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**A STUDY OF THE REMOVAL OF PHOSPHORUS FROM WATER  
BY CHEMICAL METHODS, AS WELL AS BY FILTRATION  
THROUGH A MIXED COLUMN OF CLAY AND SAND**

**A Thesis**

**Submitted to the Faculty of Graduate Studies through the  
Department of Chemical Engineering in Partial Fulfilment  
of the Requirements for the Degree of  
Master of Applied Science at the  
University of Windsor**

**by**

**Chia-su Wan**

**Windsor, Ontario**

**1972**

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## ABSTRACT

Chemical treatment using ferric chloride or Aluminum sulfate in combination with calcium hydroxide has been studied for the purpose of removing phosphorus from ortho-phosphate, ortho- and pyro-phosphate and ortho-, pyro- and tripoly-phosphate solutions in the pH range 7.5 to 9.5.

The data showed that pyro- and tripoly-phosphate could be more easily removed than ortho-phosphate in the experimental pH range. The data also showed that the combination of ferric chloride and calcium hydroxide had better settling ability than the combination of aluminum sulfate and calcium hydroxide.

With a molar ratio of 1:1 between iron or aluminum and phosphorus as ortho-phosphate and 150 mg/l of calcium hydroxide, a supernatant of about 1 mg/l P was obtained from a phosphorus solution of 10 mg/l P as ortho-phosphate, 4 mg/l P as pyro-phosphate and 6 mg/l P as tripoly-phosphate near pH 9. After filtration through a sand column, the residual phosphorus was reduced to about 0.6 mg/l P. The residual phosphorus could be further reduced to less than 0.2 mg/l P during the first eight hours and about 0.3 mg/l P even after 24 hours by using a mixed column of sand and soil to replace the sand column.

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## TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
I. INTRODUCTION	1
II. LITERATURE REVIEW	4
A. Eutrophication and Phosphorus Concentrations	4
B. Phosphorus Removal Methods	5
C. Chemical Reactions Between Phosphorus and Metal Ions (Fe, Ca and Al) in Water	5
D. Phosphorus Removal by Iron or Aluminum Salts	6
E. Phosphorus Removal by Lime	8
F. Combined Chemical Process For Phosphorus Removal	9
G. Fixation of Phosphorus by Soil	10
III. EXPERIMENTAL	13
A. Plan	13
B. Material	14
C. Apparatus	15
D. Analytical Procedures	15
E. General Experimental Procedures	16
IV. EXPERIMENTAL RESULTS AND DISCUSSIONS	19
A. Phosphorus Removal by Calcium Hydroxide, Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution	19

	Page
B. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution.	21
C. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho- and Pyro-phosphate Solution	28
D. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho-, Pyro- and Tripoly-phosphate Solution	33
E. Phosphorus Removal by a Mixed Column of Sand and Soil From Chemically Treated Supernatant Water	38
V. CONCLUSION	45
APPENDIX	
I. Solubility and Complex Formation Equilibria of Phosphate With Iron, Aluminum and Calcium	47
II. Experimental Data	48
REFERENCES	61



## LIST OF TABLES

Table	Page
1. Phosphorus Removal by Calcium Hydroxide, Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution	49
2. Phosphorus Removal by 50 mg/l of Calcium Hydroxide and Different Doses of Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution	50
3. Phosphorus Removal by 100 mg/l of Calcium Hydroxide and Different Doses of Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution	51
4. Phosphorus Removal by 150 mg/l of Calcium Hydroxide and Different Doses of Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution	52
5. Phosphorus Removal by Calcium Hydroxide From Ortho- and Pyro-phosphate Solution	53
6. Phosphorus Removal by 30 mg/l of Ferric Chloride and Different Doses of Calcium Hydroxide From Ortho- and Pyro-phosphate Solution	54
7. Phosphorus Removal by 30 mg/l of Aluminum Sulfate and Different Doses of Calcium Hydroxide From Ortho- and Pyro-phosphate Solution	55
8. Phosphorus Removal by 1:1 Molar Ratio of Ferric Chloride to Ortho-phosphate and Different Doses of Calcium Hydroxide From Ortho-, Pyro- and Tripoly-phosphate Solution	56
9. Phosphorus Removal by 1:1 Molar Ratio of Aluminum Sulfate to Ortho-phosphate and Different Doses of Calcium Hydroxide From Ortho-, Pyro- and Tripoly-phosphate Solution	57
10. Phosphorus Removal by a Mixed Column of 80% Sand and 20% Soil	58
11. Phosphorus Removal by Sand Column and Mixed Column of 80% Sand and 20% Soil From Iron and Calcium Treated Supernatant Water	59
12. Phosphorus Removal by Sand Column and Mixed Column of 80% Sand and 20% Soil From Aluminum and Calcium Treated Supernatant Water	60

## LIST OF FIGURES

Figure		Page
1.	Calcium Hydroxide With Ortho-phosphate Solution	20
2.	Ferric Chloride With Ortho-phosphate Solution	22
3.	Aluminum Sulfate With Ortho-phosphate Solution	23
4.	Ferric Chloride or Aluminum Sulfate and 50 mg/l of Calcium Hydroxide With Ortho-phosphate Solution	24
5.	Ferric Chloride or Aluminum Sulfate and 100 mg/l of Calcium Hydroxide With Ortho-phosphate Solution	25
6.	Ferric Chloride or Aluminum Sulfate and 150 mg/l of Calcium Hydroxide With Ortho-phosphate Solution	26
7.	Calcium Hydroxide With Ortho- and Pyro-phosphate Solution	30
8.	Calcium Hydroxide and 30 mg/l of Ferric Chloride With Ortho- and Pyro-phosphate Solution	31
9.	Calcium Hydroxide and 30 mg/l of Aluminum Sulfate With Ortho- and Pyro-phosphate Solution	32
10.	Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate With Ortho-, Pyro- and Tripoly-phosphate Solution (Residual Ortho-phosphate)	35
11.	Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate With Ortho-, Pyro- and Tripoly-phosphate Solution (Residual Total Phosphate)	36
12.	Phosphorus Removal by Combinations of Calcium Hydroxide and Aluminum Sulfate or Ferric Chloride at Different Calcium Hydroxide Dosage and Supernatant pH	37
13.	Phosphorus Removal by a Mixed Column of 80% Ottawa Sand and 20% Local Soil From Ortho-, Pyro- or Tripoly-phosphate Solution	38
14A.	Phosphorus Removal From The Supernatant of Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate	42

**Figure**

**Page**

- Treated Phosphate Solution by a Sand Column  
and a Mixed Column of 80% Ottawa Sand and 20%  
Local Soil (Residual Ortho-phosphate)
- 14B. Phosphorus Removal From The Supernatant of 43  
Calcium Hydroxide and Ferric Chloride or Aluminum  
Sulfate Treated Phosphate Solution by a Sand  
Column and a Mixed Column of 80% Ottawa Sand and  
20% Local Soil (Residual Total Phosphate)
15. Soil and Sand Filtration Column 44

## CHAPTER I

### INTRODUCTION

Phosphorus and nitrogen are important nutrients in waste water which promote algal growth and result in eutrophication of lakes. Since certain species of algae, especially the nuisance blue greens (1), can fix nitrogen from the air, phosphorus becomes the critical nutrient to the growth of algae. Prolific algal growth has been reported to occur at phosphorus concentration as low as 0.01 to 0.1 mg/l P (1, 2).

Conventional secondary treatment, biological oxidation, can only remove 30-50% phosphate (3). The effluents from most of these treatment plants still contain quantities of phosphate, substantially higher than the limits indicated above (4). Chemical precipitation processes can remove phosphate effectively. The most popular chemicals used are lime, iron and aluminum salts.

The reactions between metal ions and phosphate ions are very complicated, depending upon the relative concentrations of the metal ions and phosphate ions, the pH and the presence of other ions (5, 6). In general, the lime process favors higher pH and the ferric chloride or aluminum sulfate process favors lower pH.

The lime process needs recarbonation to reduce the pH of the effluent to prevent precipitation of calcium in the receiving water and calcium deposits on subsequent process equip-

ment (7). Due to its poor settling ability, coagulant aid is recommended by several authors. The iron or aluminum process needs the addition of acids to the waste water to reach the optimum pH (8) and excess chemical is needed to make the colloidal precipitate settle down (9).

Wuhrmann (10) observed that the combined chemical process (Fe and Ca) was economical both in chemical cost and sludge handling in phosphate removal. Black (11) performed a comparison test between lime with ferric chloride and lime alone and concluded that for chemical treatment alone, combination of lime and ferric chloride gave optimum phosphate removal efficiency. One pilot plant in Wisconsin using alum ( $Al/P = 2$ ) and lime ( $Al/Ca = 3/2$ ) obtained 85% removal of phosphate (12).

Since the combined chemical processes are economical in cost and can operate at a pH range between 8 and 9 which is suitable either for discharge to receiving water without any further treatment or to the activated sludge section of a sewage plant for BOD and phosphate removal, it is worthy to know more about its behavior within the pH range of 7.5 to 9.5. Therefore, the combinations of iron or aluminum and calcium salts were tested with phosphate solutions within this pH range.

The experimental data showed that both pyro- and tripolyphosphate were more easily removed than ortho-phosphate within the pH range tested. It also confirmed that the combination of iron and calcium salts had better settling ability than

the combination of aluminum and calcium salts.

In order to meet effluent total phosphate level of 0.5 mg/l P or lower, filtration is needed following sedimentation in chemical process for phosphate removal from waste water (9). A mixed column of sand and soil will not only meet the filtration requirement but also can remove some phosphate from the supernatant which is already low in phosphate content. Therefore, a sand column and a mixed column of sand and soil were also used in this study to study its effect in phosphate removal from the chemically treated supernatant.

With only 150 mg/l of  $\text{Ca(OH)}_2$  and 1:1 molar ratio of Fe or Al to ortho-phosphate, a supernatant of about 1 mg/l P was obtained from an initial concentration of 20 mg/l P. After filtration with a sand column, the residual phosphate was around 0.6 mg/l P. The residual phosphate could be further reduced to less than 0.2 mg/l P during the first eight hours and about 0.3 mg/l P even after 24 hours by using a mixed column of sand to replace the sand column.

## CHAPTER II

### LITERATURE REVIEW

#### A. Eutrophication and Phosphorus Concentrations

Excessive growth of algae in rivers and lakes is the result of water pollution. The decay of dead algae not only produces foul odours but also consumes dissolved oxygen in water, causing extensive fish kills. The situation is more serious in lakes because the dead organisms settle down to the bottom and repeat the phosphorus cycle in water. Therefore, the polluted beaches can not be used for recreation purposes and extra cost is needed to clean the raw water for domestic or industrial use.

Phosphorus and nitrogen are important nutrients in waste water which promote algal growth and result in eutrophication of lakes. Since certain species of algae, especially the nuisance blue greens (1), can fix nitrogen from the air, phosphorus becomes the critical nutrient of algal growth.

Prolific algal growth has been reported to occur at phosphorus concentration as low as 0.01 to 0.1 mg/l P (1, 2). Dryden in his research studies (13) for changing a polluted lake into a recreational lake in Lancaster, California, found that phosphorus levels below 0.5 mg/l  $\text{PO}_4$  would control nuisance growth of algae.

All in all, the dilution factor and character of receiving water along with the environmental conditions determine the lowest phosphorus concentration required at waste water

treatment plants to control the algae growth in the receiving water.

#### B. Phosphorus Removal Methods

Conventional secondary treatment, biological oxidation, can only remove 30-50% phosphate (3). The effluents from most of these treatment plants still contain substantial quantities of phosphate, higher than the limits indicated above (4).

Chemical precipitation processes can remove phosphate effectively. The most popular chemicals used are lime, aluminium and ferric salts. Other processes such as reverse osmosis and ion exchange can produce very low phosphate concentration effluents but their operational costs are higher, process capacities are small and the water needs pretreatment (14). Lanthanum salts have shown very good results in phosphate removal and are suitable for a wide pH range but again, the chemical cost is very high (8).

Since microorganisms in activated sludge can readily utilize phosphate at very low concentrations and the efficiency of the chemical process decreases as phosphate concentration decreases, it is better to combine the chemical and biological method with chemical addition prior to biological treatment from the practical viewpoint (15).

#### C. Chemical Reactions Between Phosphorus and Metal Ions (Fe, Ca and Al) in Water

Phosphorus is usually present in waste water in the form of organic phosphorus, complex inorganic phosphates and



orthophosphate (7). The rate of hydrolytic degradation of polyphosphate into orthophosphate is influenced by pH and temperature (16). The temperature effect on the rate of hydrolysis is different for each sample and the biological effect is noticeable at low temperatures (17). Very little is known about the hydrolysis of the dissolved organic phosphorus compounds (18).

The reactions between metal ions and phosphate anions are very complicated, depending upon the relative concentrations of the phosphates and metal ions, the pH and the presence of other ions (Sulfate, Carbonate, Fluoride and Organic species) (5, 6). Both adsorption and precipitation mechanisms take place during the reaction and a "mixed hydroxophosphate" is formed, especially when using a stoichiometric excess of the coagulant (19). The solubility and complex formation equilibria data of ferric, aluminum and calcium ion with phosphate ion are shown in Appendix I.

#### D. Phosphorus Removal by Iron or Aluminum Salts

Recht and co-workers (18) in their study of phosphorus removal with ferric and aluminum salts arrived at the following conclusions: (1). with orthophosphate, the removal was directly proportional to the amount of added cation up to 1:1 molar ratio, indicating the occurrence of a chemical reaction. The best pH for Al and Fe are 6 and 3.5 to 4 respectively; (2) with pyro or tripolyphosphate and a 2:1 cation to phosphate equivalence ratio, the maximum removal pH for Al and Fe are 5 and 4; (3) with tripolyphosphate and 1:1

cation to phosphate ratio, no removal occurs at several pH levels.

Their findings confirmed that polyphosphates have a strong tendency to form soluble complexes with cations (20). Therefore, it is safe to say that the removal of orthophosphate is a precipitation reaction and the removal of polyphosphate is a complex reaction of precipitation and adsorption. That is why a considerable molar excess of Al or Fe is recommended by each researcher.

The precipitate of Fe or Al with various phosphates is often colloidal especially at neutral or lower pH values (9). This is another reason why excess chemical is recommended because the additional amount of chemical can serve as a coagulant for the colloidal phosphorus precipitate.

Wuhrmann (10) in his pilot plant experiments found that at least 10 mg/l Fe must be added in excess of the stoichiometric amount for phosphate precipitation to create a precipitate that can be readily removed by sedimentation. For an influent with 6 mg/l P, 20 mg/l Fe (approximately double the stoichiometric amount) was required to get a final effluent with total phosphorus less than 0.5 mg/l P. Lime was added to maintain the pH between 7.0 and 7.2.

Rohlich's data (20) showed that at least 200 mg/l alum was required to get a 95% removal from an influent of 4.45 to 5.9 mg/l P (Al/P molar ratio = 4.1 and 3.1). The optimum pH range was 7.1 to 7.7 and mixing time is 10 to 15 minutes. Dryden (13) applied 200 to 300 mg/l of alum to an influent

of 40 mg/l  $\text{PO}_4$  and obtained less than 0.5 mg/l  $\text{PO}_4$  in the effluent after sedimentation and filtration. When alum is added directly to the activated sludge basin, a flocculation basin is needed to get better effluent clarity and total phosphorus removal (21). Pöpel (19), assuming a condition of constant pH and influent phosphate concentration, suggested an equation to calculate the dosage of Fe and Al in phosphate removal. But other factors, such as the presence of organic and inorganic substances, the duration of the flocculation period and the manner of addition of the chemicals, may well influence the final result so that the chemical dose has still to be determined experimentally (19).

#### E. Phosphorus Removal by Lime

The reaction between calcium and phosphate is also very complicated and slow to reach the solubility equilibrium (20 to 50 days at 20°C) (20). In the alkaline pH range, hydroxylapatite is the only stable calcium phosphate phase (22). The base formula of hydroxylapatite is  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  and the Ca/P molar ratios for this precipitate are in the range of 1.33 to 2.0 (16). The dosage is mainly dominated by the alkalinity of the waste water. Wuhrmann (10) suggested 1.5 times the carbonate hardness at pH 10.5-11.

