



PHOSPHORUS REMOVAL

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GENERAL INFORMATION ON PHOSPHORUS REMOVAL

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GENERAL INFORMATION ON PHOSPHORUS REMOVAL

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The key role of phosphorus in the process of eutrophication (aging of lakes and impoundments) has been known for many years. However, until recently, eutrophication of the nation's waterways was not a significant problem. Consequently, control of the phosphorus level in streams and lakes was not considered an important pollution control problem. Since the conclusion of World War II, however, the rate of eutrophication has increased to the point where it is a major water quality problem. Although other nutrients play a role in eutrophication, recent articles by Sawyer^(1,2) have indicated that much of the recent increase in eutrophication rate is linked to significant increases in phosphorus discharges to rivers and lakes. Sawyer has shown that virtually all of the increase in phosphorus discharge is due to the activities of man and has termed the resulting eutrophication, cultural eutrophication.

The major sources of phosphorus contributing to eutrophication are domestic sewage and agricultural runoff. Domestic sewage is the primary source in critical areas, and only this source will be discussed here. Phosphorus gains entrance to sewage from human body wastes (primarily urine) and through the use of condensed inorganic phosphate compounds as builders in detergent formulations. Each of these sources accounts for about half of the phosphorus in domestic sewage. Thus, while elimination of phosphorus from detergent formulations would be helpful, it would not be the total answer to the eutrophication problem. Treatment of domestic sewage to remove a significant portion of the phosphorus contributed by human wastes and detergent builders would, however, have a significant effect on eutrophication rate.

Phosphorus Removal in Conventional Treatment

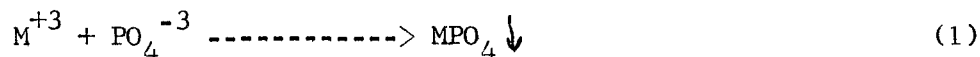
Removal of any pollutant from wastewater requires that it be converted to either an insoluble gas or an insoluble solid. Because none of the chemically stable forms of phosphorus is a gas at normal temperature and

pressure, removal from wastewater is dependent on formation of an insoluble solid. Less than 10 percent of the phosphorus discharged to municipal sewerage systems is insoluble and none of the conventional treatment techniques is particularly effective in insolubilizing this nutrient. Thus, phosphorus removal in conventional treatment systems is relatively poor. Primary treatment can remove only the 10 percent of the phosphorus which is initially insoluble. During secondary treatment, phosphorus removal is achieved by synthesis into the biomass followed by sedimentation and sludge wasting. However, municipal sewage contains a considerable excess of phosphorus over that required for biomass synthesis during complete utilization of the organic carbon present; thus, removals are generally limited to 20-40 percent⁽³⁾. Studies indicate that biological systems have the capacity for much higher removals through the mechanism of "luxury uptake"⁽⁴⁾. However, attempts to implement this phenomenon in actual plants have not been successful⁽⁵⁾. Indeed, a recent study has illustrated that luxury uptake may actually be a chemical precipitation rather than a biologically mediated phenomenon⁽⁶⁾.

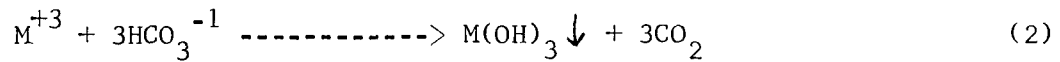
Phosphorus Removal by Chemical Precipitation

Fortunately, phosphorus forms essentially completely insoluble precipitates with a number of substances, thus high levels of removal can be obtained when appropriate doses of the proper chemicals are applied. A large variety of chemicals can be utilized for this purpose but economic factors dictate the use of salts of iron, salts of aluminum or lime.

For both the salts of aluminum and iron, the required dose is set by similar factors. The major control is the stoichiometric reaction between the metal salt and the phosphorus compound as illustrated in equation 1.



This reaction indicates a requirement of 1 mole of the metallic cation for each mole of phosphorus in the wastewater. However, a number of factors act to increase the dose of metallic salt required. As indicated by equation 2, the metal salt reacts with the alkalinity in the wastewater to form insoluble hydroxide.



