

PHOSPHATE REMOVAL FROM WASTEWATERS USING LANTHANUM PRECIPITATION



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PHOSPHATE REMOVAL FROM WASTEWATERS
USING LANTHANUM PRECIPITATION

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ABSTRACT

A parametric study was made of the use of lanthanum salts for the removal of phosphates from pure aqueous solutions of orthophosphate, pyrophosphate, and tripolyphosphate, and effluent from an activated sludge wastewater treatment plant, and the results were compared with the results of similar tests using Al(III).

The reactions of orthophosphate with both La(III) and Al(III), which result in precipitate formation and phosphate removal, were found to be complete in less than 1 sec.

Phosphate removal results indicated that La(III) is far superior to Al(III) for the precipitation of phosphates, especially condensed phosphates, in that it has a broader effective pH range and yields a lower residual phosphate concentration. For example, at a 2:1 cation-to-phosphate equivalence ratio, with phosphates at about 0.001 N , La(III) gave a residual phosphate concentration of less than 0.1 mg/l P for both ortho- and condensed phosphates over a pH range of 6 to 9. With Al(III) this same residual phosphate concentration was obtained only with orthophosphate, and only at a pH of 6.

Within the pH range for optimal phosphate removal, the reaction of La(III) with both ortho- and polyphosphates resulted in the formation of large, settleable flocs. Immediately outside this pH range, fine turbidity developed which did not settle very well. At higher pH levels outside this pH region, some residual turbidity was observed in almost all cases. No turbidity or precipitate formation was observed at very low pH levels with either ortho- or polyphosphates.

In studies at constant pH, the removal of orthophosphate was found to be directly proportional to the concentration of added lanthanum. Essentially complete removal of phosphate was observed at a $\text{La(III)}/\text{PO}_4^{-3}$ molar ratio of slightly less than 0.9. This direct stoichiometric relationship strongly suggests that phosphate removal occurs through a purely chemical reaction between the lanthanum and the orthophosphate and not through adsorption (physical or chemical) of phosphate on a precipitating metal hydroxide.

In tests with actual wastewater (secondary effluent), as with pure solutions, a lower residual phosphate level was produced over a wider pH range with La(III)

as compared with Al(III). At a 2:1 cation-to-phosphate equivalence ratio, a residual phosphate concentration of less than 0.1 mg/l P was obtained with La(III) over a pH range of 4.5 to 8.5; Al(III) gave this residual concentration only over a pH range of 5 to 6.5, and left 0.3 mg/l P at a pH of 7. Thus lanthanum is effective for the removal of phosphates from domestic wastewater (pH ~7 to 8) without pH adjustment. To reach the optimum precipitation pH of 6 with aluminum, large quantities of acid, or a considerable excess of aluminum salt, must be added to the wastewater to overcome its natural buffer capacity.

Based on the above data, further studies of the use of lanthanum salts for phosphate removal from wastewater, including pilot plant testing, appear warranted.

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INTRODUCTION

Phosphorus and nitrogen compounds, which are present in domestic wastewater in appreciable amounts, are important nutrients. The discharge of large quantities of these nutrients into natural waters promotes the growth of algae and results in eutrophication of lakes and similar deterioration of water quality in receiving streams. In recent years, the rapid population growth and the astonishing economic and industrial expansion experienced in many areas of the world have placed a growing burden on the available water resources. This has generated an increasing need for abatement of water pollution, and reclamation and reuse of wastewaters. Accordingly, considerable effort has been directed toward the development of economical methods to achieve a high degree of wastewater treatment and to effect near complete removal of undesirable nutrients.

Although both nitrogen and phosphorus compounds are essential to algae growth, phosphorus is generally considered to be a more critical nutrient because, unlike nitrogen, it can enter a receiving body of water only by influx of phosphorus containing compounds. In contrast, certain species of algae, particularly the nuisance blue-greens, have been reported to be capable of satisfying their nitrogen demand by direct utilization of the atmospheric nitrogen.⁽¹⁾ Thus, control of eutrophication may best be achieved through control of phosphorus. For this reason, the major portion of the research effort on the elimination of nutrients from wastewaters has been directed toward the development of economical methods for the removal of phosphates.