Magnesium is also important in phosphate removal with calcium. Its effect is to increase phosphate solubility at pH values below 9, but to decrease the solubility at higher pH values and has no effect at pH 10.5 or higher (23).

Schmid (15) in his investigation discovered that the

orthophosphate will adsorb onto the polyphosphate floc at a pH near 7.0 and polyphosphate will adsorb onto the orthophosphate floc at higher pH. The polyphosphate mixture also adsorbs onto the calcium carbonate precipitate and results in phosphate carry over because when phosphate is adsorbed onto the surface of calcium carbonate crystal nuclei, the nuclei will not grow and will be hard to settle down.

Sludge recirculation will not only improve the rate of precipitation and clarification but also can reduce the dose about one-half and operate at 1 pH unit lower (24).

#### F. Combined Chemical Process For Phosphorus Removal

The lime process needs recarbonation to reduce the pH of the effluent to prevent precipitation of calcium in the receiving water and calcium deposits on subsequent process equipment (7). Due to its poor settling ability, coagulant aid is recommended by several authors. The iron or aluminum process needs the addition of acids to the wastewater to reach the optimum pH (8) and excess chemical is needed to make the colloidal precipitate settle down (9).

Wuhrmann (10) applied 1 to 2 mg/l of Fe as a flocculation aid in the lime process and obtained a sparkling clear effluent along with excellent compacting character of the excess sludge. This led to his further investigation of the combined chemical process of Fe and lime. With the addition of 10 mg/l  $\text{Fe}^{3+}$  and 100-150 mg/l of calcium hydroxide, he obtained similar degree of phosphate removal but the chemical costs and the amount of excess sludge was less. Black (11)

performed a comparison test between lime with ferric chloride and lime alone and concluded that for chemical treatment alone, combination of lime and ferric chloride gave optimum phosphate removal efficiency. One pilot plant in Wisconsin using alum ( $Al/P \approx 2$ ) and lime ( $Al/Ca = 3/2$ ) obtained 85 % removal of phosphate (12).

The combination of ferric chloride with lime has better settling ability than the combination of alum and lime (10, 25). But ferric chloride is more expensive than alum in North America. Another disadvantage of ferric chloride is that its sludge may release phosphate during digestion (24).

#### G. Fixation of Phosphorus by Soil

The fixation of phosphate by soil is largely due to the free Al and Fe oxide content in the soil (26-28). Coleman (27), in investigating the difference of phosphate fixation between coarse and fine clay fraction of kaolinitic and montmorillonitic clays (fine clay contained about twice amount of free Al and Fe than coarse clay), found that fine clay fractions adsorbed twice the amount of phosphate as coarse clay fractions did. But after removal of the Al and Fe oxides, both adsorbed almost the same amount of phosphate and had no pH effect on phosphate adsorption.

Other authors (29-31) had studied the effect of pH, time of contact, the concentration of phosphate in the solution, certain ions and organic matter in the fixation of phosphate by soil. Black (30) concluded that the fixation was caused mainly by replacement of the hydroxyl ions exposed on the

kaolinite lattice layer and the maximum fixation pH range was corresponding to the minimum solubility of Al and Fe hydroxide. The phosphate, fixed by replacement of the hydroxide groups, was easily washed out by water (28, 30). The hydroxyl replacement will not take place from a very dilute phosphate solution unless the clay has a large amount of surface accessible to the phosphate in solution. The presence of organic matter in the clay can increase its phosphate fixation and the more the calcium carbonate in the clay, the more the fixed phosphate is exchangeable.

The pH of solution is very important in the fixation of phosphate by soil. Above a pH of 5, the amount of phosphate fixed in a month is only slightly more than the amount fixed in one day (28, Figure 1). Jackson (32) found that the Fe and Al phosphate fraction decreased, while the calcium phosphate fraction increased with increased pH. Since the phosphate fixation is mainly by free Al and Fe oxide in the soil and the hydroxyl replacement takes place at lower pH, his findings agree with the previous authors.

In the fixation of phosphate by soil, some authors favor the precipitation theory while other authors favor the adsorption theory. Actually, both precipitation and adsorption are involved. The precipitation or adsorption is dependent on pH and the phosphate concentration in the solution. In moderately acidic medium (pH 4) with a high phosphate concentration, the reaction process may be precipitation (33). In a slightly acidic to neutral medium (pH 6 to 7) with a dilute

phosphate solution, phosphate is adsorbed on the surface of free Al and Fe oxides (33).

### CHAPTER III

#### EXPERIMENTAL WORK

##### A. Plan

1. Prepare calibration curve of phosphate concentration vs percent transmission of the spectronic 20 colorimeter with standard ortho-phosphate solution.

2. Phosphate removal by calcium hydroxide, aluminum sulfate or ferric chloride from ortho-phosphate solution (3.262 mg/l P or 10 mg/l  $\text{PO}_4$ ).

3. Phosphate removal by combinations of calcium hydroxide and ferric chloride or aluminum sulfate from ortho-phosphate solution (3.262 mg/l P or 10 mg/l  $\text{PO}_4$ ).

4. Phosphate removal by combinations of calcium hydroxide and ferric chloride or aluminum sulfate from ortho- and pyro-phosphate solution (3.262 mg/l P as ortho- and 1.631 mg/l P as pyro- or 10 mg/l  $\text{PO}_4$  as ortho- and 5 mg/l  $\text{PO}_4$  as pyro-). The doses of ferric chloride and aluminum sulfate were fixed and selected from the results of step 3.

5. Phosphate removal by 1:1 molar ratio of Fe or Al to ortho-P and three different doses of calcium hydroxide from ortho-, pyro- and tripoly-phosphate solution (10 mg/l P as ortho-, 4 mg/l P as pyro- and 6 mg/l P as tripoly-). This phosphate concentration is in the range of North America's raw sewage phosphate content.



6. Phosphate removal by a sand or mixed column of sand and soil (80% Ottawa sand and 20% local soil) from ortho-, pyro- or tripoly-phosphate solution.

7. Phosphate removal by a sand or mixed column of sand and soil in step 6 from the supernatant of step 5.

## B. Material

### 1. Chemicals

All chemicals used in the experiments were reagent grade.

a. Sodium phosphate dibasic ( $\text{Na}_2\text{HPO}_4$ ), sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ) and sodium phosphate tripoly ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) were used to prepare ortho-, pyro- and tripoly-phosphate solutions.

b. Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ) and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) were used to prepare the reagent solutions in phosphate removal experiments.

c. Adjustment of pH was made by the addition of HCl or NaOH solutions.

d. Other chemicals; such as potassium persulfate, phenolphthalein, ammonium molybdate, stannous chloride, glycerine, benzene, methanol and isobutanol, which were used in the determination of phosphate concentration were also reagent grade.

### 2. Preparation of Solutions

a. All phosphate solutions were prepared daily.

b. Both calcium hydroxide and aluminum sulfate solu-

tions were prepared daily. The ferric chloride solution was prepared just before the experiments in order to minimize the aging effect.

c. Other solutions used in the analysis of phosphate concentration were prepared according to the directions of Standard Methods (34).

### 3. Sand and Soil

The size between 16 to 32 mesh of Ottawa sand and local soil (by screening) were used to prepare the sand and mixed column for filtration and phosphate removal from the supernatant of chemically treated phosphate solution.

### C. Apparatus

1. Phipps and Bird Six Place Stirrer

Phipps and Bird, Inc., Richmond, Va.

2. Direct reading pH Meter (Model 23A)

Electronic Instruments Ltd., Richmond, Surrey, England.

3. Spectronic 20 Colorimeter

Bausch and Lomb Co., Rochester, N.Y.

4. Filtration Columns (As shown in Figure 15)

5. Other apparatus such as hot plate, glass-ware etc.

### D. Analytical Procedures

All phosphate determinations were done according to the procedures described in Standard Methods (34). In which, the persulfate digestion method for poly-phosphate and the benzene isobutanol extraction modification of the stannous chloride method were used

## E. General Experimental Procedures

### 1. Jar Test Experiments

All the chemical solutions were prepared in mg/ml concentration. The amount of distilled water for each test was calculated by subtracting the total volume of chemical solutions needed from one liter. For example, the amount of distilled water for the test of 30 mg/l ferric chloride and 100 mg/l of calcium hydroxide with 10 mg/l ortho-phosphate solution was 860 ml.

a. Add distilled water and phosphate solutions into one liter beaker.

b. Start stirring.

c. Add the reagent solutions (In combined chemical experiments, calcium hydroxide is added three minutes after the addition of ferric chloride or aluminum sulfate).

d. After three minutes of the addition of reagent solutions, adjust the solution pH with HCl or NaOH for a period of four minutes and record the pH as solution pH at the end of this period.

e. Transfer the beaker to Jar Test Apparatus for flocculation at 30 rpm and a period of 20 minutes.

f. Let the flocculated solution settle down for a period of 30 minutes.

g. Take sample from the settled portion and record the pH as supernatant pH.

h. Determine the phosphate concentrations according

the Standard Methods (34).

## 2. Filtration Column Experiments

a. Prepare the supernatant according to the above procedure in a 70-liter plastic drum.

b. Take the supernatant out by the Syphon method and maintain the suction opening at one third from the bottom of the drum with opening facing upward in order to avoid any disturbance of the settled sludge.

c. Transfer the supernatant into the head tank of the filtration column.

d. Open the drain valve of the sand (or mixed) column and let the supernatant enter the column until the whole column is wet.

e. Close all the valves except the inlet valve and adjust the supernatant level in the column by vent valve.

f. Open the drain valve and adjust the flow rate.

g. Open the vent valve (this valve can be closed to get a higher head) and the valve connected to the movable plastic tube to measure the pressure drop by reading the water level in the tube. The pressure drop is calculated by subtracting the column head with the head indicated in the movable tube.

h. Adjust the drain valve to make the flow rate constant.

i. Take sample from the supernatant sampling valve and drain valve at desired time. At the mean time, also measure the pressure drop in the column.

j. At the end of one test run, change the sand and soil for next test.

k. The phosphate analysis is the same as in the former portion.

## CHAPTER IV

### EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Phosphorus Removal by Calcium Hydroxide, Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution

All the samples were filtered through 0.45  $\mu$  membrane and the results were shown in Table 1 and plotted in Figures 1-3. The plots of M/P molar ratio vs residual phosphate at different pH were converted from corresponding plots of pH of the solution vs residual phosphate at different chemical doses.

##### 1. Ortho-phosphate Removal by Calcium Hydroxide (Figure 1)

Ortho-phosphate cannot be precipitated with calcium hydroxide at pH near 7.0 (15). From the plot of Ca/P molar ratio vs residual phosphate, it is obvious that the slope of the lines at pH 7.5 and 8.0 are almost the same. The slope of the line at pH 8.5 is slightly different from the lines at pH 7.5 and 8.0 and the slope change of the line at pH 9.0 is very sharp. This indicates that precipitation did take place at pH 9.0 so that a larger phosphate removal result was obtained.

Since the distilled water used in the experiments was only single distilled and not freshly prepared some carbon dioxide had been dissolved during the storage period. Therefore, the small amount of phosphate removal at lower pH (7.5 and 8.0) by higher doses calcium hydroxide in the experiments might be due to some adsorption of ortho-phosphate on the surface of calcium carbonate flocs.

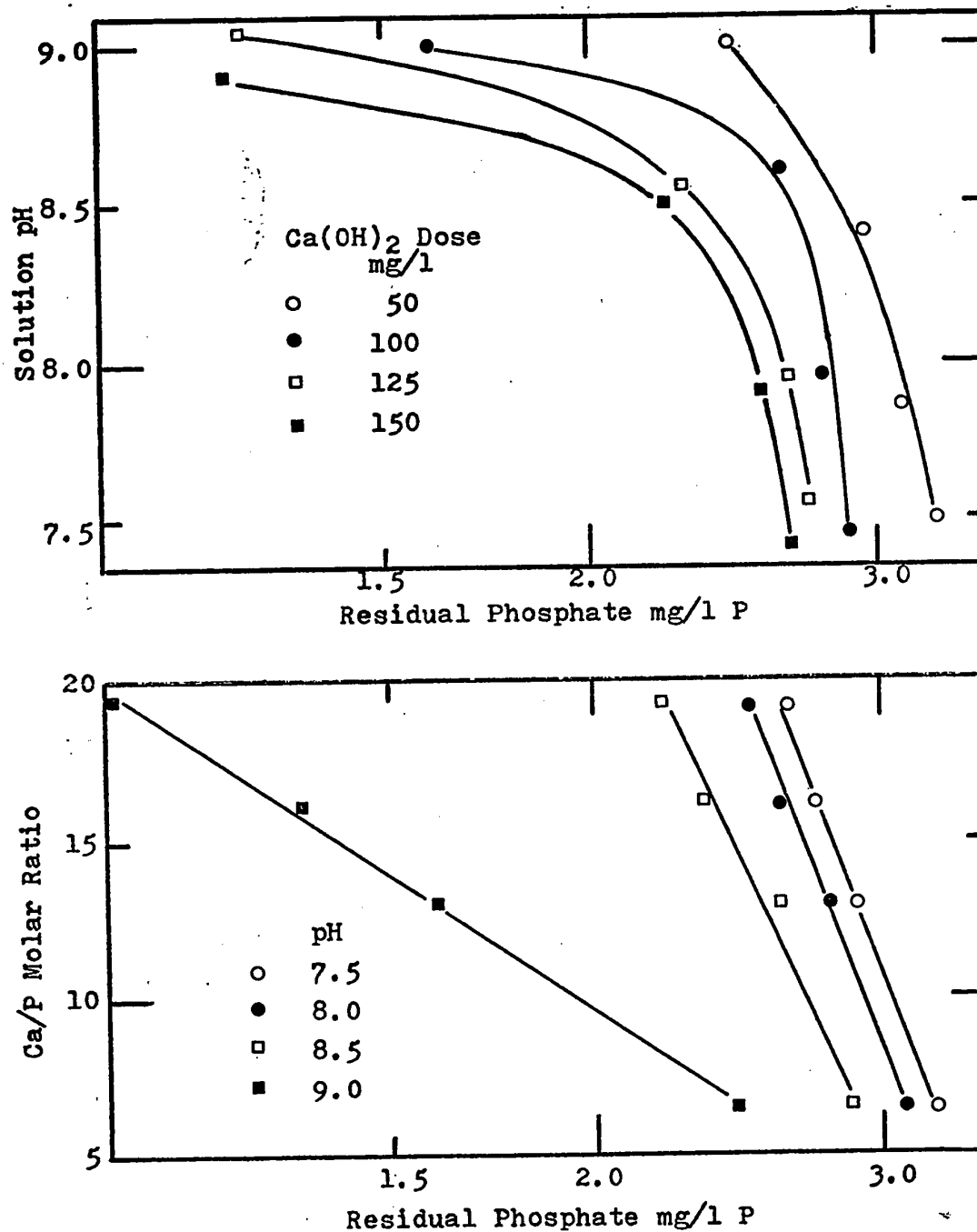


Figure 1 Calcium Hydroxide With Ortho-phosphate Solution  
(Initial Phosphate Concentration, 3.262 mg/l P  
or 10 mg/l  $\text{PO}_4$ )

## 2. Phosphorus Removal by Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution

The best pH range for ortho-phosphate removal by iron is 3.5 to 4.0 and by aluminum 6.0 (18). The experimental data confirmed the fact that the amount of residual phosphate increased as pH increased within the test pH range.

From Figures 2 and 3, it is clear that aluminum sulfate is more pH sensitive in phosphate removal than ferric chloride. At pH 9, only a little phosphate removal was obtained even when larger doses were applied. But at lower pH, less residual phosphate results were obtained by aluminum sulfate than by ferric chloride at corresponding M/P molar ratios. The lower pH (7.5) used in the experiments is closer to the optimum pH of aluminum in ortho-phosphate removal.

In general, for ortho-phosphate removal by calcium hydroxide, ferric chloride or aluminum sulfate alone, better results can be obtained by applying excess amounts of chemicals and operating near their individual optimum pH ranges.