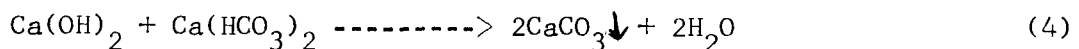
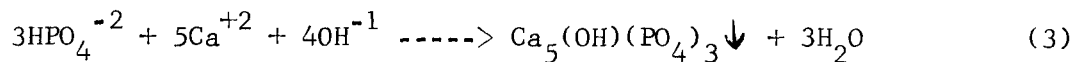
Although this is a competing reaction with the phosphorus precipitation, the metal consumed is not wasted as the hydroxide formed is an excellent flocculant of the phosphorus precipitates of equation 1. Another factor which tends to increase metal dosage over that theoretically required is pH. Figure 1 illustrates that aluminum phosphate is least soluble at pH 6 and iron phosphate is best precipitated at pH 4⁽⁷⁾. It is usually best to use additional metal salt rather than adjust the pH of the sewage from its normal range of 7-8. Another factor which influences coagulant dose is the presence of suspended organic solids in the wastewater. A portion of the metal salt added will be required for coagulation of these materials, again increasing the dose requirement.

The dose required to achieve any specified degree of phosphorus removal cannot be specified with great precision because of the factors discussed above. It is best to conduct bench-scale jar tests on the wastewater to be treated to establish the metal salt dose requirement. Average of results from many installations which can serve as a rough guide are given in Table 1⁽³⁾.

TABLE 1
AVERAGE METAL SALT DOSE REQUIRED FOR
SPECIFIED PERCENT PHOSPHORUS REMOVAL

<u>% P Removal</u>	<u>Dose Metal Salt Mole Ratio M⁺³/P</u>
75	1.4
85	1.7
95	2.3

The reaction of lime with wastewater constituents is given in equations 3 and 4:



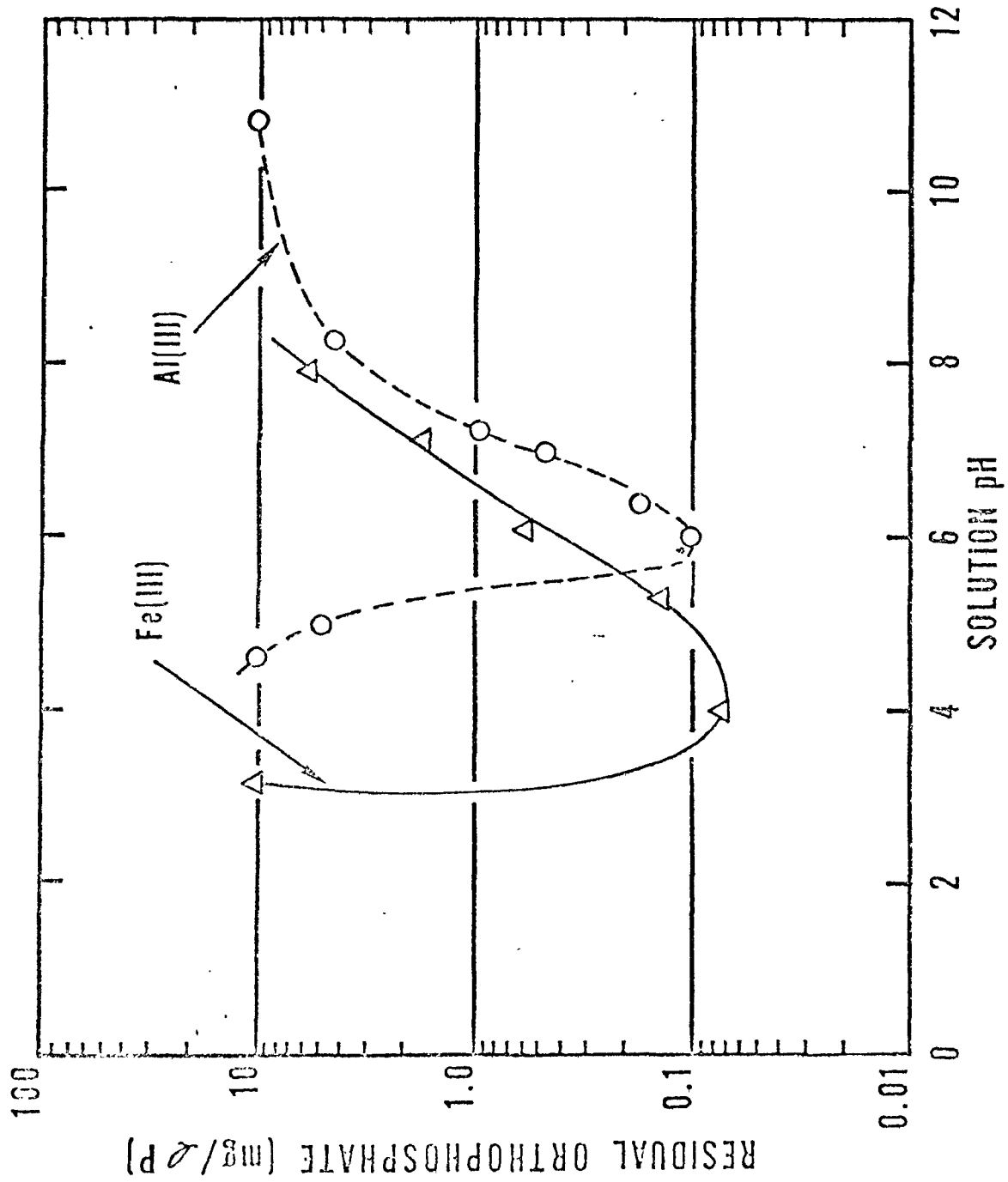
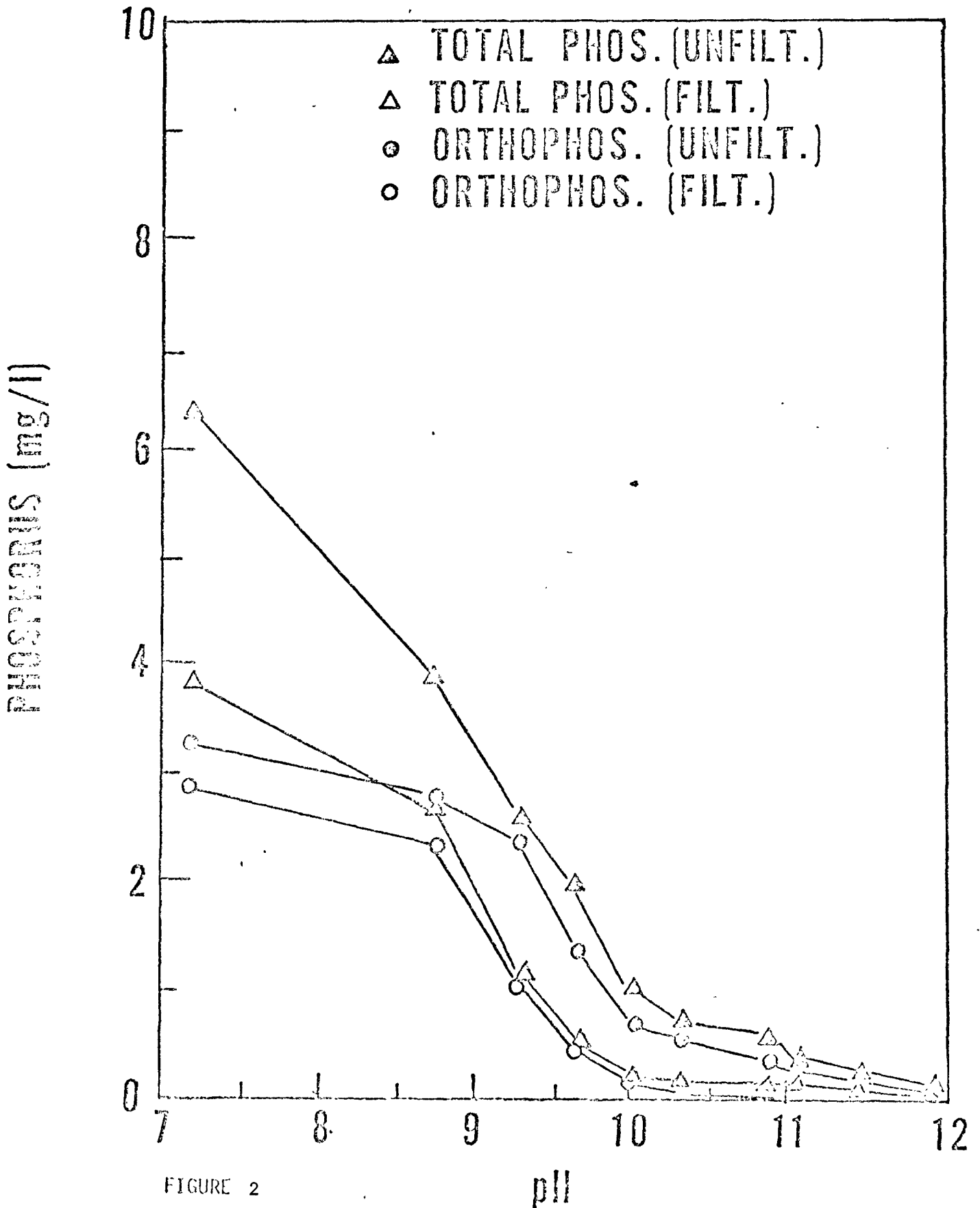