Phosphorus may be present in the wastewater in the form of organic phosphorus, inorganic condensed phosphates, and orthophosphates. Most of the organically-bound phosphorus compounds in the wastewater are present as particulate organic matter and as bacterial cells. Very little is known about the dissolved organic phosphorus compounds produced by bacterial metabolism and cell lysis. Inorganic condensed phosphates such as tripolyphosphate and pyrophosphate originate mainly in household detergents. Orthophosphate is an end-product of microbial degradation of phosphorus-containing organic compounds; it is also excreted in the urine and is the product of enzymatic hydrolysis of condensed phosphates. Orthophosphate is the phosphorus form most readily available for biological utilization. The concentrations of the various forms of phosphorus in a domestic wastewater are subject to wide

hourly and daily fluctuations. Wastewaters received at or discharged from different plants also contain varying concentrations of phosphates depending on the type of community served and the nature of the biological treatment employed. Finstein and Hunter⁽²⁾ studied phosphate concentration in three activated sludge and three trickling filter plants and found that in the influent to the biological treatment units inorganic condensed phosphates constituted 15 to 75% of the total phosphorus, the value varying on a daily cycle, and that about 50% of the condensed phosphates were hydrolyzed to orthophosphate on their passage through the treatment plants.

To date, the most common method of secondary wastewater treatment is biological oxidation. The microorganisms present in the wastewater degrade the complex organic molecules into simpler products, thereby acquiring energy and material for their growth and the synthesis of new cells. As the supply of the available food diminishes, the starving bacteria agglomerate into large flocs which are removed by settling. Although conventional biological treatment processes can result in a substantial reduction of the carbonaceous organic matter, due to the unique nutritional requirements of sewage bacteria, only 20 to 40% of the phosphorus compounds initially present in the raw wastewater is converted into removable cell material. Accordingly, the effluents from most conventional biological treatment units still contain substantial quantities of phosphates (about 5 to 30 mg/l $P^{(2)}$) which have to be essentially completely removed if serious deterioration of water quality in the receiving stream is to be avoided. Phosphorus concentrations over 0.01 mg/l in natural waters have been shown to lead to the development of massive algae growth.⁽³⁾

Of the several methods available for the removal of phosphates, chemical precipitation (often called coagulation) using aluminum, ferric, and calcium salts has received the widest attention and is considered the most promising of these.⁽⁴⁾ Aluminum and ferric salts both hydrolyze in solution to an appreciable extent; their effectiveness in precipitating phosphate depends on pH. The pH of maximum phosphate removal is close to 5 for aluminum and is near 4 for ferric salts.⁽⁵⁾ The pH of most wastewaters, however, lies in the range of 7 to 8. To reach the optimum precipitation pH with aluminum and ferric salts, large quantities of acid must be added to the wastewater to overcome its natural buffer capacity. In practice, the requirement for addition of acid is often partially eliminated by the addition of excess quantities of aluminum and ferric salts. Even

then, the extent of phosphate removal has been reported to be unsatisfactory. For example, Lea et al⁽⁶⁾ reported that in a pilot plant evaluation of phosphate removal using alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, phosphate removals, varying from 77 to 89.3%, were achieved with an alum dose of 200 mg/l when the concentration of soluble phosphate in the influent was in the range of 4 to 6 mg/l P. An appreciable amount of the precipitated phosphate did not settle out but was lost in the effluent. The phosphate removal efficiency could be raised to 99% by filtration of the effluent. However, considering that such a large excess of alum was used (aluminum to phosphate molar ratios in the range of 3:1 to 5:1), the effective molar capacity of aluminum to remove phosphate is very low.

The effectiveness of aluminum and ferric salts in precipitating condensed inorganic phosphates has been the subject of some controversy. Sawyer,⁽¹⁾ for example, reported that both aluminum and ferric salts are highly effective in removing all forms of phosphate. According to Stumm,⁽⁷⁾ however, tripolyphosphates are not removed effectively by coagulation with either Al(III) or Fe(III) due to the formation of soluble complexes such as $\text{MP}_3\text{O}_{10}^{-2}$.