### B. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution

The results were shown in Tables 2 to 4 and plotted in Figures 4 to 6. For convenience of comparison, the corresponding data for these two combinations of chemicals were plotted in the same figure.

1. Since calcium favors higher pH (above 9) and ferric chloride or aluminum sulfate favor lower pH (4 for iron and 6 for aluminum) in ortho-phosphate removal, it can be under-



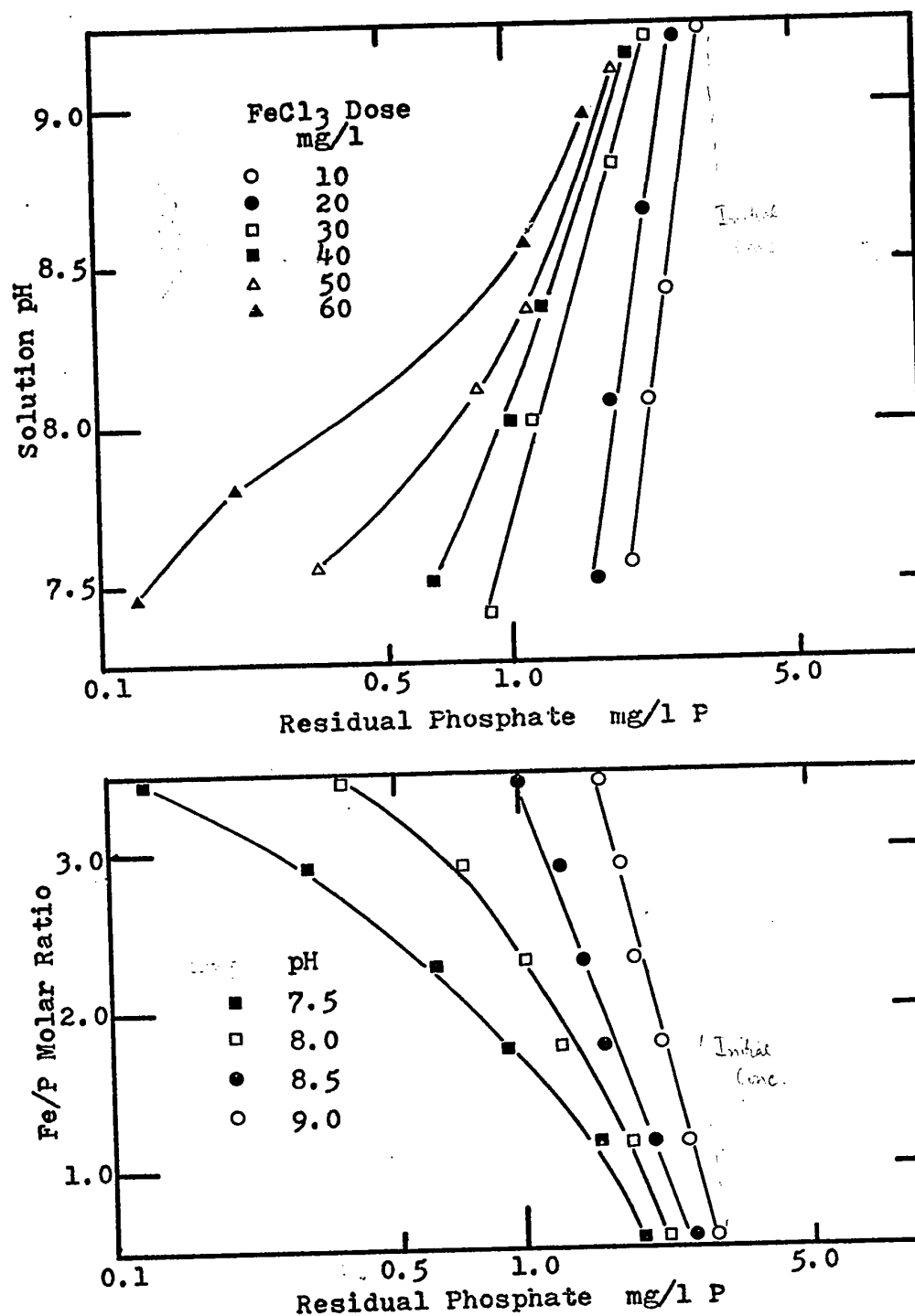


Figure 2 Ferric Chloride With Ortho-phosphate Solution  
(Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$ )

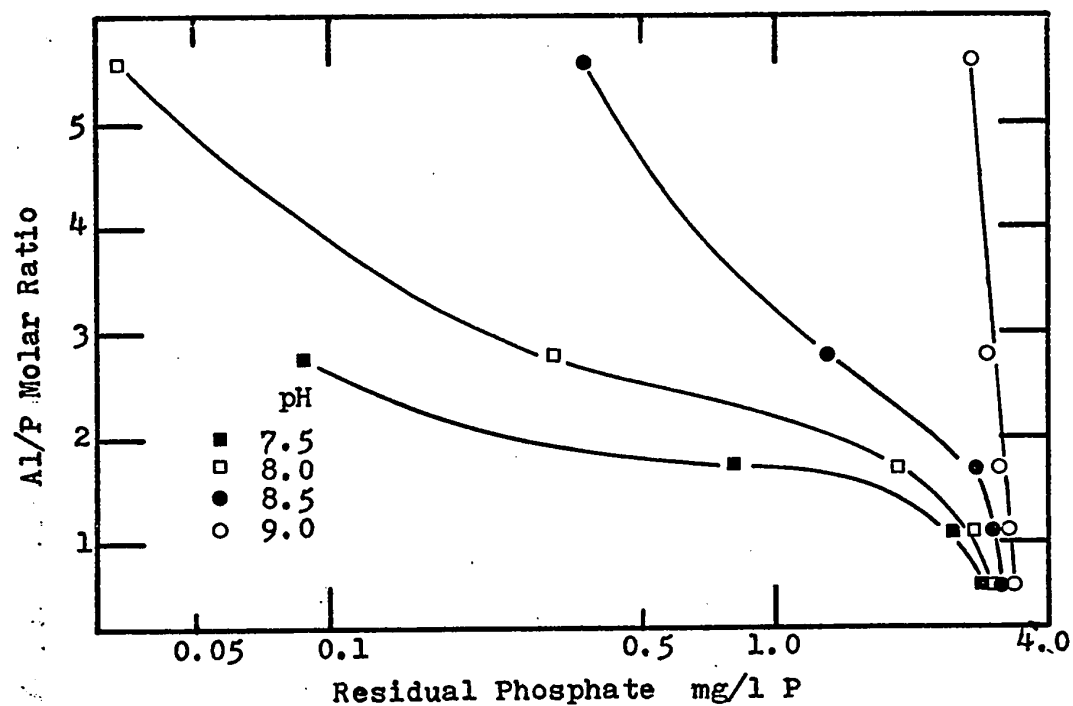
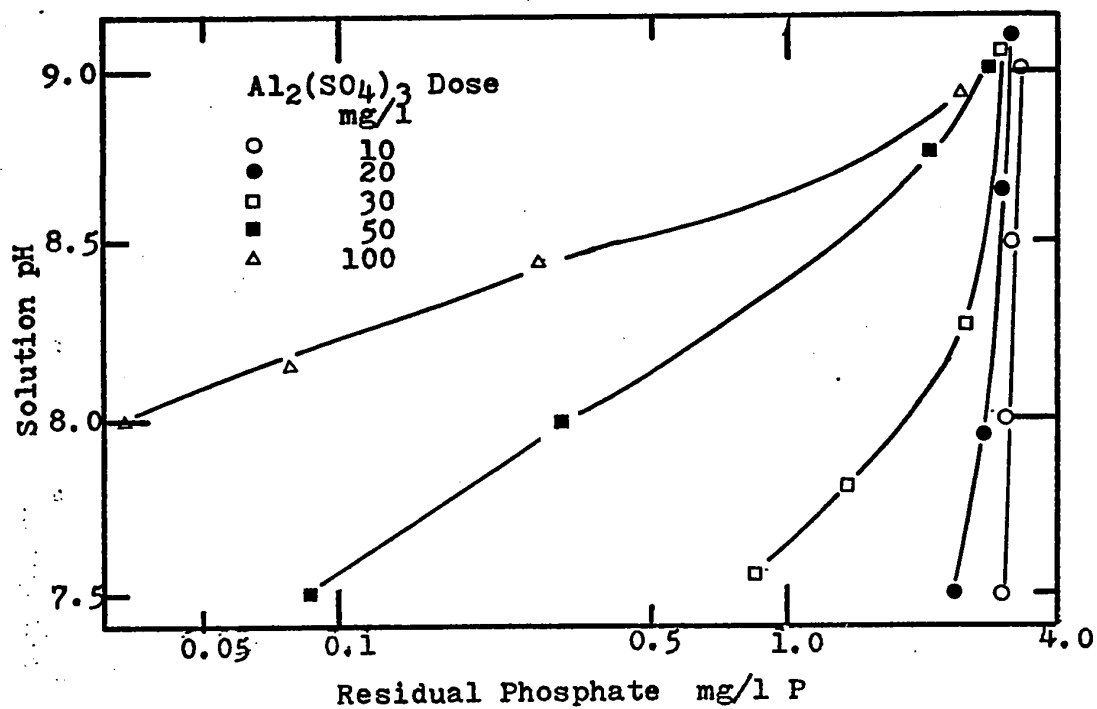


Figure 3 Aluminum Sulfate With Ortho-phosphate Solution (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$ )

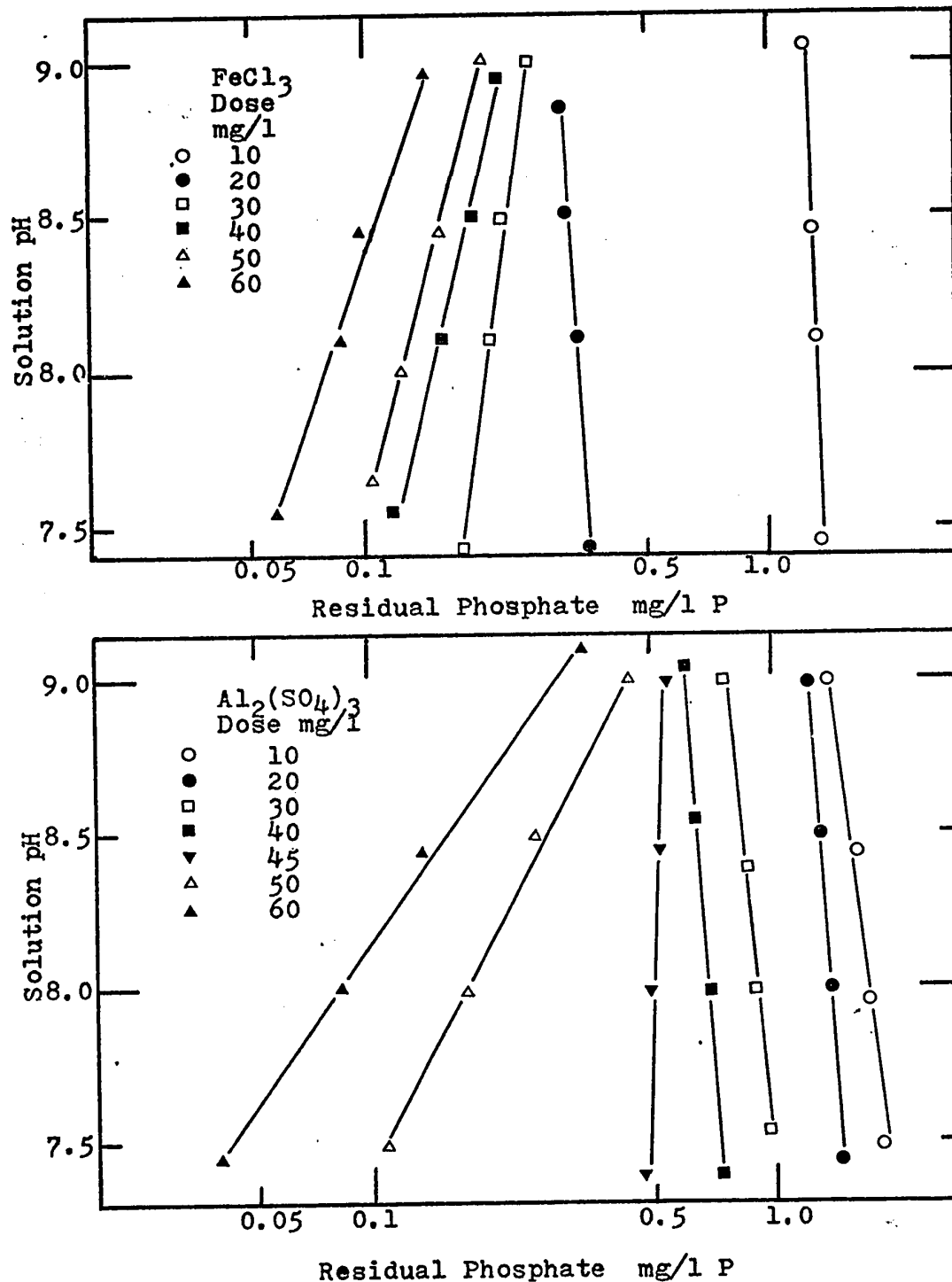


Figure 4 Ferric Chloride or Aluminum Sulfate and 50 mg/l of Calcium Hydroxide With Ortho-phosphate Solution. (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$ )

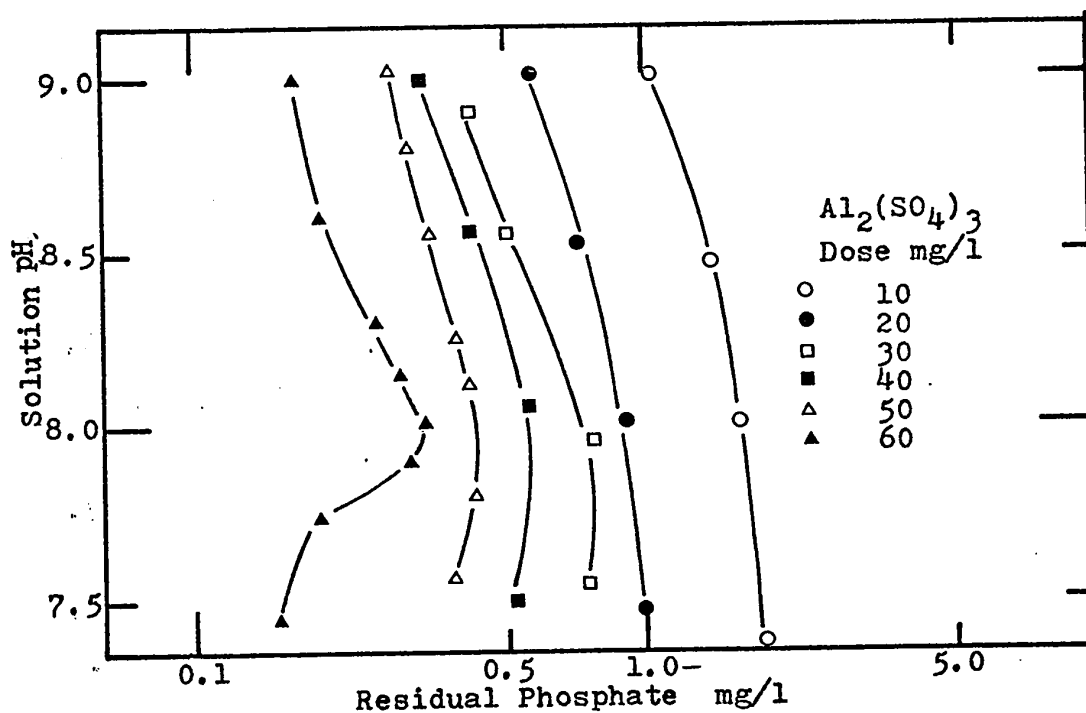
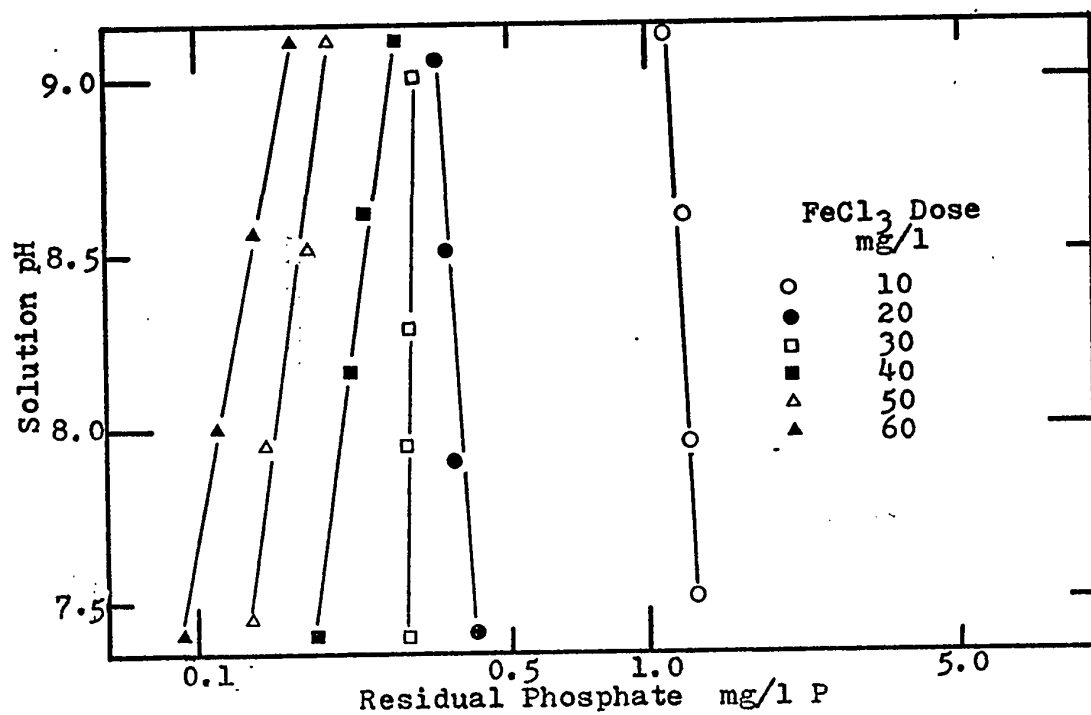