FIGURE 1
PRECIPITATION OF ORTHOPHOSPHATE WITH Al (III) AND Fe (III)
AT A 2:1 CATION-TO-ORTHOPHOSPHATE MOLAR RATIO (Ref. 17)

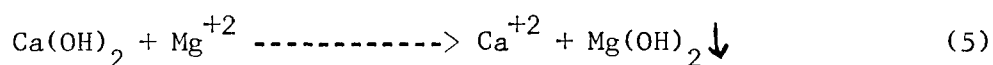
LIME PRECIPITATION AND PHOSPHORUS REMOVAL FROM RAW WASTEWATER.



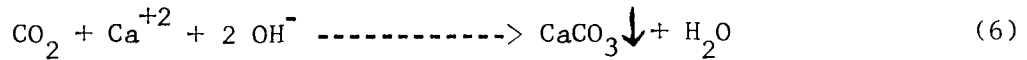
Equation 3 represents the formation of the insoluble compound calcium hydroxyapatite. The kinetics of this reaction as well as the stoichiometry are pH dependent. Elevated pH values 9.5-11.5 are required to ensure good phosphorus removal by precipitation and liquid solids separation techniques. Figure 2 illustrates this pH effect⁽⁸⁾. Thus, while pH was a secondary factor in establishing the dose requirement with iron or aluminum as the precipitant, it is the primary factor when calcium is utilized.

In order to reach the pH range which will ensure good phosphorus removals, the alkalinity demand of the wastewater must be met, as illustrated in equation 4. Because the bicarbonate concentration in wastewater is much higher than the phosphorus concentration (several hundred mg/l vs. \approx 10 mg/l), therefore, most of the lime dose required to achieve effective phosphorus removal is used to meet the alkalinity demand. Here a situation exists similar to that occurring when metal salts are used for phosphorus removal; i.e., the product of the cation alkalinity reaction serves as a flocculant of the phosphorus precipitate. Thus, the reaction of the lime with the alkalinity does not completely waste the lime.

When reaction 4 is complete, the pH of the wastewater is in the range of 9.5-10.0. For wastewater with moderate to high levels of alkalinity (> 200 mg/l), sufficient calcium carbonate is formed under these conditions to effectively bring down the hydroxyapatite. After sedimentation, the pH is reduced to < 8 by the addition of CO₂. This process is referred to as single-stage lime precipitation. If the alkalinity of the wastewater is low > 150 mg/l, however, insufficient calcium carbonate is formed. For this situation, the pH must be raised above 11 which will ensure precipitation of magnesium hydroxide according to equation 5:



Magnesium hydroxide is a gelatinous precipitate which will effectively scavenge hydroxyapatite from solution. Adding excess lime to raise the pH to high levels results in a wastewater containing excess calcium. The calcium is reduced by carbonation with CO₂. As illustrated in equation 6, this reduces the pH and results in a second precipitation of calcium carbonate:

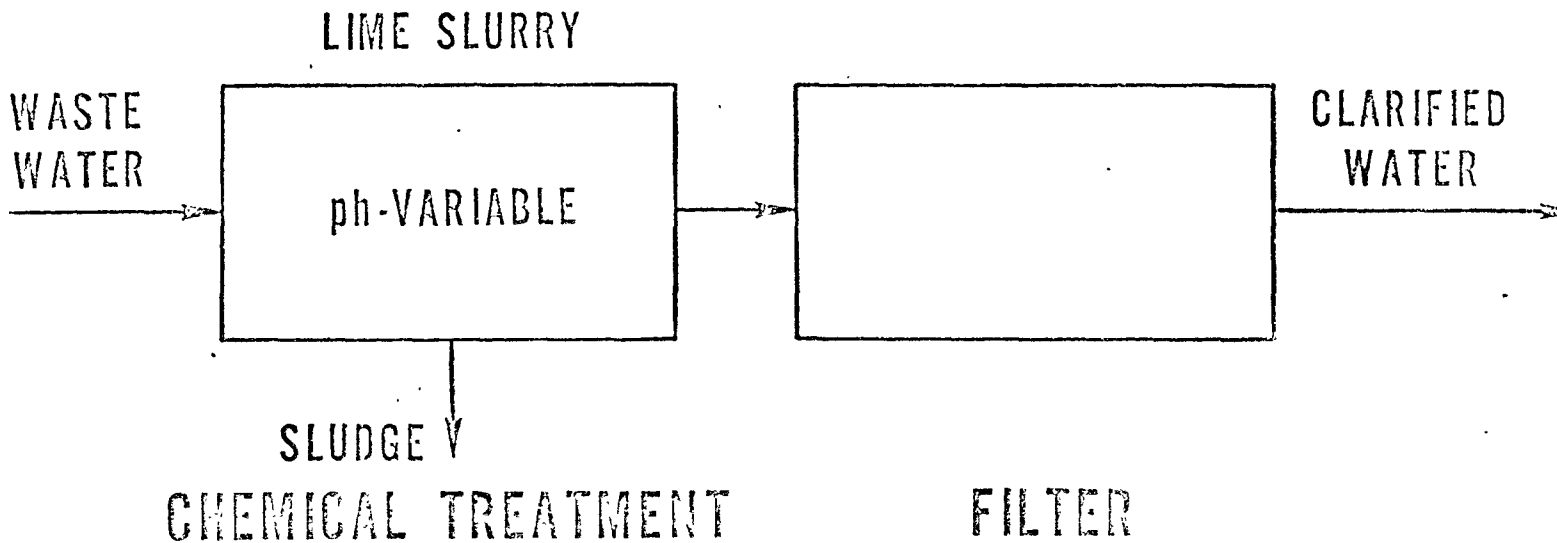


The second precipitation is carried out in a sedimentation tank separate from that in which hydroxyapatite, calcium carbonate and magnesium hydroxide precipitation takes place. The recarbonation reaction is complete at pH 9.5-10.0, which is the same end point pH as in the single stage process. A second dose of CO₂ is then applied to reduce the pH below 8. The final pH reduction in the two-stage and single-stage processes is utilized to prevent post precipitation of CaCO₃ in other treatment units. Flow diagrams of the single-stage and two-stage lime precipitation processes are given in Figure 3.

Table 2 gives a list of chemicals which are useful for phosphorus precipitation. Small doses of organic polymer may also be required to aid flocculation. In selecting the chemical for use at any particular site, the factors listed in Table 3 should be taken into account. It is clear that the cost of the chemical is only one factor among many which bear on the ultimate cost of phosphorus removal. Of prime importance is dewatering and ultimate disposal of sludges. Here, lime has an advantage because lime sludges are more easily dewatered than iron or aluminum sludges. In addition, lime sludge can be recalcined to reusable lime in an incinerator. However, large capital expenditures such as an incinerator can only be justified at large treatment plants.

Phosphorus removal is achieved by precipitation followed by liquid solids separation. For the most part, the usual liquid-solids separation equipment in a treatment plant can be utilized for phosphorus removal. This results in a considerable savings in capital as well as integration of phosphorus removal into conventional treatment plant operation. In addition, it has been found that the use of chemical precipitants in conventional treatment can markedly upgrade performance of the treatment plant. This results from coagulation of organic suspended and colloidal solids by the chemicals added to precipitate phosphorus.