In the case of aluminum, disagreement has been expressed by some investigators on the effect of contact time on the efficiency of phosphate precipitation. Stumm,⁽⁷⁾ for example, reported that under proper pH conditions and at low cation-to-phosphate ratios, the cation-orthophosphate reaction occurring is $\text{M}^{+3} + \text{H}_2\text{PO}_4^- = \text{MPO}_4 + 2\text{H}^+$, provided that sufficient time is allowed for the precipitation to occur. In the actual practice, however, even under optimum pH conditions, far more than equivalent quantities of metal salts are required for complete precipitation of phosphates. Also, Lea et al⁽⁶⁾ reported that in the treatment of sewage plant effluent with alum, mixing and flocculation time in excess of 12 minutes resulted in a decrease in soluble phosphate removal.

Calcium salts are effective in precipitating phosphate at very high pH levels. The calcium is generally added to the wastewater in the form of unslaked lime (CaO) which serves the additional purpose of raising the pH. Because of the large buffer capacity of most wastewaters, however, considerable amounts of lime are required to raise the pH high enough to effect good phosphate removal. Residual phosphate concentrations of less than 0.01 mg/l P have been reported with lime dosages exceeding 500 mg/l CaO.⁽⁸⁾ Recarbonation of the wastewater

following lime treatment is also necessary if the discharge of a highly alkaline effluent is to be avoided.

Because of the special pH requirements and the low efficiencies of aluminum, ferric, and calcium salts in precipitating phosphates, there has been considerable interest in developing better methods for phosphate removal. In some preliminary work at Atomics International, the salts of lanthanum, the most abundant of the trivalent rare earth cations, were shown to be effective in precipitating orthophosphate from solution. (It should be noted that there is an abundant supply of the rare earths in nature so that application of lanthanum to the treatment of domestic wastewater on a wide scale will not be limited by any shortage.⁽⁹⁾)

Based on these very promising results, the present investigation was undertaken. This investigation had as its principal objectives the carrying out of a parametric study of phosphate precipitation with lanthanum and the comparison of the lanthanum precipitation results with the data obtained using aluminum. Specifically, an evaluation was made of the effects of pH and reagent concentration on phosphate removal, the rate of phosphate precipitation, and the nature and characteristics of the precipitates. Although effluent from a biological wastewater treatment plant was used in some of the experiments, most of the precipitation studies were made on pure solutions of ortho-, pyro-, and tripolyphosphates.

EXPERIMENTAL

This section describes the materials, apparatus, and procedures used generally during the course of the investigation. Special methods and modifications are described with the results where appropriate.

Materials

Reagent grade sodium monohydrogen (ortho-) phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, and aluminum nitrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, and lanthanum nitrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ of 99.9% purity, obtained from Molycorp (Molybdenum Corp. of America), were used to prepare pure solutions. All La(III) and Al(III) solutions were prepared fresh daily. Adjustment of pH was made using reagent grade HCl or NaOH. All other reagents used were the

purest grade available. Double distilled water was used to prepare reagent solutions.

The orthophosphate solution used in most experiments contained 12 mg/l P Na_2HPO_4 (11.8×10^{-4} equivalents/l PO_4^{-3} or 3.86×10^{-4} M). This concentration was selected as representative of that to be encountered in a typical secondary effluent. An 18 mg/l P solution of tetrasodium pyrophosphate and 21.6 mg/l P solution of sodium tripolyphosphate, each containing the same number of equivalents per liter of the anion as the orthophosphate solution, were used in the experiments with condensed phosphates.

The wastewater (secondary effluent) used in these studies was obtained from the Tapia Park Treatment Plant of the Las Virgenes Municipal Water District in Calabasas, California. This treatment plant is a small (~2 mgd) activated sludge plant which serves a primarily residential community. It employs an aerobic sludge digestion process with the supernatant liquor returned to the head of treatment plant. The small amount of large bacterial flocs which were present in the effluent was removed by prior filtration through coarse filter paper.

