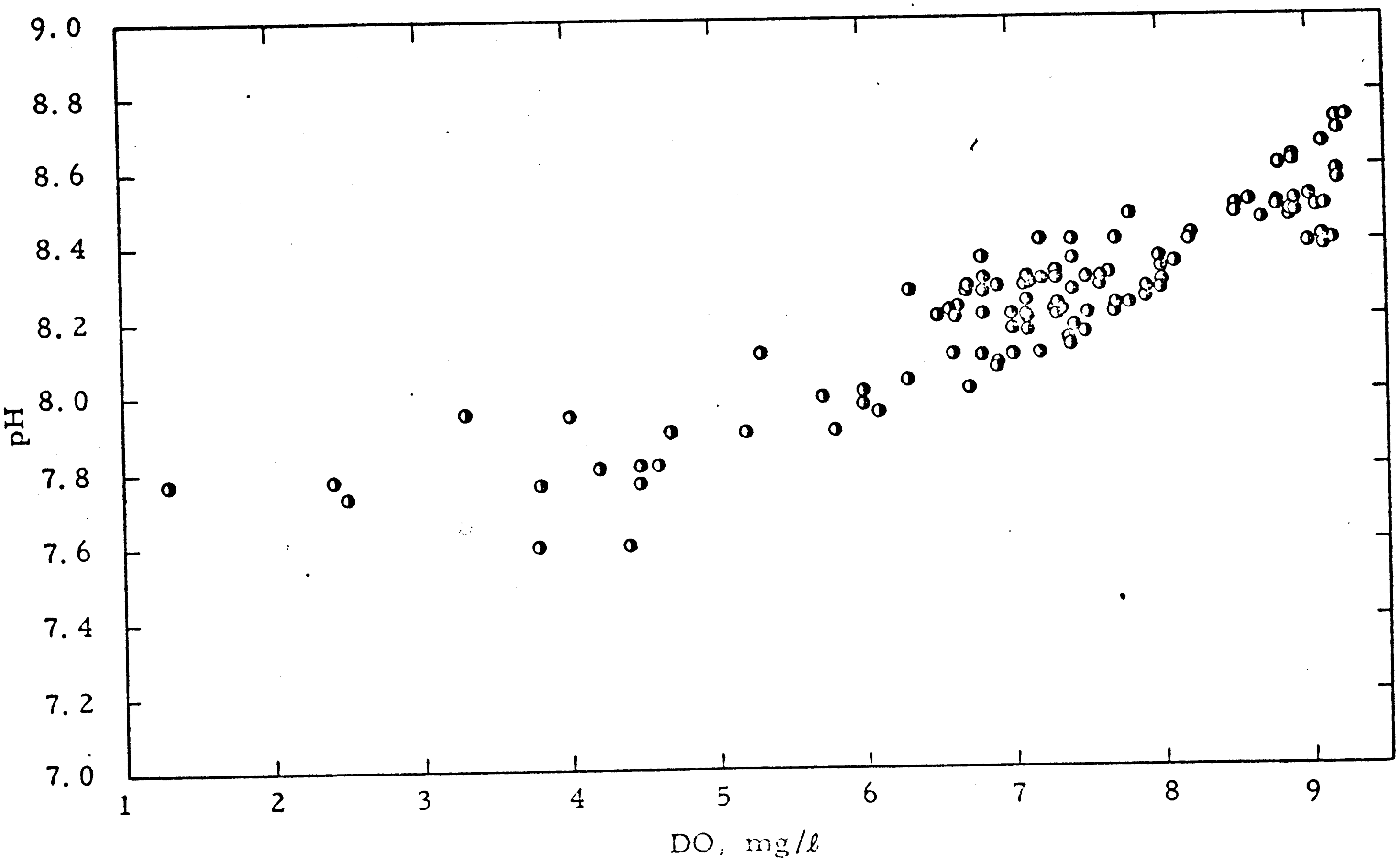

FIGURE 3. ILLUSTRATION THAT MIXED LIQUOR DO REFLECTS MIXED LIQUOR pH IN PILOT PLANT EXPERIMENTS

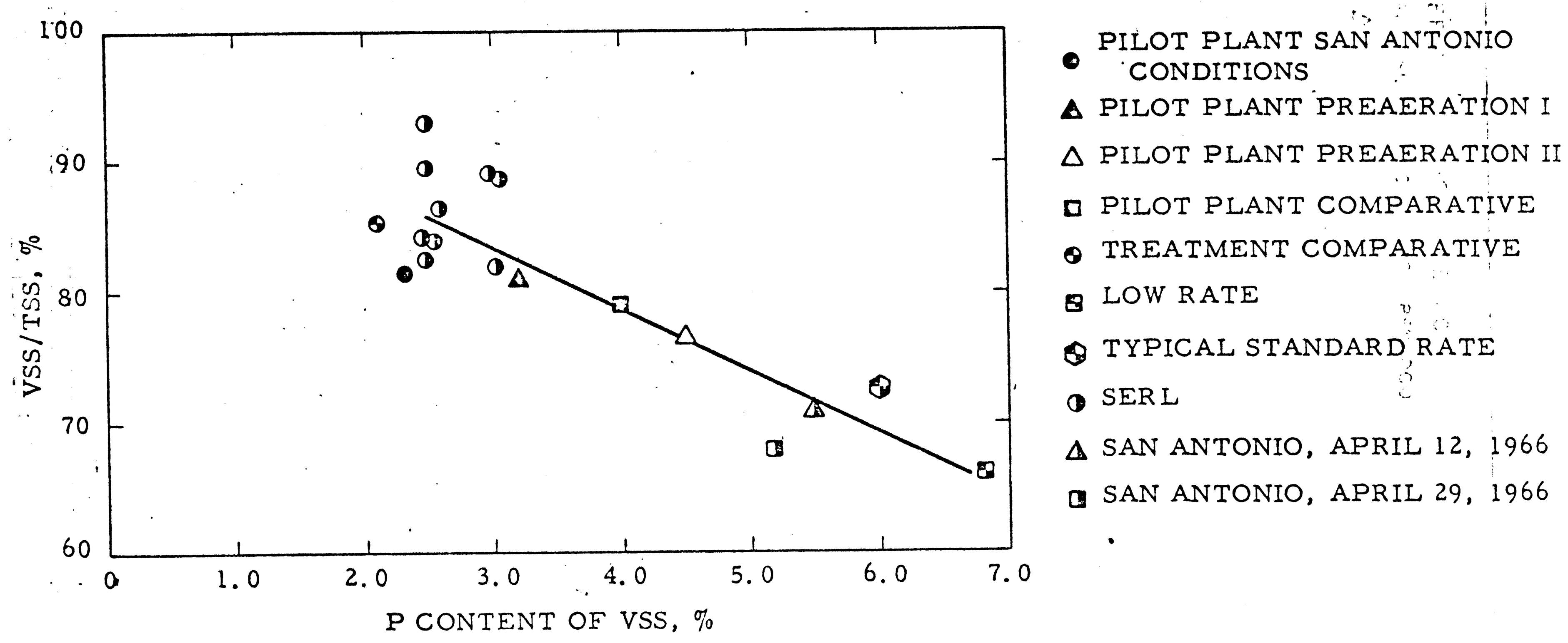

FIGURE 5. CORRELATION OF ACTIVATED SLUDGE PHOSPHATE CONTENT AND VOLATILE FRACTION

product $[Ca^{+2}]$ [Σ orthophosphate] and pH (Figure 6). While this correlation at the present time is empirical it does provide a consistent representation of the data and confirms the hypothesis that the solubility of calcium phosphate in sewage systems is a function of pH.

Several activated sludge treatment operating parameters claimed to be necessary for enhanced phosphate removal (Connell and Vacker [7], Levin and Shapiro [5]) do not appear to be significant. High DO concentrations _per se_ did not cause enhanced phosphate removal in these experiments. Connell and Vacker [7] report that the particular organic loading of 0.5 lb BOD/lb MLSS-day and the particular MLSS concentration of 1000 mg/ℓ were most favorable for enhanced phosphate removal. Pilot-plant-activated-sludge experiments showed that enhanced phosphate removals could occur at a wide range of organic loadings and MLSS concentrations. Other correlations of Vacker, Connell, and Wells [10] relating enhanced removal of phosphate to sludge volume index, effluent nitrate content, effluent SS concentration, and the effluent ammonia concentration, were not substantiated.