Figure 5 Ferric Chloride or Aluminum Sulfate and 100 mg/l of Calcium Hydroxide With Ortho-phosphate Solution. (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l PO<sub>4</sub>)

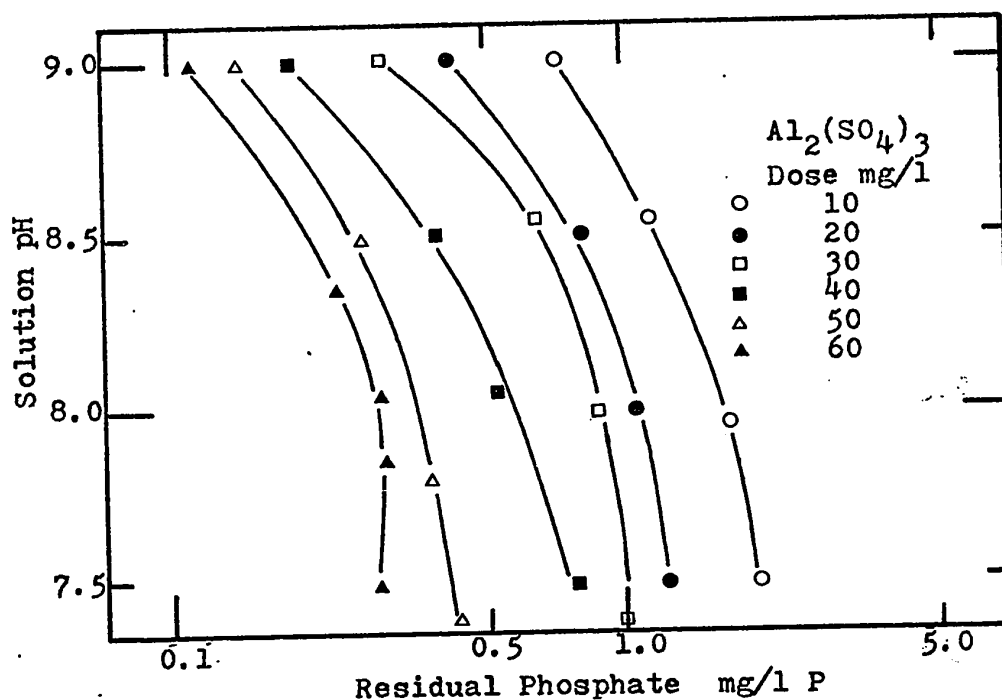
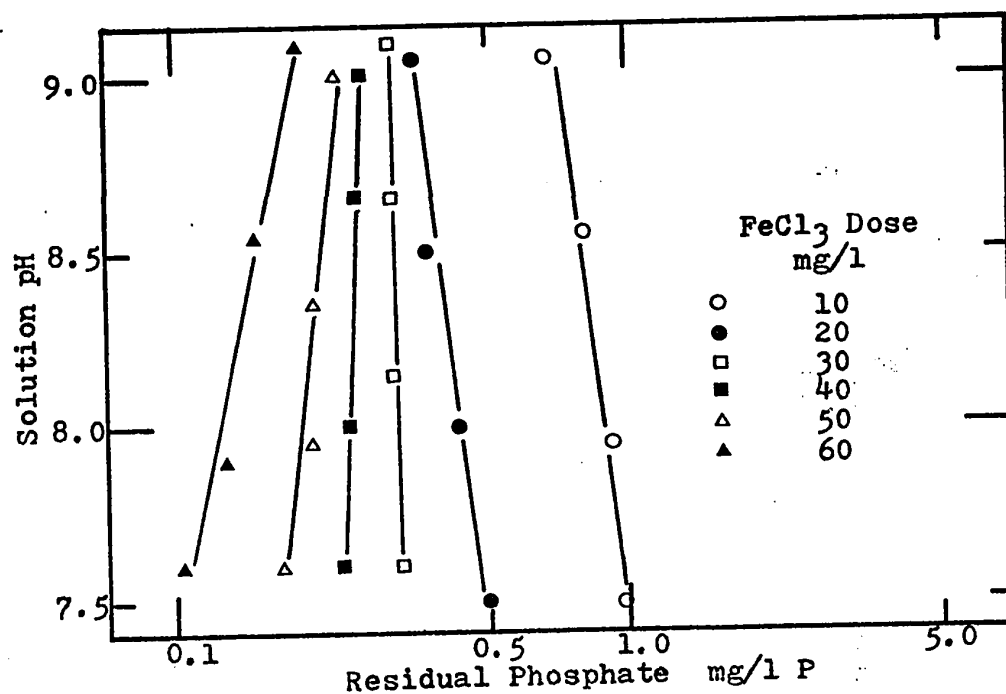


Figure 6 Ferric Chloride or Aluminum Sulfate and 150 mg/l of Calcium Hydroxide With Ortho-phosphate Solution (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$ )

stood that there must be some combination which has almost no effect of pH in the ortho-phosphate removal within this experimental range. The combination of 150 mg/l of calcium hydroxide and 30 mg/l of ferric chloride showed a vertical line in the plot of the pH of the solution vs residual phosphate in Figure 6. For the combination of calcium hydroxide and aluminum sulfate, there is likely to be a similar vertical line between 40 and 45 mg/l of aluminum sulfate and 50 mg/l of calcium hydroxide (Figure 4).

2. For the combination of calcium hydroxide and ferric chloride, the difference in phosphate removal between 10 and 20 mg/l of ferric chloride with the same amount of calcium hydroxide is very significant (Figures 4 to 6). Similar situations for aluminum sulfate and calcium hydroxide can be found with higher calcium hydroxide doses (100 and 150 mg/l; Figures 5 and 6). This suggests that significant ortho-phosphate removal by combined chemicals of calcium and iron or aluminum can be achieved when the molar ratio of Fe or Al to P is larger than 1 (with 20 mg/l of  $\text{FeCl}_3$  or  $\text{Al}_2(\text{SO}_4)_3$ , the M/P molar ratio is 1.16 or 1.11).

3. From Figure 5, it is clear that the combination of 100 mg/l of calcium hydroxide and aluminum sulfate shows a maximum residual phosphate near pH 8. The combination of 100 mg/l of calcium hydroxide and 60 mg/l of aluminum sulfate is a good example to show the maximum residual phosphate near pH 8.

4. It is also very obvious that for a fixed amount of

calcium hydroxide, the combined chemical method favors higher pH in ortho-phosphate removal when the dose of ferric chloride or aluminum sulfate is small; otherwise, it favors lower pH.

5. Almost all the combinations of calcium and iron showed linear relationship when the pH of the solution vs residual phosphates were plotted in the experimental range (7.5 to 9.0; Figures 4 to 6). For calcium and aluminum, only the combinations of 50 mg/l of calcium hydroxide and different doses of aluminum sulfate showed a linear relationship (Figure 4).

6. In the experimental pH range, higher calcium hydroxide dose did not achieve a proportionately higher ortho-phosphate removal.

7. Because the combination of 30 mg/l of ferric chloride and different amounts of calcium hydroxide showed very little pH effect, this combination was selected for the following steps. For convenience of comparison, the same combination of aluminum sulfate and calcium hydroxide was also selected.

C. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho- and Pyro-phosphate Solution

1. Phosphate Removal by Calcium Hydroxide Only (Table 5 and Figure 7)

a. Comparing the plots of residual ortho- and total phosphate in Figure 7, the residual total phosphates are only slightly more than the residual ortho-phosphate. The plots indicate that pyro-phosphate can be easier removed by calcium at this experimental pH range (8.1 to 9.5).

b. Again, when Figure 7 is compared with Figure 1, even the residual total phosphates in Figure 7 are much less than the corresponding data of residual ortho-phosphates in Figure 1 (same initial ortho-phosphate concentrations). This indicates that pyro-phosphate can be precipitated by calcium at this pH range and some ortho-phosphate can be adsorbed on the pyro-phosphate flocs. Schmid (15) found that ortho-phosphate could adsorb on the polyphosphate floc at a pH near 7.0. Therefore, it can be said that the difference in residual phosphate between Figures 1 and 7 is due to adsorption.

c. In terms of percent of total phosphate removal, calcium hydroxide alone is not effective in the experimental pH range. For example, the highest dose (150 mg/l) at pH 9 produced a supernatant with 1.22 mg/l P before filtration and 0.72 mg/l P after filtration (85% and 75% of total phosphate removal).

## 2. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate (Tables 6 and 7; Figures 8 and 9)

a. In general, the phosphate removal data for calcium and iron showed better results compared to that of calcium and aluminum.

b. Similarly with single chemical of calcium hydroxide, the data showed that the amount of residual total phosphates were slightly more than the amount of residual ortho-phosphates, indicating that pyro-phosphate could be easier removed at the experimental pH range.



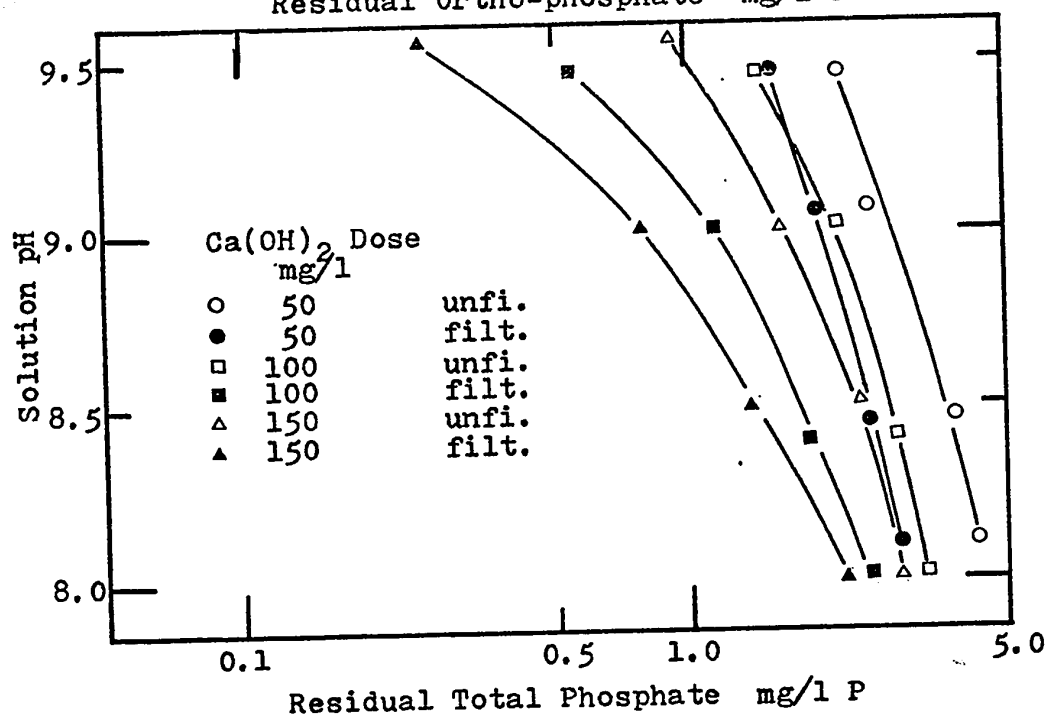
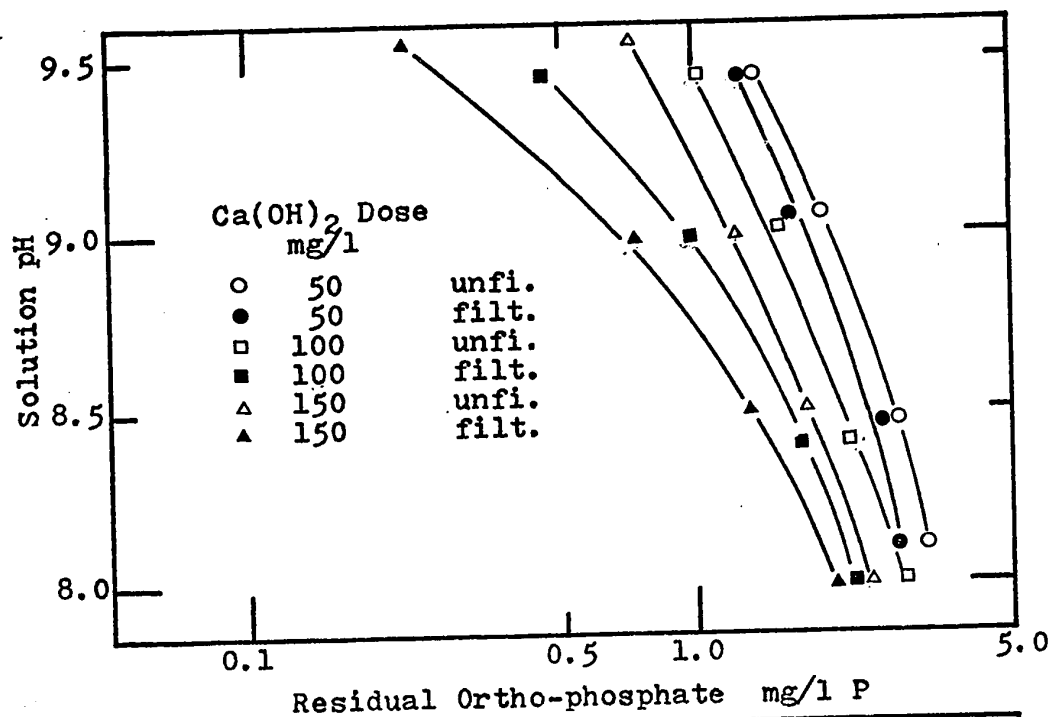


Figure 7 Calcium Hydroxide With Ortho and Pyro Phosphate Solution (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$  of Ortho and 1.161 mg/l P or 5 mg/l  $\text{PO}_4$  of Pyro Phosphate).