SINGLE STAGE LIME TREATMENT



TWO STAGE LIME TREATMENT

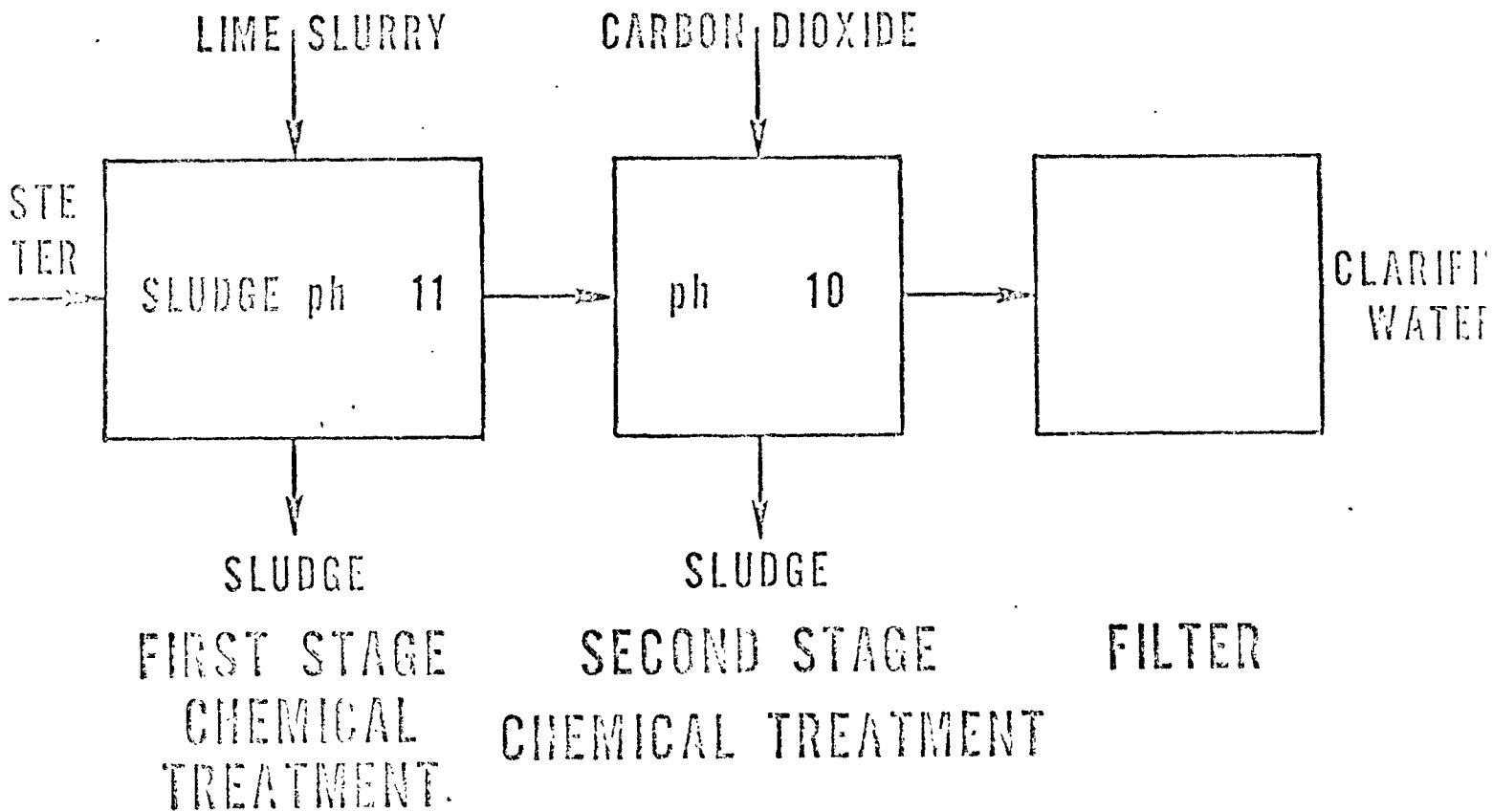


FIGURE 3

TABLE 2

CHEMICALS FOR PHOSPHORUS REMOVAL

Ferric Chloride	FeCl_3
Ferric Sulfate	$\text{Fe}_2(\text{SO}_4)_3$
Ferrous Chloride	FeCl_2
Ferrous Sulfate	FeSO_4
Alum	$\text{Al}_2(\text{SO}_4)_3$
Sodium Aluminate	NaAlO_2
Steel Mill Pickling Liquor	$\text{FeCl}_2 + \text{FeSO}_4$
Lime	$\text{Ca}(\text{OH})_2$

TABLE 3

FACTORS AFFECTING CHOICE OF CHEMICAL
FOR PHOSPHORUS REMOVAL

- Influent Phosphorus Level
- Wastewater Suspended Solids and Alkalinity
- Chemical Cost Including Transportation
- Reliability of Chemical Supply
- Sludge Handling Facilities
- Ultimate Disposal Methods
- Compatibility with Other Treatment Processes in Plant
- Potential Adverse Environmental Effects