The following is a partial analysis of the filtered effluent used in the phosphate precipitation experiments with La(III) and Al(III):

pH	7.8
Temperature (°C)	17.5
Conductivity (at 17.5°C)(mmhos/cm)	2.17
Turbidity (JTU)	0.73
Orthophosphate (mg/l P)	7.75
Total phosphate (mg/l P)	7.75
Polyphosphate (by difference)(mg/l)	0

Apparatus

Commercial Items

All "jar test" precipitation experiments were conducted using Phipps and Bird six-place stirrers (Phipps and Bird, Inc., Richmond, Va.). The metallic paddles supplied with the instruments were replaced with clear plastic paddles to avoid possible metallic contamination of test solutions. Radiometer PHM 26

and PHM 28 pH meters (Radiometer Co., Copenhagen) and a Beckman Model 96 Zeromatic pH meter (Beckman Instrument Co., Fullerton, Calif.) were used for pH measurements. All conductivity determinations were made with Radiometer Model CDM2e conductivity meters (Radiometer Co., Copenhagen). The conductivity cell was modified by drilling numerous holes in the glass envelope to permit more rapid passage of the solution into the space between the electrode surfaces. A Radiometer automatic titration control unit, type TTT 11 (Radiometer Co., Copenhagen) was used in conjunction with the Radiometer pH meters for the constant pH precipitation experiments. A Moseley Model 7100 B two-pen strip chart recorder (Hewlett-Packard Co., Pasadena, Calif.) was used for recording of pH and conductivity in the reaction rate studies. Turbidity measurements were made with a Hach Laboratory Turbidimeter Model 2100 (Hach Chemical Co., Ames, Iowa). Most of the colorimetric analyses were made with a Bausch and Lomb Spectronic 20 Colorimeter/Spectrophotometer (Bausch and Lomb Co., Rochester, N. Y.). Some colorimetric analyses were obtained using a Cary Model 14 recording spectrophotometer (Cary Instruments, Monrovia, Calif.) with a 10 cm light path. A Beckman Model DU Spectrophotometer-Flame Photometer (Beckman Instrument Co., Fullerton, Calif.) was used for the flame-photometric determination of lanthanum. All x-ray diffraction analyses were made on a Norelco 50 kv Diffractometer (Norelco, New York, N. Y.). Weights of precipitates in the study of weight loss on drying and heating were determined using a Mettler M5 Micro Analytical Balance (Mettler Instrument Corp., Hightstown, N. J.) of ± 0.001 mg stated precision.

Kinetics Apparatus

To obtain reliable data on the rates of the phosphate precipitation reactions, a special reaction kinetics apparatus, shown schematically in Figure 1, was designed and constructed. In this apparatus provision is made for monitoring pH and residual phosphate and cation concentrations under steady-state conditions. The metal salt and phosphate solutions flow by gravity from separate reservoirs into a 50 ml reaction flask where they are rapidly mixed with a magnetic stirrer. The mixture then travels through a long 16 mm OD tube assembled from 4-ft Pyrex sections connected by short pieces of rubber hose, with openings for sampling or for insertion of a pH probe electrode. Samples of the flowing solution mixture are withdrawn under vacuum through 450 m μ membrane