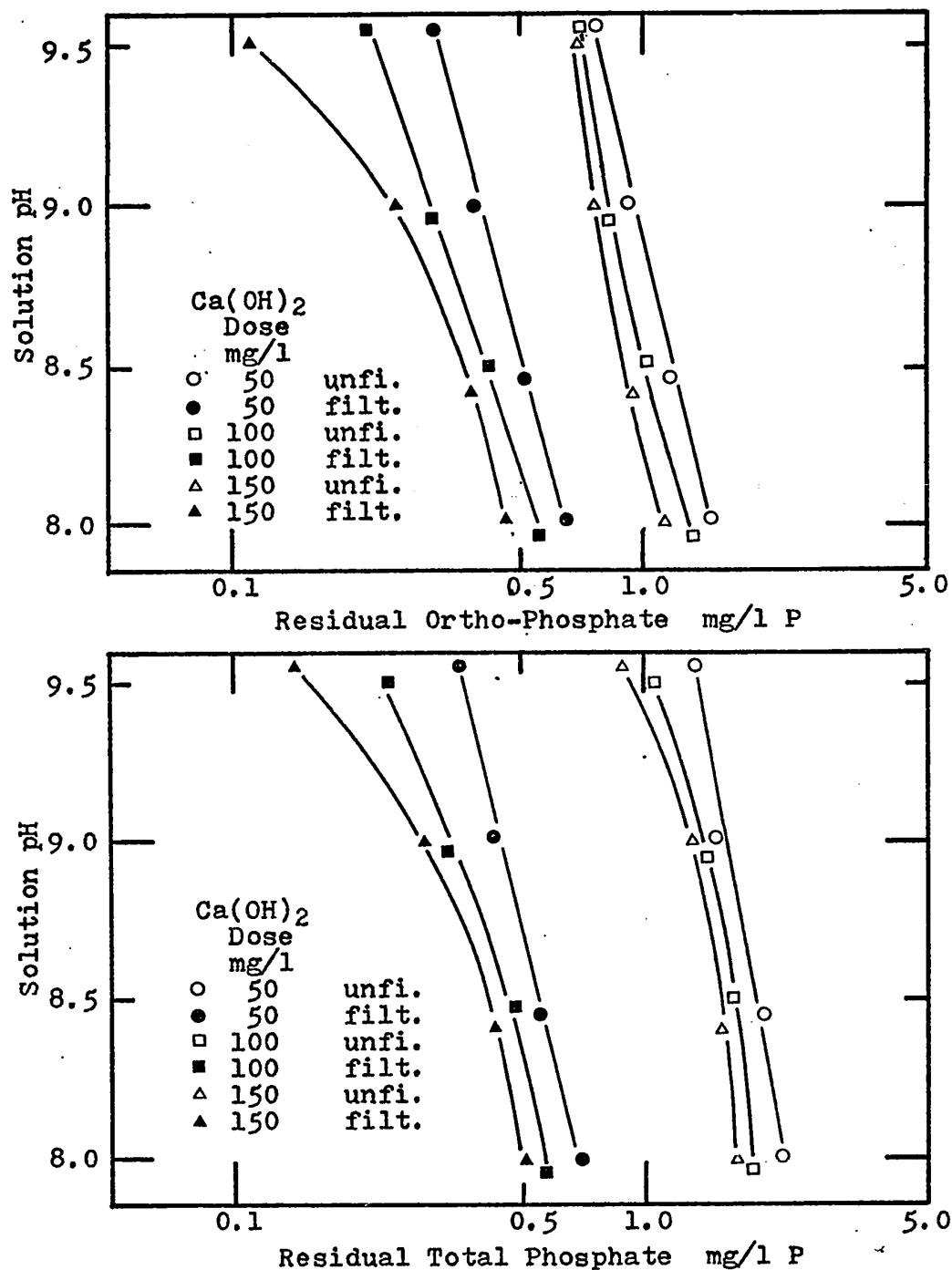


Figure 8 Calcium Hydroxide and 30 mg/l of Ferric Chloride With Ortho and Pyro Phosphate Solution (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$  of Ortho-phosphate and 1.161 mg/l P or 5 mg/l  $\text{PO}_4$  of Pyro-phosphate)

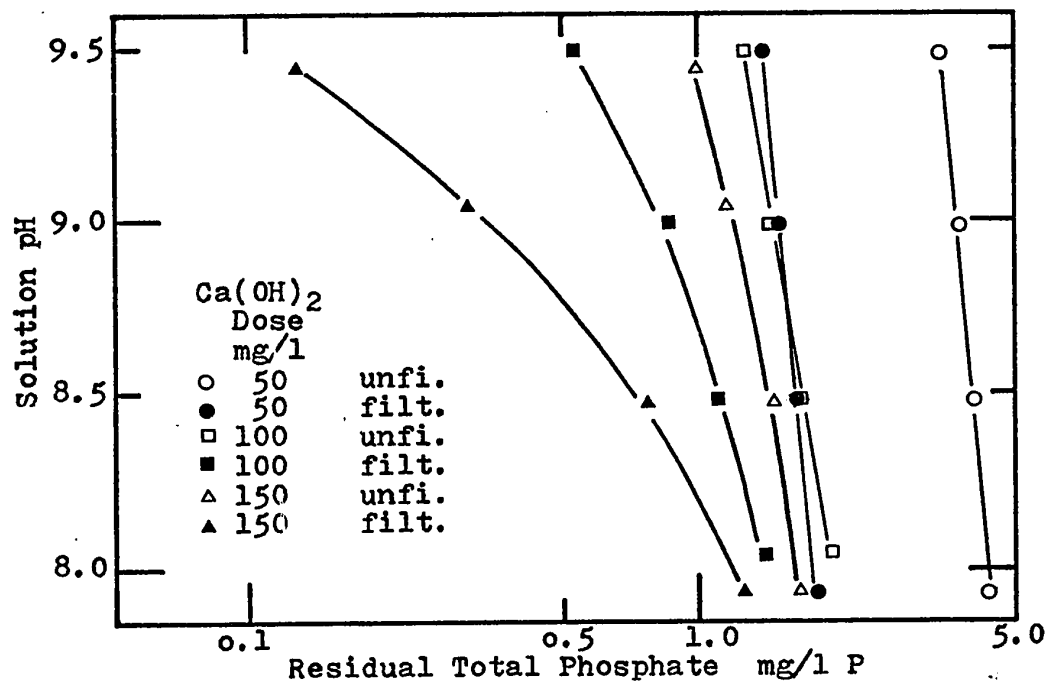
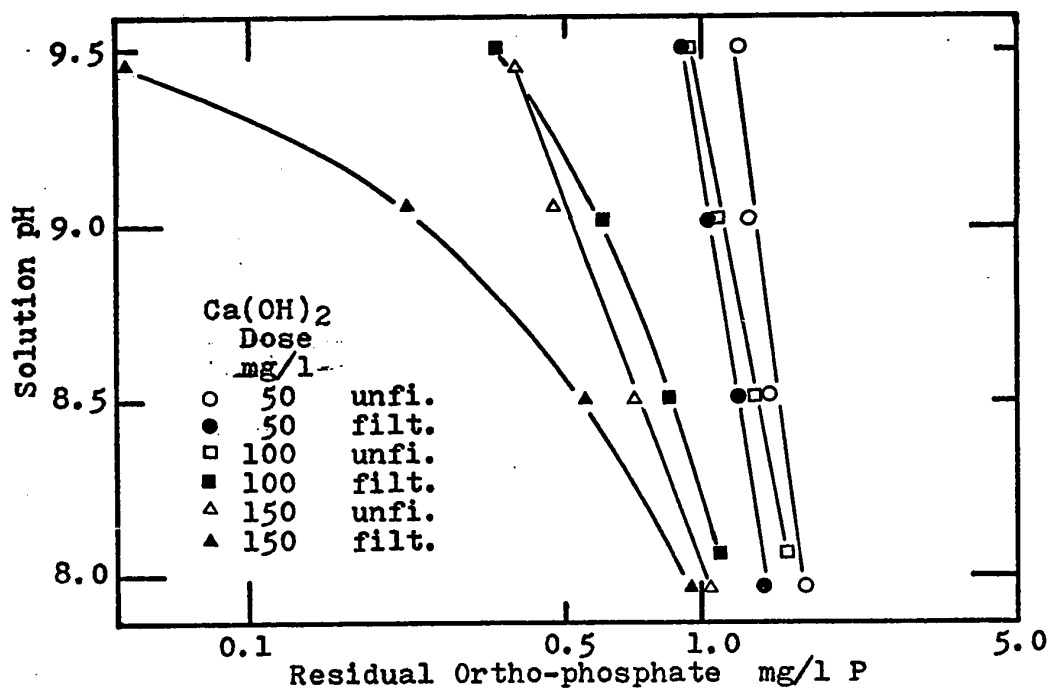


Figure 9 Calcium Hydroxide and 30 mg/l of Aluminum Sulfate With Ortho and Pyro Phosphate Solution (Initial Phosphate Concentration, 3.262 mg/l P or 10 mg/l  $\text{PO}_4$  of Ortho-phosphate and 1.161 mg/l P or 5 mg/l  $\text{PO}_4$  of Pyro-phosphate)

c. The difference in residual phosphates between filtered and unfiltered samples were significant (Figures 8 and 9).

d. The corresponding data for unfiltered samples were selected from Tables 5 to 7 to make the following table to show that the combined chemical method could improve the phosphate removal ability.

Chemical	Dose mg/l	Solution pH	Initial P mg/l	Residual P mg/l	Percent Removal
Ca(OH) <sub>2</sub>	100	8.0	4.89	3.27	33.1
Ca(OH) <sub>2</sub> FeCl <sub>3</sub>	100 30	7.95	4.89	1.79	63.4
Ca(OH) <sub>2</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	100 30	8.05	4.89	1.57	67.9

D. Phosphorus Removal by Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate From Ortho-, Pyro- and Tripoly-phosphate Solution (Tables 8 and 9; Figures 10 to 12)

Because iron and aluminum are more favorable in ortho-phosphate removal than calcium in the experimental pH range, and their removal ability is proportional to the M/P molar ratio up to 1, 1:1 molar ratio of iron and aluminum to ortho-phosphate was selected to combine with different doses of calcium hydroxide in this step. All the data were based on the supernatant pH.

1. The data also showed that more pyro- and tripoly-phosphate had been removed than the ortho-phosphate (Figures 10 and 11).

2. The difference in residual phosphate for both ortho-

34

and total phosphate between 50 and 100 mg/l of calcium hydroxide was significantly larger than 100 and 150 mg/l of calcium hydroxide. This indicated that calcium hydroxide doses above 100 mg/l are not economical.

3. In terms of percent removal of phosphate, the combinations of more than 100 mg/l of calcium hydroxide and 1:1 molar ratio of Fe or Al to ortho-phosphate showed 90% or more removal between pH 8.5 and 9.0.

4. By selecting corresponding data from Tables 5 to 9 for the following table, it is clear that higher initial phosphate concentration does not require proportional higher chemical dose.

Chemical	Dose mg/l	M/P (ortho-) Molar Ratio	pH	Initial P mg/l	Residual P mg/l (unfilt.)	Percent Removal
Ca(OH) <sub>2</sub>	100		8.40	4.89	2.81	42.5
Ca(OH) <sub>2</sub> FeCl <sub>3</sub>	100 30	1.74	8.50	4.89	1.63	66.7
Ca(OH) <sub>2</sub> FeCl <sub>3</sub>	100 52.4	1.0	8.60	20.0	2.15	89.3

5. For unfiltered samples, the combination of iron and calcium is better than the combination of aluminum and calcium in phosphate removal. But for filtered samples, taken at high pH (near 9), the combination of aluminum and calcium is better.

6. Some HCl had been added to lower the pH. According to the data of O.W.R.C. (25, Figure 3), the amount of calcium hydroxide used in these experiments when applied to sewage showed a pH between 9.0 and 9.1. Therefore, the natural buffer characteristic of sewage may eliminate the need of chemicals

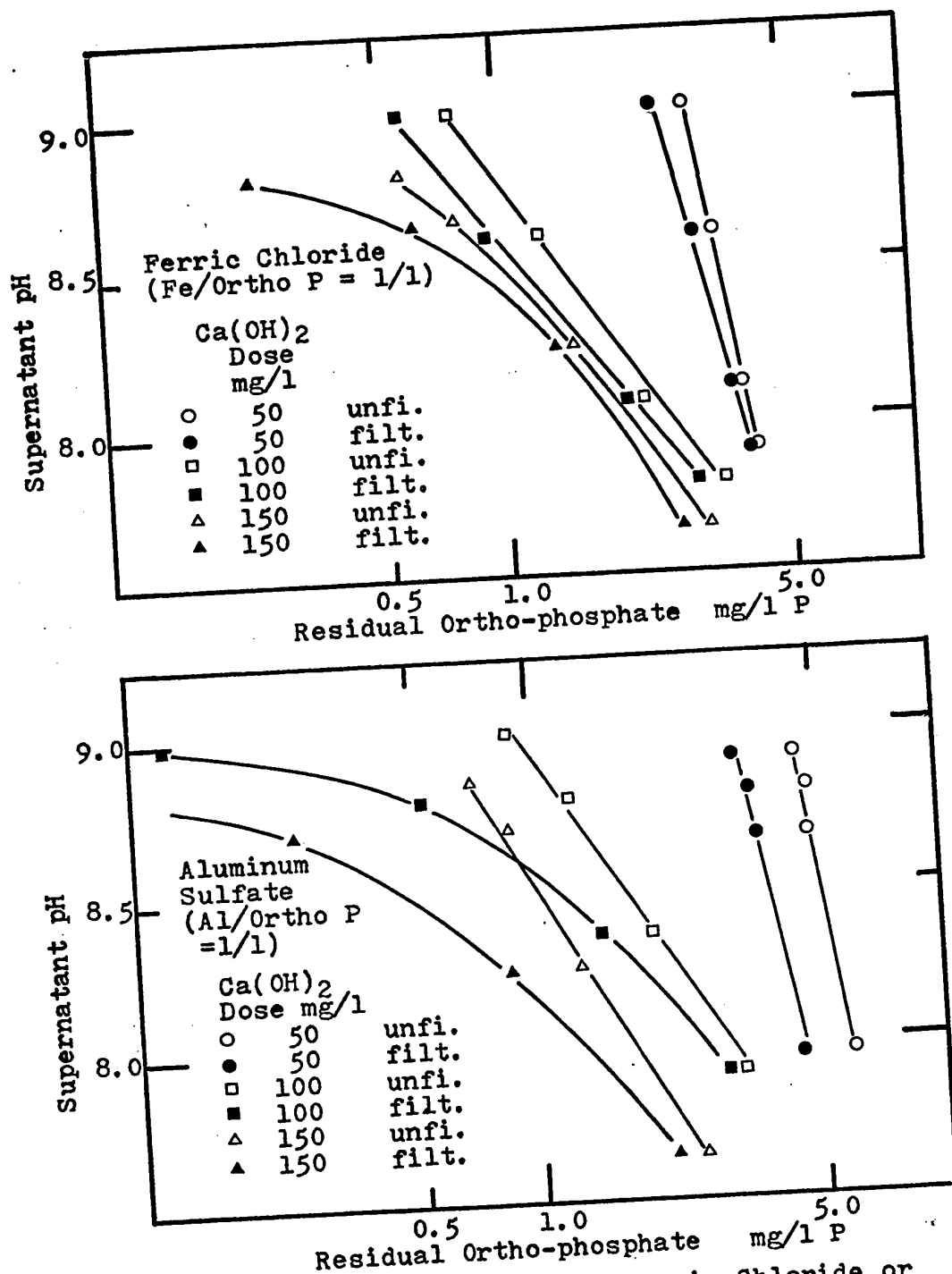


Figure 10 Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate With Ortho, Pyro and Tripoly Phosphate Solution (Initial Phosphate Concentration; 10 mg/l P of Ortho, 6 mg/l P of Tripoly and 4 mg/l P of Pyro) (Residual Ortho-phosphate)