That enhanced removal of phosphate in an activated sludge system takes place by a precipitation mechanism has been demonstrated conclusively by this research. Moreover, in hard water sewages such as those of San Antonio and VCSD, the precipitation is largely as a calcium phosphate. However, it should be noted that the residual dissolved orthophosphate concentrations obtained at San Antonio at the pH values reported by Connell and Vacker [7] for this plant are much lower than would be predicted by the correlation curve in Figure 6. Moreover, the dissolved orthophosphate residuals obtained in the

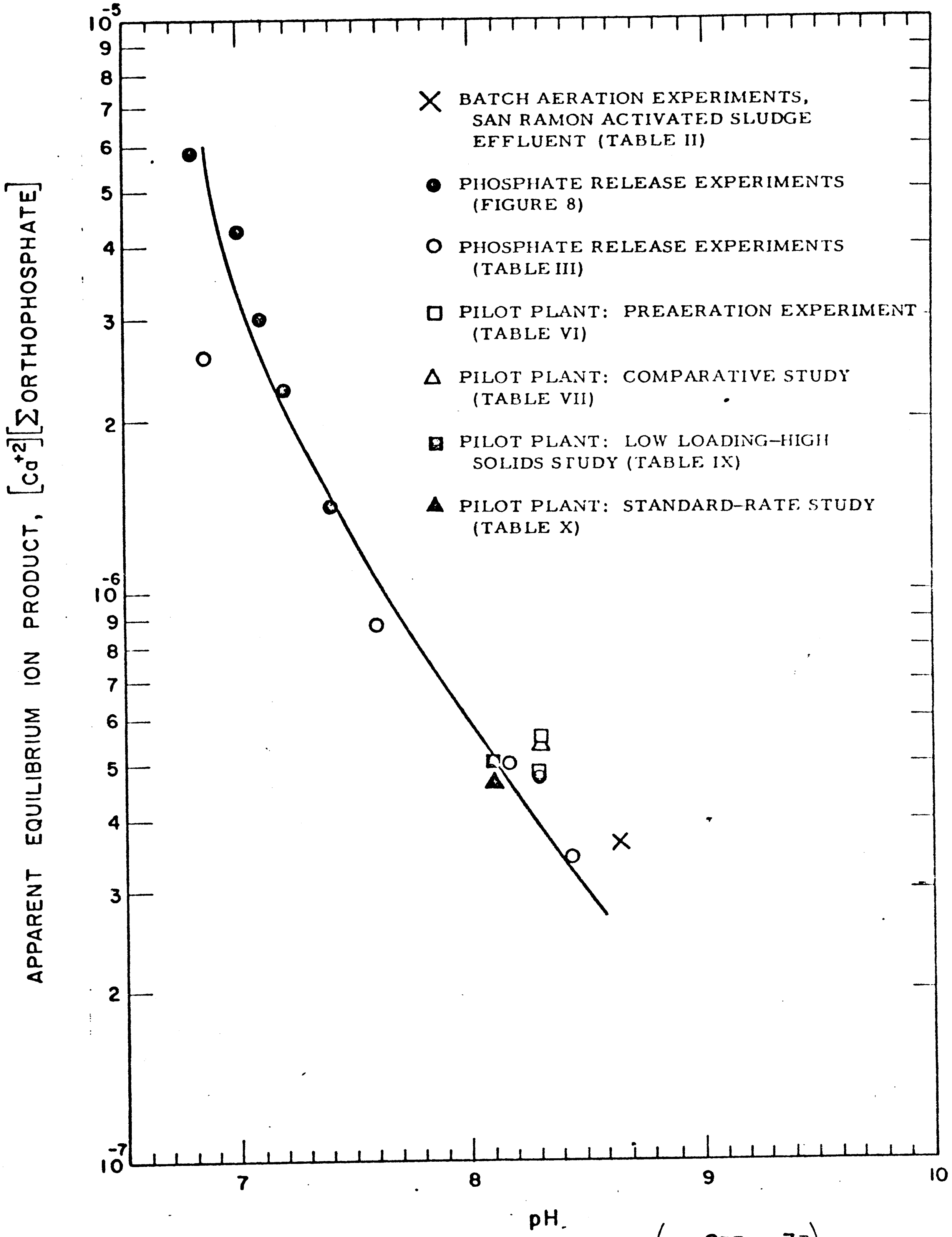

FIGURE 6. CORRELATION OF APPARENT Ksp $\left([Ca^{+2}][PO_4^{-3}]\right)$ WITH pH

pilot plant experiments at no time approached those low values of < 1 mg/ℓ P reported for the Rilling Road Plant at San Antonio [7]. It is possible therefore that other phosphate precipitants, that produce lower equilibrium dissolved orthophosphate concentrations, are present in San Antonio sewage. Analyses of activated sludge samples [10] taken from the Rilling Road Plant at San Antonio, when this plant was achieving $> 90\%$ phosphate removal showed high levels of calcium, aluminum, zinc and iron all of which form sparingly soluble phosphates at typical mixed liquor pH's. If one assumes that these metals were present in the activated sludge as their phosphate salts they account for a sludge P content of about 3% on a VSS basis. The total phosphate content of these sludge samples was approximately 5%. Therefore, the inorganic phosphates can account for the sludge P content in excess of the 2% typically incorporated into activated sludge by biological means.