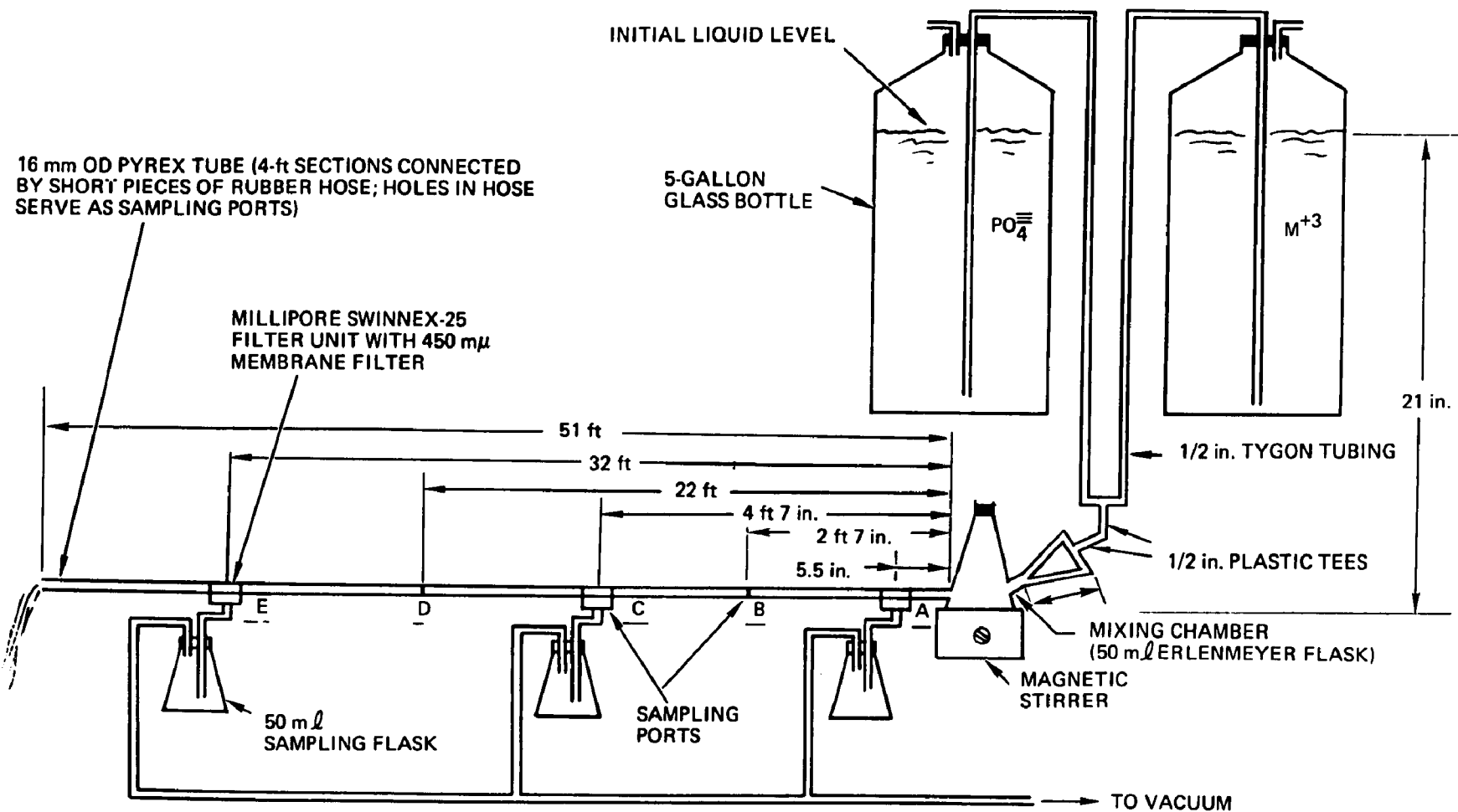


Figure 1. Schematic Diagram of the Reaction Kinetics Apparatus
(Not Drawn to Scale)

filters installed in Millipore Swinnex-25 filter units (Millipore Corp., Bedford, Mass.), modified and attached to small flow-through cells. These cells are placed in the flow line so that the flowing liquid passes directly over the entire filtration area (see Figures 2 and 3). The filtrates collected in this manner represent the liquid phase prevailing at the sampling ports. The time of solution travel to each port is thus the true reaction time prior to filtration. After collection, the filtrates are analyzed for residual phosphate and metal ion content.

It was originally intended that the conductivity of the solution mixture also be monitored at several points in the flow line. However, this did not prove to be feasible because the available conductivity cell caused an excessive reduction in flow rate.

The mixing apparatus was shown to be effective by reacting a dilute solution of sodium hydroxide, with phenolphthalein indicator added, with a dilute HCl solution. No color was observed in the fluid leaving the mixing flask. Indeed, little, if any, color was observed beyond the point where the two streams entered the flask.

In the initial reaction rate experiments an average total solution flow of 65 ml/sec was used. At this flow rate, the approximate total travel time from the start of the mixing to the observation ports, A, B, C, D, and E (see Figure 1) are 1.3, 2.7, 4.3, 15.6, and 22.2 sec, respectively. In later experiments the time of solution travel to the first port was reduced to less than 1 sec by further elevating the solution reservoirs and by shortening the flow line. A photograph of the apparatus in this arrangement is presented in Figure 3.