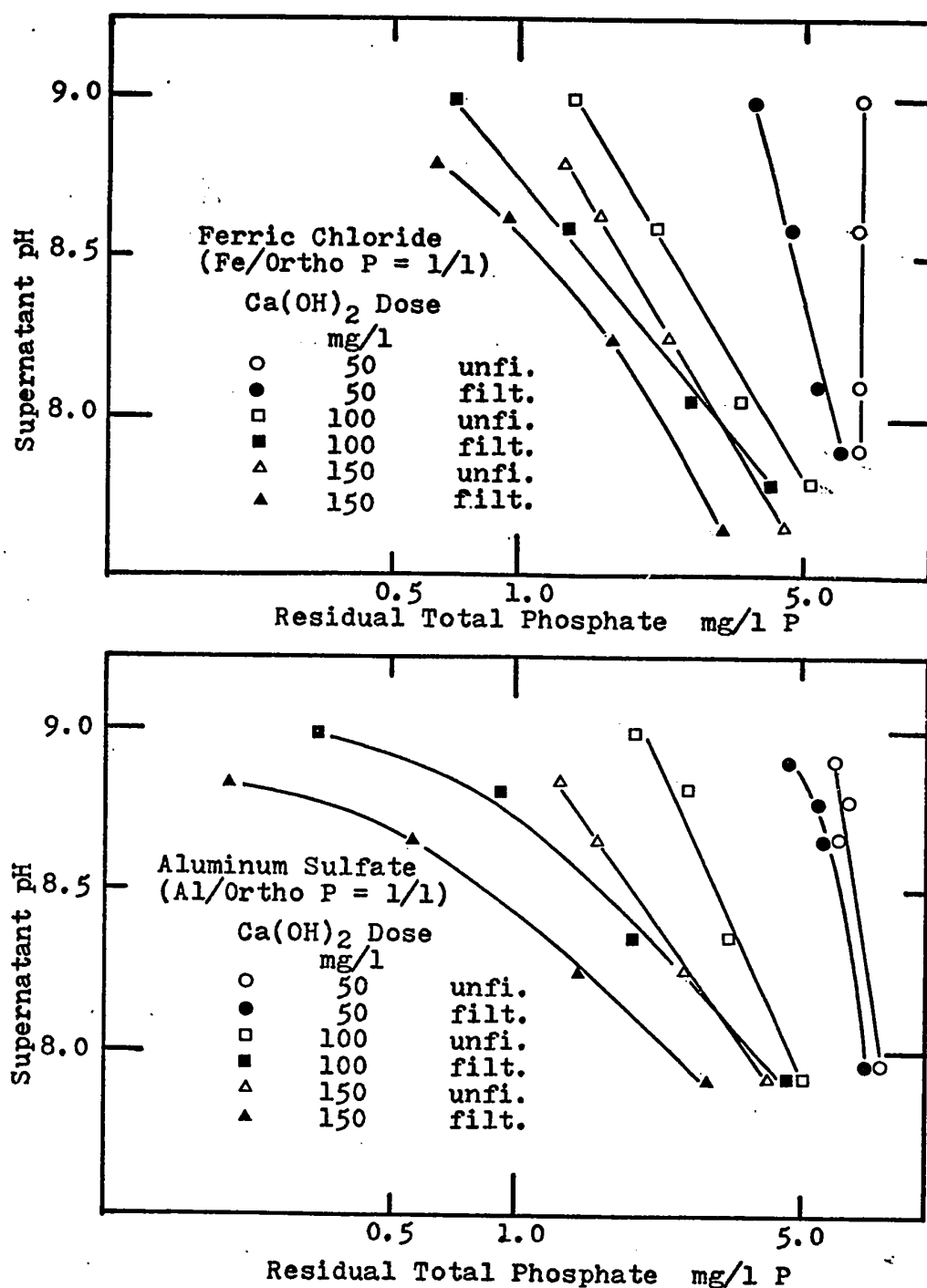


Figure 11 Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate With Ortho, Pyro and Tripoly Phosphate Solution (Initial Phosphate Concentration; 10 mg/l P of Ortho, 6 mg/l P of Tripoly and 4 mg/l P of Pyro) (Residual Total Phosphate)

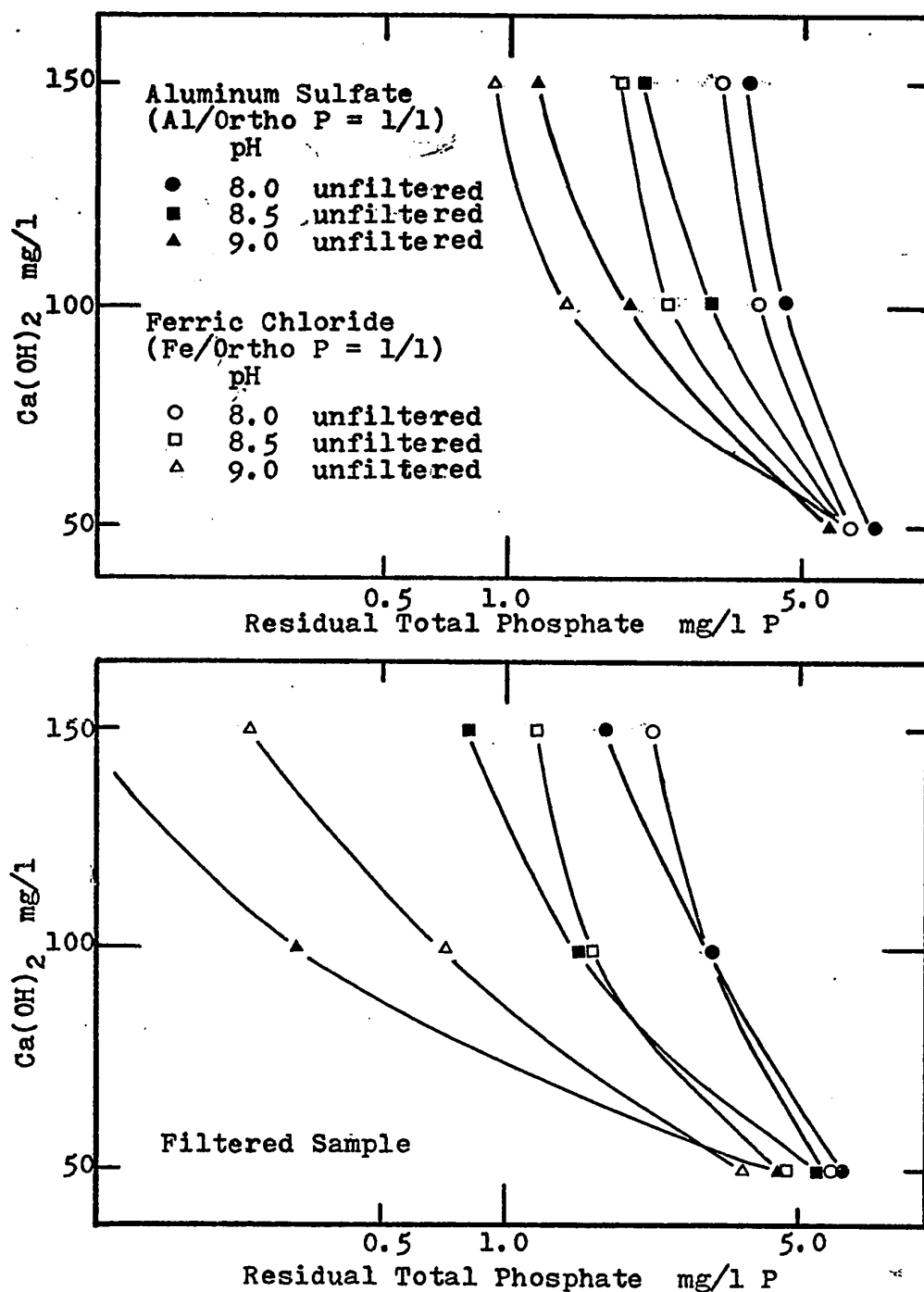


Figure 12 Phosphate Removal by Combinations of Calcium Hydroxide and Aluminum Sulfate or Ferric Chloride at Different Calcium Hydroxide Dosage and Supernatant pH (Data from Figures 10 and 11)



to lower the pH when the combined chemical process is used in phosphate removal.

E. Phosphorus Removal by a Mixed Column of Sand and Soil From Chemically Treated Supernatant Water(80% sand and 20% soil)

The soil was taken from a field in Essex County, Ontario that had not been fertilized for one year. It contains approximately equal proportions (50%) of illite and vermiculite in the clay fraction. The illite is a group of minerals with a basic structure of  $(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)(Si_{8-y} \cdot Al_y)O_{20}$ . Vermiculites are hydrous silicates derived generally from the alteration of mica(35).

1. Phosphorus Removal From Phosphate Solution (Table 10 and Figure 13)

a. No detectable phosphate removal was obtained in the filtrate of sand column with phosphate solutions.

b. The ortho-phosphate fixation ability of the mixed column dropped rapidly and less than 4% of ortho-phosphate could be fixed after six hours. In comparison, pyro- and tri-poly-phosphate were easily retained by soil, about 40% of pyro- and 20% of tripoly-phosphate could be retained after six hours.

c. The phosphate, fixed by hydroxyl replacement in soil, is easily washed out by water (26, 28). The poor ortho-phosphate fixation ability of the mixed column indicated that hydroxyl replacement might have taken place.

2. Phosphorus Removal From Chemically Treated Supernatant (Tables 11 and 12; Figures 14A and 14B)

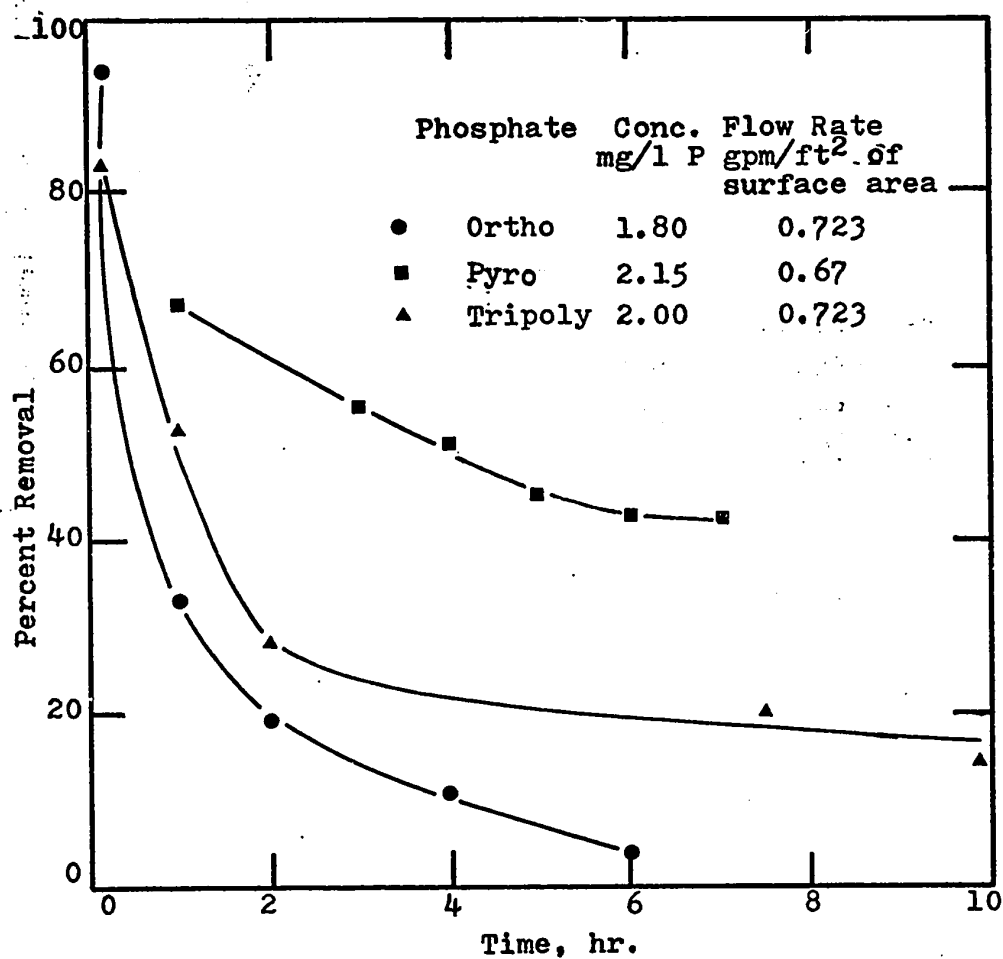


Figure 13 Phosphorus Removal By a Mixed Column of 80% Ottawa Sand and 20% Local Soil From Ortho, Pyro or Tripoly Phosphate Solution

Because large quantities of water were needed to run these experiments, tap water was used to make the supernatant after an analysis revealed that the phosphate content of tap water was only about 0.01 mg/l P.

a. Since a large enough tank was not available, six batches of supernatant were prepared in 70-liter plastic drum for each test to keep flow continuously through the columns during the test period. The large difference in the amount of residual phosphate present in the supernatant might have been due to different mixing and flocculating speed during preparation because the stirring speed could not be controlled properly by a transformer. As stated before in the literature (20), mixing and flocculating are important factors in phosphate removal.

b. The residual total phosphate was almost constant during the first eight hours; then steadily increased with time, indicating that the soil started to lose its ortho-phosphate fixation ability between 5 to 7 hours from starting time. This phenomenon was similar to the one observed before when ortho-phosphate solution was used .

c. From the residual phosphate data of supernatant, the iron and calcium treated supernatant showed less residual total phosphate content, proving that this combination had better settling ability than the combination of aluminum and calcium. But again, after filtration through sand column both filtrates showed almost the same amount of total phosphate content.

d. The pressure drop data indicated that the filtration column were more easily clogged by filtering the aluminum and calcium treated supernatant in comparison to the iron and calcium treated supernatant.

e. In terms of phosphate removal, the data could not indicate which supernatant was more suitable for the mixed column of sand and soil.

f. In order to know the relationship between retention time and phosphate removal by mixed column of sand and soil, the flow rate was reduced from 0.56 gpm/sq. ft. of surface area to 0.46 gpm/sq. ft. of surface area at the eighteenth hour in these two experiments. The data showed less residual total phosphate in the 24th hour's sample than the 18th hour's sample, although the tendency was more residual phosphate as time went on (Tables 11 and 12).