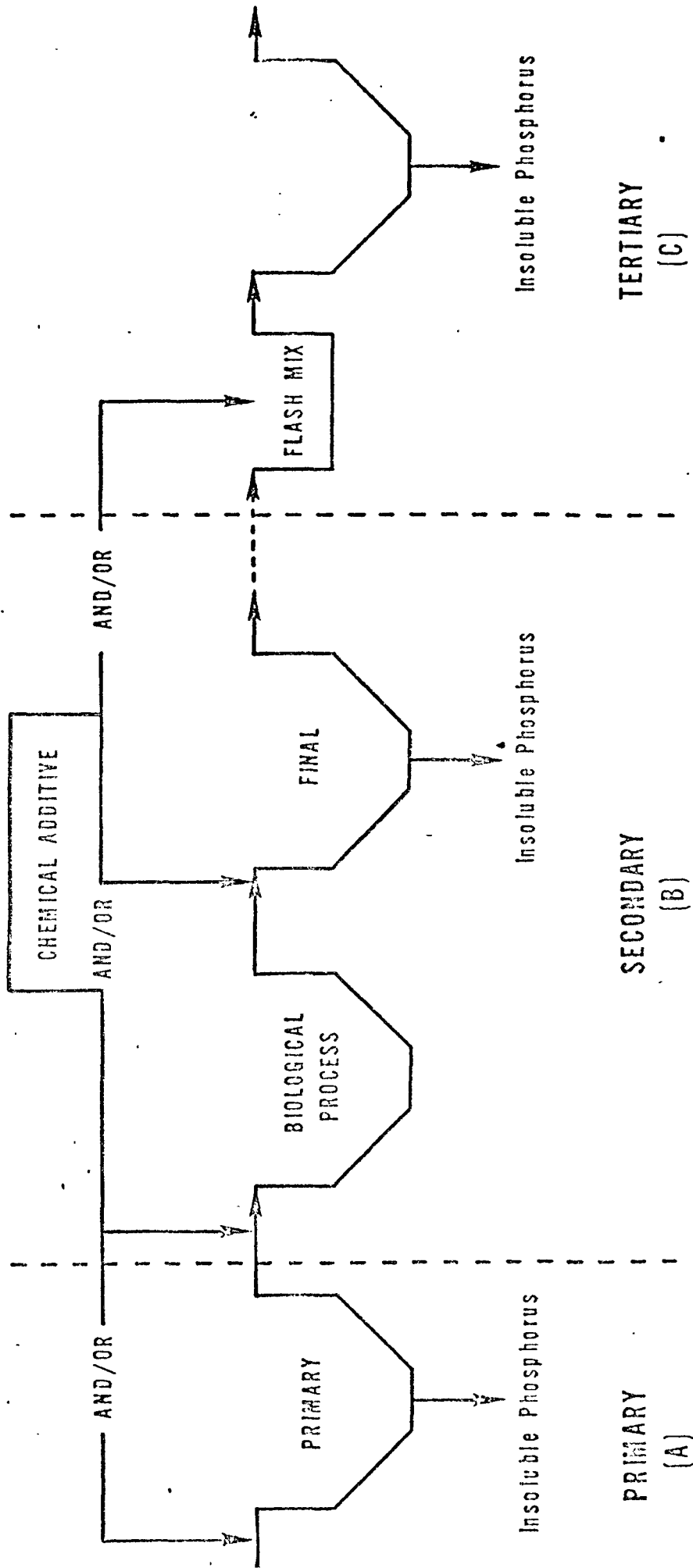


FIGURE 4

LOCATIONS FOR CHEMICAL CONTROL OF PHOSPHORUS

Figure 4 illustrates a conventional treatment plant with the three general sections in which phosphorus removal can be carried out. Chemical can be added either:

- a. Just before the primary tank with removal taking place in the primary.
- b. In the secondary (biological) section of the plant with removal in the secondary sedimentation tank.
- c. In a tertiary stage as was discussed in the section on suspended solids removal.

Table 4 illustrates typical results obtained with phosphorus removal in the primary, secondary, or tertiary. As can be seen, good removals are obtained in all sections, however, the lowest levels of phosphorus remaining are achieved in the tertiary addition. One reason for this is that a filter is usually included in the tertiary plant, thus better removal of fine precipitates is achieved. In addition, when the flow reaches this section of the plant all the complex phosphorus forms which are more difficult to precipitate have been hydrolyzed to orthophosphate which is the easiest to precipitate.

In plants where removal in the primary was practiced a major effect to note is the significant increase in BOD and suspended solids removal achieved over the removal usually obtained in the primary tank. This may be important in helping to meet water quality standards for BOD and suspended solids if the treatment plant is overloaded.