The nature of the calcium phosphate precipitate cannot be conclusively stated at this time because of inconclusive data and because of the complexity, both ionic and organic, of the system in which precipitation takes place.

The literature on calcium phosphate precipitation [11-15] indicates that under the conditions of the laboratory and pilot plant experiments, hydroxyapatite is the thermodynamically stable crystalline species. However, the precipitates obtained in this work generally tended to have lower Ca:P ratios than hydroxyapatite. However, non-stoichiometric basic calcium phosphates with Ca:P ratios of less than the 1.66 required for hydroxyapatite have been widely reported [16-20].

A further complicating factor in these systems that makes a determination of the nature of the precipitate exceedingly difficult is that they are also supersaturated with $CaCO_3$. Indeed experiments showed that $CaCO_3$ was precipitated and incorporated into activated sludge under the conditions where enhanced phosphate removal was achieved.

Attempts to determine the nature of the precipitate by x-ray crystallographic analysis of activated sludge containing high phosphate levels failed to show any crystallinity. It would, therefore, seem that any precipitates that form are poorly crystalline. This observation is in agreement with Bachra et al. [11] who have shown in carbonate-phosphate systems, that high C:P ratios and the presence of Mg^{+2} tend to encourage the formation of amorphous precipitates.

V. Conclusions

1. The conventionally designed and operated combination of primary and secondary treatment processes can remove a maximum of 20% – 30% of an influent 10 mg P/ℓ by biological means.
2. Enhanced phosphate removal by the activated sludge process in hard water sewages is caused by the precipitation of a calcium phosphate followed by the enmeshing of the precipitate into the activated sludge floc.
3. The degree of calcium phosphate precipitation in activated sludge mixed liquor and in activated sludge effluents are largely controlled by pH which, in turn, in an activated sludge aeration basin is largely controlled by the CO_2 content of the mixed liquor.
4. DO concentration in the mixed liquor or in a sludge blanket in the secondary clarifier has no influence on the precipitation of calcium phosphate and has no involvement in the enhanced removal of phosphate by activated sludge. A high DO concentration in mixed liquor is an indicator that the CO_2 content of the aerating air is low and that the pH of the mixed liquor is high. A low DO concentration in a sludge blanket is indicative of a high CO_2 concentration and low pH. Thus, high DO is fortuitously correlated with the conditions that favor phosphate precipitation while low DO concentrations represent conditions unfavorable for calcium phosphate precipitation.

5. The normal total phosphate content of activated sludge volatile solids, when biological incorporation of phosphate is the only mechanism of phosphate incorporation, is between 2% – 3% P. Enhanced phosphate removal produced activated sludges with up to 6.8% P on a VSS basis. Similarly, enhanced phosphate removal produced activated sludges with calcium levels of up to 10.0% Ca on a VSS basis compared with the approximately 2.0% Ca incorporated biologically into activated sludge.
6. An empirical correlation between the apparent equilibrium ion product $[Ca^{+2}]$ $[\Sigma$ orthophosphate$]$ and pH was developed which fitted all laboratory and pilot plant data and which can be used as a predictive tool to determine the required chemical additions to produce given effluent dissolved phosphate concentration.
7. All experiments, both laboratory and pilot plant, resulted in the removal (incorporation into activated sludge) of mole ratios of Ca:P of between about 1.3 – 2.1. The nature of the precipitate cannot be conclusively stated. It was determined, however, that $CaCO_3$ precipitated from San Ramon sewage under conditions that allowed calcium phosphate precipitation.
8. X-ray crystallographic analysis failed to show crystallinity in the precipitates incorporated into activated sludge.
9. Pilot-plant experiments showed that organic loading, mixed liquor DO concentration, MLSS concentration, are <u>without influence</u> in the enhanced removal of phosphate by activated sludge.

10. It appears that the enhanced removal of phosphate at the Rilling Road Plant of San Antonio, Texas, cannot be explained on the basis of a biological mechanism such as "luxury uptake."

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