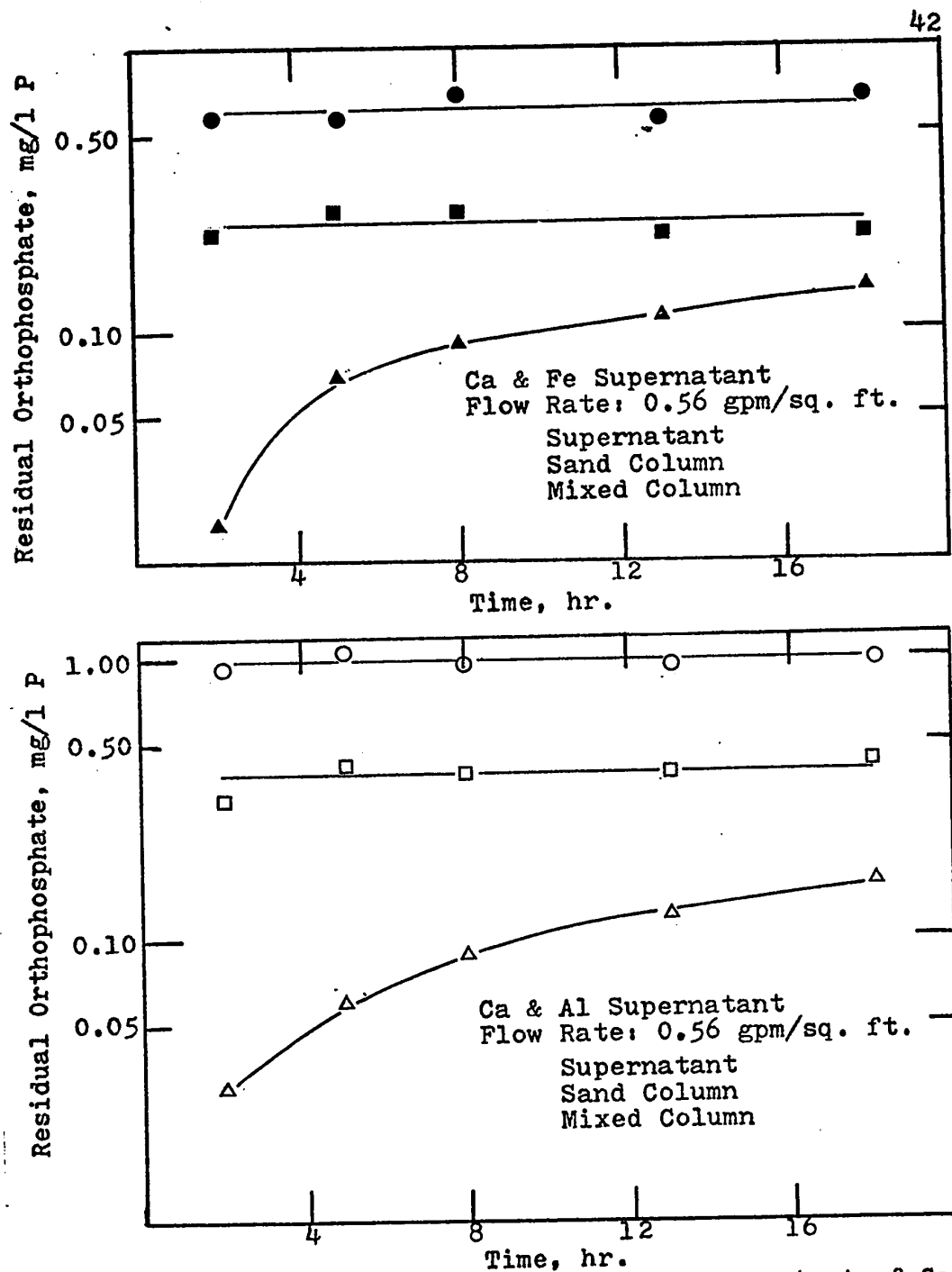


Figure 14A Phosphorus Removal From The Supernatant of Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate Treated Phosphate Solution by a Sand Column and a Mixed Column of 80% Ottawa Sand and 20% Local Soil (Residual Orthophosphate)

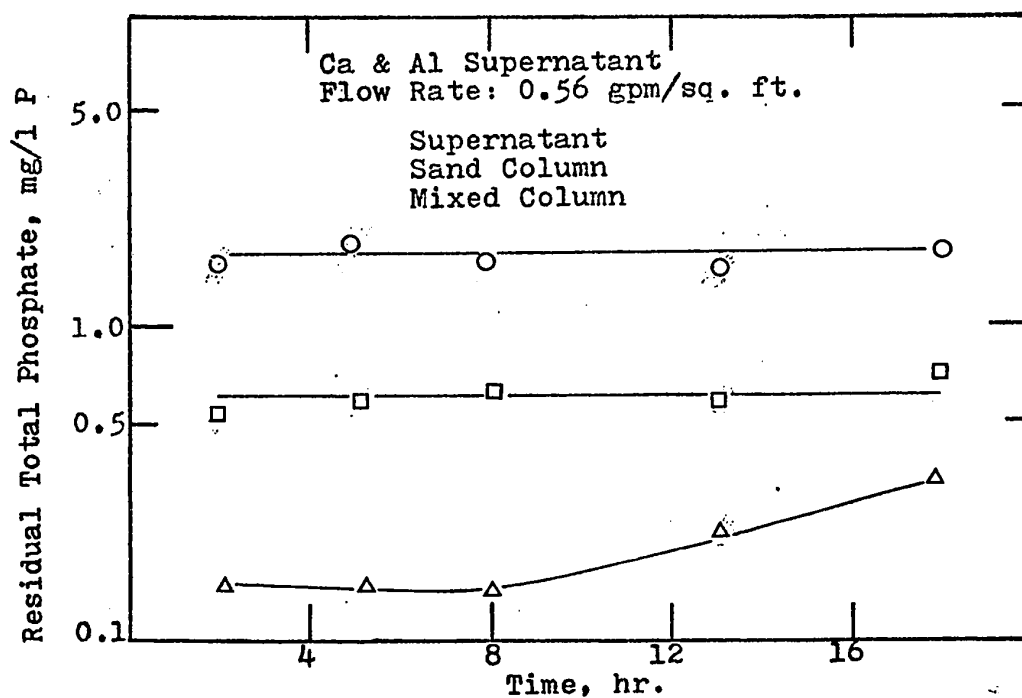
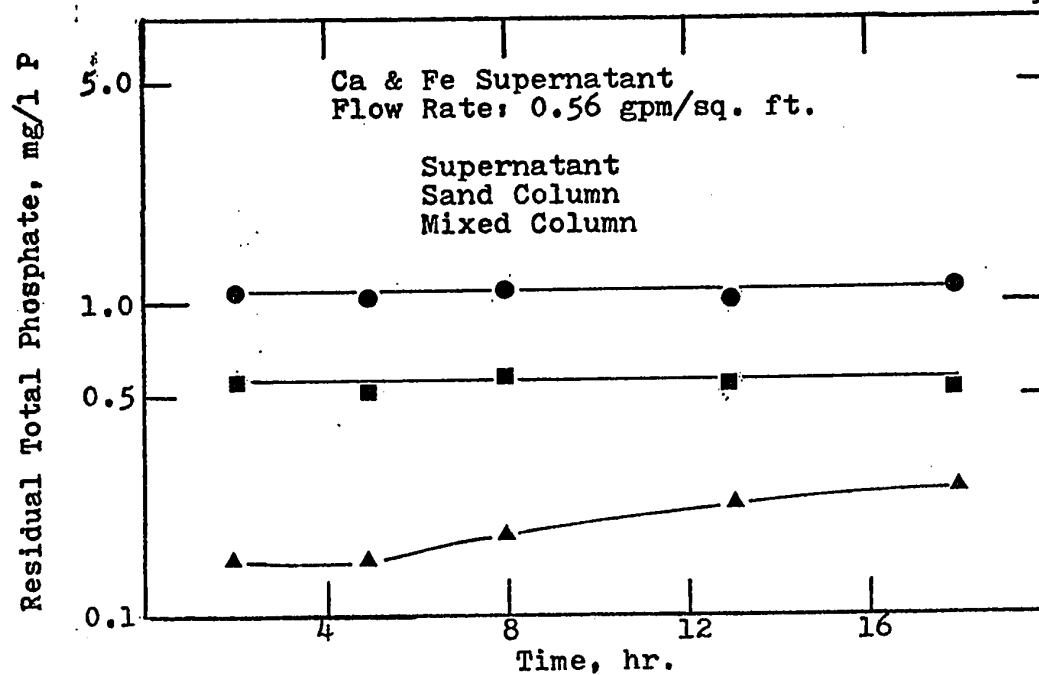


Figure 14B Phosphorus Removal From The Supernatant of Calcium Hydroxide and Ferric Chloride or Aluminum Sulfate Treated Phosphate Solution by a Sand Column and a Mixed Column of 80% Ottawa Sand and 20% Local Soil (Residual Total Phosphate)

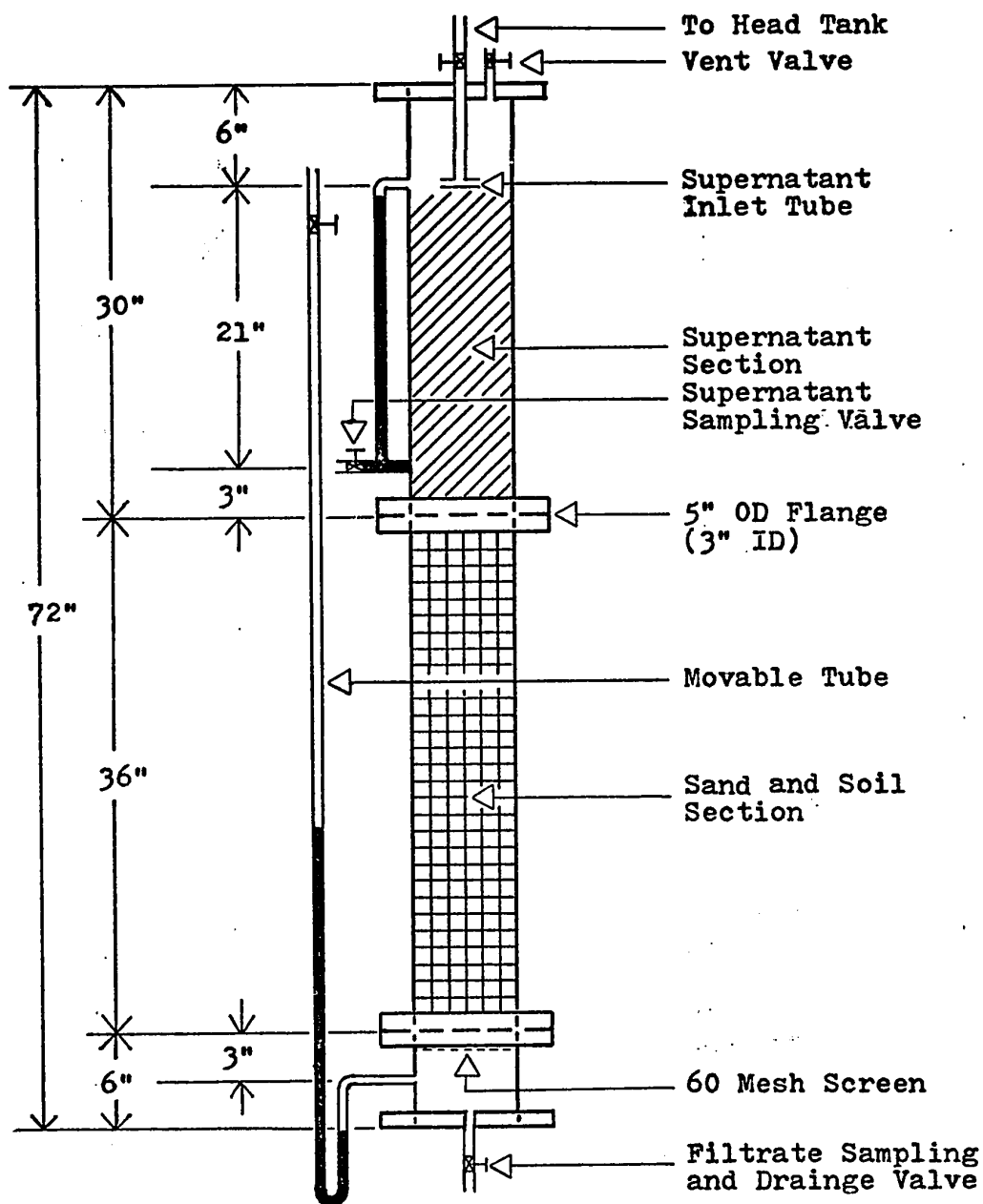


Figure 15 Soil and Sand Filtration Column  
(Not to Scale)

## CHAPTER V

### CONCLUSION

After investigation of phosphorus removal from ortho-phosphate, ortho- and pyro-phosphate and ortho-, pyro- and tripoly-phosphate solutions, pyro- and tripoly-phosphate could be more easily removed than ortho-phosphate in the experimental pH range between 7.5 to 9.5. The data showed that the ortho-phosphate removal could be improved in the presence of pyro- and tripoly-phosphate. The data also showed that pyro- and tripoly-phosphate, which are more difficult to be removed by single chemical method, could be easily removed by combined chemical method of calcium hydroxide and ferric chloride or aluminum sulfate.

1:1 molar ratio of ferric chloride or aluminum sulfate to ortho-phosphate in combinations with different amounts of calcium hydroxide was chosen in the last step of the test with ortho-, pyro- and tripoly-phosphate solution. With a combination of 150 mg/l of calcium hydroxide ( $\text{Ca}/\text{total P} = 3.14$ ) and 52.4 mg/l of ferric chloride or 55.2 mg/l of Aluminum sulfate ( $\text{Fe or Al}/\text{ortho-phosphate} = 1$ ), the total phosphorus content could be reduced to about 1.2 mg/l P from an initial concentration of 10 mg/l P as ortho-, 4 mg/l P as pyro- and 6 mg/l P as tripoly-phosphate without filtration at pH near 9. Similar results were also obtained when tap water was used to make the supernatant for filtration column experiments.



For unfiltered samples, the combination of iron and calcium showed less residual phosphate in the supernatant water than the combination of aluminum and calcium. But, after passing through a sand column both filtrates showed almost the same amount of residual total phosphate.

The reason why soil lost its ortho-phosphate fixation ability so rapidly might be that the ortho-phosphate fixation by soil was due to hydroxyl replacement which could be easily washed out by water (28, 30).

The data in Table 11 showed that the sand column could reduce the ortho-phosphate content in the iron and calcium treated supernatant from an average of 0.59 mg/l P to about 0.24 mg/l P. The mixed column could reduce the ortho-phosphate content to 0.02 mg/l P in the first two hours and 0.18 mg/l P at the 24th hour. For total phosphate removal, the sand column could reduce it from an average of 1.09 mg/l P to about 0.58 mg/l P. The mixed column could reduce it to less than 0.18 mg/l P during the first eight hours and 0.26 mg/l P at the 18th hour.

Mixed column could not only remove those particles which were non-settling but also could remove some phosphate from the chemically treated supernatant which was already low in phosphate content. This could not be achieved economically by chemical method.

# APPENDIX I

## Solubility and Complex Formation Equilibria of Phosphate With Iron, Aluminum and Calcium

No.	Equilibrium	Log of Equilibrium Constant,* 25°C
<u>I. Solubility of Phosphates</u>		
1	$\text{Fe}^{+3} + \text{PO}_4^{-3} = \text{FePO}_4(\text{s})$	23
2	$\text{Al}^{+3} + \text{PO}_4^{-3} = \text{AlPO}_4(\text{s})$	21
3	$\text{Ca}^{+2} + 2\text{H}_2\text{PO}_4^{-} = \text{Ca}(\text{H}_2\text{PO}_4)_2(\text{s})$	1
4	$\text{Ca}^{+2} + \text{HPO}_4^{-2} = \text{CaHPO}_4(\text{s})$	6
5	$10\text{Ca}^{+2} + 6\text{PO}_4^{-3} + 20\text{H}^{-} = \text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6(\text{s})$	90
6	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6(\text{s}) + 6\text{H}_2\text{O}$ $= 4(\text{Ca}_2(\text{HPO}_4)(\text{OH})_2) + 2\text{Ca}^{-2} + 2\text{HPO}_4^{-2}$	17
<u>II. Complex Formation With Orthophosphate</u>		
7.	$\text{Fe}^{+3} + \text{H}_2\text{PO}_4^{-} = \text{FeH}_2\text{PO}_4^{+2}$	1.8
8.	$\text{Fe}^{+3} + \text{HPO}_4^{-2} = \text{FeHPO}_4^{+}$	8.3
9.	$a\text{Fe}^{+3} + b\text{H}_n\text{PO}_4^{3-n} = \text{Fe}_a(\text{H}_n\text{PO}_4)_b^{3a-b(3-n)}$	Evidence
10.	$a\text{Al}^{+3} + b\text{H}_n\text{PO}_4^{3-n} = \text{Al}_a(\text{H}_n\text{PO}_4)_b^{3a-b(3-n)}$	Evidence
11.	$\text{Ca}^{+2} + \text{H}_2\text{PO}_4^{-} = \text{CaH}_2\text{PO}_4^{+}$	1
12.	$\text{Ca}^{+2} + \text{HPO}_4^{-2} = \text{CaHPO}_4$	2.5

\* This table is taken from reference (20) and the equilibrium constants given here are approximate

**APPENDIX II**  
**EXPERIMENTAL DATA**

Table 1

Phosphorus Removal by Calcium Hydroxide, Ferric Chloride or Aluminum Sulfate From Ortho-phosphate Solution

Initial Ortho-phosphate Concentration: 3.262 mg/l P

Chemical mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l
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Calcium Hydroxide

50	7.50	3.26	7.85	3.10	8.40	2.95	9.0	2.43
100	7.45	2.87	7.95	2.77	8.60	2.63	9.0	1.60
125	7.55	2.71	7.95	2.64	8.55	2.28	9.05	1.22
150	7.40	2.64	7.90	2.54	8.50	2.23	8.90	1.20

Ferric Chloride (Anhydrous)

10	7.55	1.92	8.05	2.18	8.40	2.44	9.20	3.03
20	7.50	1.63	8.05	1.73	8.65	2.15	9.20	2.64
30	7.40	0.86	8.0	1.14	8.80	1.83	9.20	2.28
40	7.50	0.62	8.0	1.0	8.35	1.20	9.15	2.04
50	7.55	0.33	8.10	0.83	8.35	1.14	9.10	1.88
60	7.45	0.12	7.75	0.21	8.55	1.14	8.95	1.57

Aluminum Sulfate (Anhydrous)

10	7.50	2.94	8.0	3.03	8.50	3.10	9.0	3.25
20	7.50	2.35	7.95	2.71	8.65	2.95	9.10	3.16
30	7.55	0.83	7.80	1.34	8.25	2.48	9.05	3.0
50	7.50	0.09	8.0	0.31	8.75	2.02	9.0	2.87
100	7.50	0.01	8.0	0.03	8.15	0.08	8.45	0.28
							8.90	2.40

Note: 1. All the samples were filtered with 0.45  $\mu$  membrane.  
2. Solution pH was measured before flocculation.