In plants where the chemical is added in the secondary section, it has been observed that much more stable operation of the activated sludge is obtained than before chemical addition. The effect of the chemical is to weigh the sludge down, preventing its loss when a filamentous or dispersed growth predominates. Even in plants which have historically exhibited excellent performance, chemical addition has improved performance by helping maintain a higher concentration of activated sludge in the aeration tank. This is illustrated by the data in Table 5 from parallel operation for one year at Penn State University ⁽⁹⁾. It has been found best to add the chemical between the biological reactor and the final sedimentation tank rather than at the head end of the secondary tank.

Table 6 summarizes the advantages and disadvantages of carrying out phosphorus removal in the various sections of a treatment plant.

TABLE 4

PHOSPHORUS REMOVAL EXPERIENCES

PRIMARY	Place	Chemical	P		BOD		S.S.		Reference
			% Removal	Effluent	% Removal	% Removal	% Removal	% Removal	
	Grayling, Michigan	FeCl ₂	72	4.4	78	58			(10)
	Washington, D.C.	Lime	95	0.45	82	88			(11)
	Mentor, Ohio	Pickle Liquor	83.5	-	59	74			
SECONDARY									
	Pomona, Calif.	Alum	80-93						(12)
	Manassas, Virginia	Alum		1.0					(13)
	Richardson, Texas			0.5-0.75					(14)
TERTIARY									
	Nassau County, N.Y.	Alum		0.08					(16)
	Lake Tahoe, Calif.	Lime		0.14					(15)
	Lebanon, Ohio	Lime		0.1-0.5					(17)

TABLE 5
COMPARISON OF ACTIVATED SLUDGE PERFORMANCE
WITH AND WITHOUT ALUM ADDITION

<u>Parameter</u>	<u>Influent</u> <u>mg/l</u>	<u>Effluent, mg/l</u>	
		<u>Alum</u>	<u>Normal</u>
S.S.	110	22	26
BOD	71	9	13
COD	172	55	68
Soluble P	6.7	0.36	6.7
Total P	10.0	1.4	7.3

TABLE 6

ADVANTAGES AND DISADVANTAGES OF P REMOVAL
IN VARIOUS SECTIONS OF A TREATMENT PLANT

ADVANTAGES

<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
1. Applicable to all plants	1. Lowest Capital	1. Lowest P in Effluent
2. Increased BOD & Suspended Solids Removal	2. Lower Chemical Dose than Primary	2. Most Efficient Metal Use
3. Lowest Degree of Metal Leakage	3. Improved Stability of Activated Sludge	3. Lime Recovery Demonstrated
	4. Polymer not Required	

DISADVANTAGES

<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
1. Least Efficient Utilization of Metal	1. Careful pH Control to get P < 1 mg/l	1. Highest Capital Cost
2. Polymer Required for Flocculation	2. Overdose of Metal may cause Low pH Toxicity	2. Highest Metal Leakage
3. Sludge More Difficult to Dewater than Primary Sludge	3. Cannot Use Lime Because of Excessive pH	

The cost of adding phosphorus removal to existing treatment plants is given in Table 7. The lowest cost option is addition in the secondary because capital expenditure for chemical feed equipment and extra sludge handling equipment are least in this mode. However, removals below 1 mg/l P are difficult. The most costly option is tertiary because of the high capital cost. However, an excellent quality effluent is obtained which is very low in phosphorus, BOD and suspended solids. Note the higher tertiary cost here than for the upgrading system. This is due to higher chemical doses, and additional sludge handling difficulties. Table 8 lists a number of plants where phosphorus removal is being conducted or is in the planning stages.

TABLE 7

ECONOMICS OF PHOSPHORUS REMOVAL

Cost Cents per 1000 Gallons

Plant Size, MGD	<u>1</u>	<u>10</u>	<u>100</u>
Chemical Addition Point			
Primary	6-8	3-5	3-4
Secondary	6-7	3.5-4.0	3.0-3.5
Tertiary	28	12	6

TABLE 8

INSTALLATIONS PRACTICING OR PLANNING PHOSPHORUS REMOVAL

<u>Location</u>	<u>Capacity, MGD</u>	<u>Status</u>
Chicago, Illinois	30	Design
Seattle, Washington	20	Design
Pomona, California	2	In Operation
S. Lake Taltee, California	7.5	In Operation
Piscattaway, Maryland	5	Construction
Colorado Springs, Colorado	2	In Operation
Richardson, Texas	1	In Operation
Blue Plains	300	In Operation
El Lago, Texas	0.5	Construction
Hatfield Twp., Pa.	5.0	In Operation

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