Table 2

Phosphorus Removal by 50 mg/l of Calcium Hydroxide  
and Different Doses of Ferric Chloride or Aluminum  
Sulfate From Ortho-phosphate Solution

Initial Ortho-phosphate Concentration: 3.262 mg/l P

Chemical mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l
<u>Ferric Chloride (Anhydrous)</u>								
10	7.45	1.34	8.10	1.32	8.45	1.29	9.05	1.24
20	7.40	0.35	7.85	0.34	8.10	0.33	8.85	0.31
30	7.40	0.17	8.10	0.20	8.50	0.21	9.0	0.25
40	7.55	0.11	8.10	0.15	8.50	0.18	8.95	0.21
50	7.65	0.10	8.0	0.12	8.45	0.15	9.0	0.19
60	7.55	0.06	8.10	0.085	8.45	0.096	8.95	0.14
<u>Aluminum Sulfate (Anhydrous)</u>								
10	7.50	1.86	7.95	1.73	8.45	1.66	9.0	1.39
20	7.45	1.48	8.0	1.39	8.50	1.48	9.0	1.24
30	7.55	0.96	8.0	0.88	8.40	0.85	9.0	0.75
40	7.40	0.74	8.0	0.70	8.55	0.64	9.05	0.60
45	7.40	0.47	8.0	0.49	8.50	0.51	9.0	0.55
50	7.50	0.104	8.0	0.17	8.50	0.25	9.0	0.51
60	7.45	0.04	8.0	0.08	8.45	0.13	9.10	0.33

Note: 1. All the samples were filtered with 0.45  $\mu$  membrane  
2. Solution pH was measured before flocculation

Table 3

Phosphorus Removal by 100 mg/l of Calcium  
Hydroxide and Different Doses of Ferric Chloride  
or Aluminum Sulfate From Ortho-phosphate Solution  
Initial Ortho-phosphate Concentration: 3.262 mg/l P

Chemical mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l
<u>Ferric Chloride (Anhydrous)</u>								
10	7.50	1.27	7.95	1.24	8.60	1.21	9.15	1.14
20	7.40	0.41	7.90	0.37	8.60	0.36	9.05	0.35
30	7.40	0.29	7.95	0.29	8.30	0.30	9.0	0.31
40	7.40	0.18	8.15	0.22	8.60	0.24	9.10	0.28
50	7.45	0.13	7.95	0.14	8.50	0.18	9.10	0.20
60	7.40	0.09	8.0	0.11	8.55	0.134	9.05	0.16
<u>Aluminum Sulfate (Anhydrous)</u>								
10	7.35	1.81	8.0	1.60	8.45	1.40	9.0	1.03
20	7.45	0.96	8.0	0.90	8.50	0.72	9.0	0.58
30	7.55	0.73	7.95	0.75	8.55	0.49	8.90	0.42
40	7.50	0.51	8.05	0.54	8.55	0.41	8.95	0.32
50	7.55	0.37	7.80	0.41	8.10	0.40	8.25	0.38
	8.55	0.33	8.80	0.30	9.0	0.28		
100	7.40	0.15	7.75	0.18	7.90	0.30	8.0	0.33
	8.15	0.28	8.30	0.25	8.60	0.19	9.0	0.17

Note: 1. All the sample were filtered with 0.45  $\mu$  membrane  
2. Solution pH was measured before flocculation

Table 4

Phosphorus Removal by 150 mg/l of Calcium  
Hydroxide and Different Doses of Ferric Chloride  
or Aluminum Sulfate From Ortho-phosphate Solution  
Initial Ortho-phosphate Concentration: 3.262 mg/l P

Chemical mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l	pH	Res. P mg/l
<u>Ferric Chloride (Anhydrous)</u>								
10	7.50	0.98	7.95	0.91	8.55	0.80	9.05	0.65
20	7.50	0.49	8.0	0.42	8.50	0.36	9.05	0.34
30	7.60	0.31	8.15	0.30	8.65	0.30	9.10	0.30
40	7.60	0.23	8.0	0.23	8.50	0.24	9.0	0.26
50	7.60	0.17	7.95	0.20	8.35	0.20	9.0	0.23
60	7.60	0.10	7.90	0.13	8.55	0.15	9.10	0.19
<u>Aluminum Sulfate (Anhydrous)</u>								
10	7.50	1.99	7.95	1.70	8.55	1.13	9.0	0.72
20	7.50	1.21	8.0	1.04	8.50	0.80	9.0	0.41
30	7.40	0.98	8.0	0.85	8.55	0.64	9.0	0.29
40	7.50	0.78	8.05	0.52	8.50	0.38	9.0	0.18
50	7.40	0.42	7.80	0.36	8.50	0.26	9.0	0.14
60	7.50	0.28	7.85	0.29	8.05	0.28	8.50	0.23
	9.0	0.12						

Note: 1. All the samples were filtered with 0.45  $\mu$  membrane  
2. Solution pH was measured before flocculation

Table 5

Phosphorus Removal by Calcium Hydroxide  
 From Ortho- and Pyro-phosphate Solution  
 Initial Phosphate Concentration: Ortho- 3.262 mg/l P  
 Pyro- 1.631 mg/l P

Ca(OH) <sub>2</sub> mg/l	pH	Residual filtered mg/l	Ortho-phosphate unfiltered mg/l	Residual filtered mg/l	Total Phosphate unfiltered mg/l
50	8.10	2.76	3.16	2.77	4.24
	8.45	2.61	2.76	2.41	3.75
	9.05	1.60	1.91	1.90	2.48
	9.45	1.29	1.35	1.50	2.12
100	8.0	2.28	2.84	2.48	3.27
	8.40	1.70	2.12	1.76	2.81
	9.0	0.93	1.58	1.11	2.10
	9.45	0.36	1.01	0.55	1.44
150	8.0	2.0	2.35	2.12	2.84
	8.50	1.32	1.79	1.34	2.38
	9.0	0.72	1.22	0.78	1.57
	9.55	0.23	0.74	0.25	0.91

Note: 1. 0.45  $\mu$  membrane was used in filtration.  
 2. Solution pH was measured before flocculation.



Table 6  
 Phosphorus Removal by 30 mg/l of Ferric  
 Chloride and Different Doses of Calcium  
 Hydroxide From Ortho- and Pyro-phosphate Solution  
 Initial Phosphate Concentration: Ortho- 3.262 mg/l P  
 Pyro- 1.631 mg/l P

Ca(OH) <sub>2</sub> mg/l	pH	Residual filtered mg/l	Ortho-phosphate unfiltered mg/l	Residual filtered mg/l	Total Phosphate unfiltered mg/l
50	8.0	0.64	1.47	0.69	2.15
	8.45	0.51	1.17	0.55	1.96
	9.0	0.39	0.91	0.42	1.47
	9.55	0.31	0.78	0.35	1.31
100	7.95	0.55	1.31	0.57	1.79
	8.50	0.42	1.01	0.48	1.63
	8.95	0.30	0.82	0.32	1.40
	9.50	0.21	0.72	0.24	1.04
150	8.0	0.47	1.14	0.51	1.70
	8.40	0.38	0.95	0.42	1.53
	9.0	0.25	0.78	0.29	1.31
	9.55	0.11	0.73	0.14	0.89

Note: 1. 0.45  $\mu$  membrane was used in filtration.  
 2. Solution pH was measured before flocculation.

Table 7

Phosphorus Removal by 30 mg/l of Aluminum  
Sulfate and Different Doses of Calcium  
Hydroxide From Ortho- and Pyro-phosphate Solution

Initial Phosphate Concentration: Ortho- 3.262 mg/l P  
1.631 mg/l P

Ca(OH) <sub>2</sub> mg/l	pH	Residual filtered mg/l	Ortho-phosphate unfiltered mg/l	Residual filtered mg/l	Total Phosphate unfiltered mg/l
50	7.95	1.37	1.66	1.47	3.59
	8.50	1.21	1.39	1.34	3.26
	9.0	1.04	1.27	1.27	3.03
	9.50	0.91	1.22	1.22	2.65
100	8.05	1.08	1.53	1.13	1.57
	8.50	0.83	1.27	0.88	1.31
	9.0	0.60	1.04	0.70	1.17
	9.50	0.35	0.91	0.44	1.12
150	7.95	0.95	1.01	1.01	1.32
	8.50	0.55	0.70	0.64	1.26
	9.05	0.22	0.47	0.25	0.95
	9.45	0.05	0.38	0.105	0.82

Note: 1. 0.45  $\mu$  membrane was used in filtration.

2. Solution pH was measured before flocculation.

Table 8

Phosphorus Removal by 1:1 Molar Ratio of Ferric Chloride to Ortho-phosphate and Different Doses of Calcium Hydroxide From Ortho-, Pyro- and Tripoly-phosphate Solution

Initial Phosphate Concentration: Ortho- 10 mg/l P

Pyro- 4 mg/l P

Tripoly- 6 mg/l P

Ca(OH) <sub>2</sub> mg/l	pH	Residual Ortho-phosphate filtered mg/l	Residual Ortho-phosphate unfiltered mg/l	Residual Total Phosphate filtered mg/l	Residual Total Phosphate unfiltered mg/l
50	7.90	3.95	4.10	6.10	6.80
	8.10	3.60	3.70	5.30	6.70
	8.60	3.05	3.40	4.70	6.70
	9.0	2.42	2.95	3.70	6.75
100	7.80	2.85	3.40	4.05	5.05
	8.05	1.95	2.10	2.60	3.40
	8.60	0.87	1.25	1.30	2.15
	9.0	0.58	0.77	0.68	1.35
150	7.65	2.60	3.10	3.10	4.30
	8.25	1.35	1.55	1.65	2.25
	8.65	0.61	0.88	0.97	1.55
	8.80	0.24	0.58	0.61	1.20

Note: 1. 0.45  $\mu$  membrane was used in filtration.

2. Supernatant pH was measured after sedimentation.

Table 9

Phosphorus Removal by 1:1 Molar Ratio of Aluminum  
Sulfate to Ortho-phosphate and Different Doses of Calcium  
Hydroxide From Ortho-, Pyro- and Tripoly-phosphate Solution

Initial Phosphate Concentration: Ortho- 10 mg/l P

Pyro- 4 mg/l P

Tripoly- 6 mg/l P

Ca(OH) <sub>2</sub> mg/l	pH	Residual filtered mg/l	Ortho-phosphate unfiltered mg/l	Residual filtered mg/l	Total Phosphate unfiltered mg/l
50	7.95	4.30	5.85	6.70	7.60
	8.65	3.55	4.70	5.30	6.0
	8.80	3.45	4.80	5.40	6.10
	8.90	3.0	4.60	4.30	5.90
100	7.90	2.85	3.10	3.70	4.90
	8.35	1.42	1.90	1.85	3.20
	8.80	0.52	1.25	0.88	2.60
	9.0	0.12	0.85	0.31	1.90
150	7.90	2.05	2.45	2.80	4.20
	8.25	0.85	1.25	1.35	2.50
	8.70	0.25	0.88	0.54	1.55
	8.85	0.05	0.70	0.19	1.25

Note: 1. 0.45  $\mu$  membrane was used in filtration.

2. Supernatant pH was measured after sedimentation.

Table 10  
Phosphorus Removal by a Mixed Column of  
80% Ottawa Sand and 20% Local Soil

Type of Phosphate	Concentration mg/l	Flow Rate gpm/ft <sup>2</sup> of surface area	Time From Start hr.	Residual Phosphate mg/l	% Removal
Ortho-phosphate	1.80	0.723	0.16	0.12	93.3
			1.0	1.22	32.2
			2.0	1.45	19.4
			4.0	1.60	11.1
			6.0	1.73	3.9
Pyro-phosphate	2.15	0.67	1.0	0.67	68.8
			3.0	0.95	55.8
			4.0	1.05	51.6
			5.0	1.17	45.6
			6.0	1.24	42.3
Tripoly-phosphate	2.0	0.723	7.0	1.24	42.3
			0.16	0.34	83.0
			1.0	0.95	52.5
			2.0	1.44	28.0
			4.0	1.48	26.0
			7.5	1.60	20.0
			10.0	1.73	13.5
			12.0	1.63	18.5

Note: Between 16 to 32 mesh of sand and soil were used.

Table 11

Phosphorus Removal by a Sand Column and a Mixed  
Column of 80% Sand and 20% Soil From Iron  
and Calcium Treated Supernatant Water

Initial Phosphate Concentration: Ortho- 10 mg/l P  
Pyro- 4 mg/l P  
Tripoly- 6 mg/l P

Chemical Dose:  $\text{Ca(OH)}_2$  150.0 mg/l  
 $\text{FeCl}_3$  52/4 mg/l (Fe/Ortho P = 1)

Supernatant pH: 9.5 Flow Rate: 0.56 gpm/ft<sup>2</sup> of surface area

Time From Start hr.	Pressure Drop inch of water		Type of Phosphate	Phosphate in Supernatant mg/l	Phosphate in Filtrate, mg/l	
	Sand Column	Mixed Column			Sand Column	Mixed Column
2	26	31	Ortho-	0.58	0.21	0.02
			Total	1.08	0.57	0.15
5	26	33	Ortho-	0.56	0.26	0.07
			Total	1.06	0.51	0.15
8	28	38	Ortho-	0.65	0.26	0.09
			Total	1.09	0.59	0.18
13	30	46	Ortho-	0.54	0.21	0.11
			Total	1.07	0.57	0.23
18	36	57	Ortho-	0.65	0.22	0.14
			Total	1.13	0.55	0.26
24	44	58*	Ortho-	0.57	0.26	0.18*
			Total	1.11	0.59	0.24*

\* The flow rate was reduced to 0.46 gpm/ft<sup>2</sup> of surface area.

Table 12

Phosphorus Removal by a Sand Column and a Mixed Column of 80% Sand and 20% Soil From Aluminum and Calcium Treated Supernatant Water

Initial Phosphate Concentration: Ortho- 10 mg/l P  
Pyro- 4 mg/l P  
Tripoly- 6 mg/l P

Chemical Dose:  $\text{Ca(OH)}_2$  150.0 mg/l  
 $\text{Al}_2(\text{SO}_4)_3$  55.2 mg/l (Al/Orth P = 1)

Supernatant pH: 9.5 Flow Rate: 0.56 gpm/ft<sup>2</sup> of surface area

Time From Start hr.	Pressure Drop inch of water Sand Column Mixed Column		Type of Phosphate	Phosphate in Supernatant mg/l	Phosphate in Filtrate, mg/l Sand Column Mixed Column	
2	24	37	Ortho-	0.98	0.31	0.03
			Total	1.59	0.51	0.15
5	26	43	Ortho-	1.05	0.41	0.06
			Total	1.83	0.58	0.15
8	28	51	Ortho-	0.97	0.39	0.09
			Total	1.65	0.62	0.14
13	31	56	Ortho-	0.96	0.39	0.12
			Total	1.63	0.59	0.22
18	41	63	Ortho-	0.95	0.42	0.16
			Total	1.74	0.71	0.33
24	47	63*	Ortho-	1.10	0.39	0.20*
			Total	1.80	0.70	0.31*

\* The flow rate was reduced to 0.46 gpm/ft<sup>2</sup> of surface area.

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