Analytical Procedures

The stannous chloride method described in Standard Methods⁽¹⁰⁾ was used for all orthophosphate determinations. With this method, the 2 cm light path of the Bausch and Lomb Spectronic 20 permitted phosphate concentrations as low as 0.01 mg/l P to be detected. Using the 10 cm light path of the Cary Model 14, phosphate concentrations as low as 0.002 mg/l P could be determined. The polyphosphates were hydrolyzed to orthophosphate by boiling with acid⁽¹⁰⁾ and determined as orthophosphate. The benzene-isobutanol extraction modification of the stannous chloride method as recommended in the Standard Methods⁽¹⁰⁾ for obtaining increased sensitivity and avoidance of certain interferences was used in

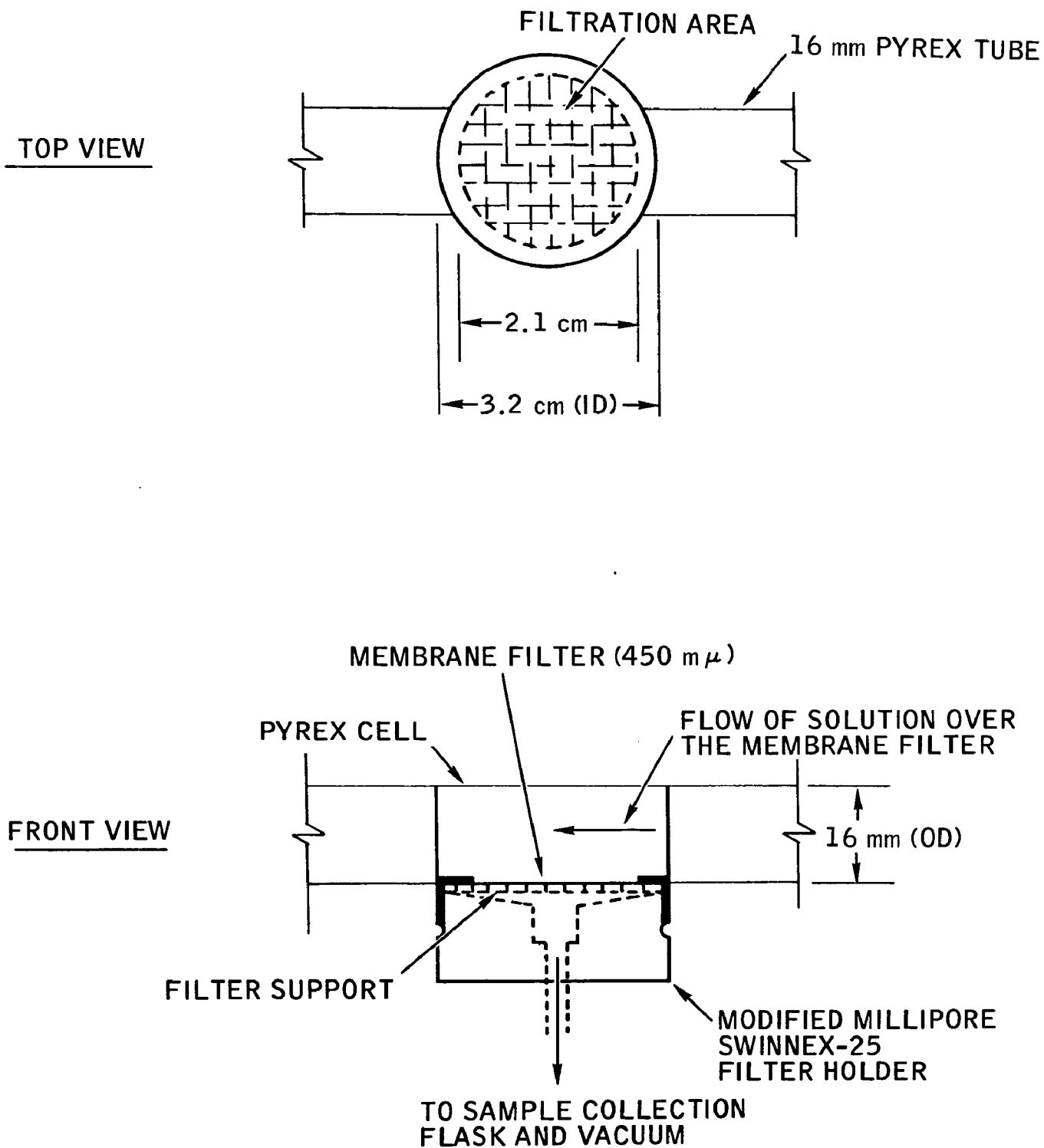


Figure 2. Schematic Diagram of the Flow-Through Sampling Port
Used in the Reaction Kinetics Apparatus

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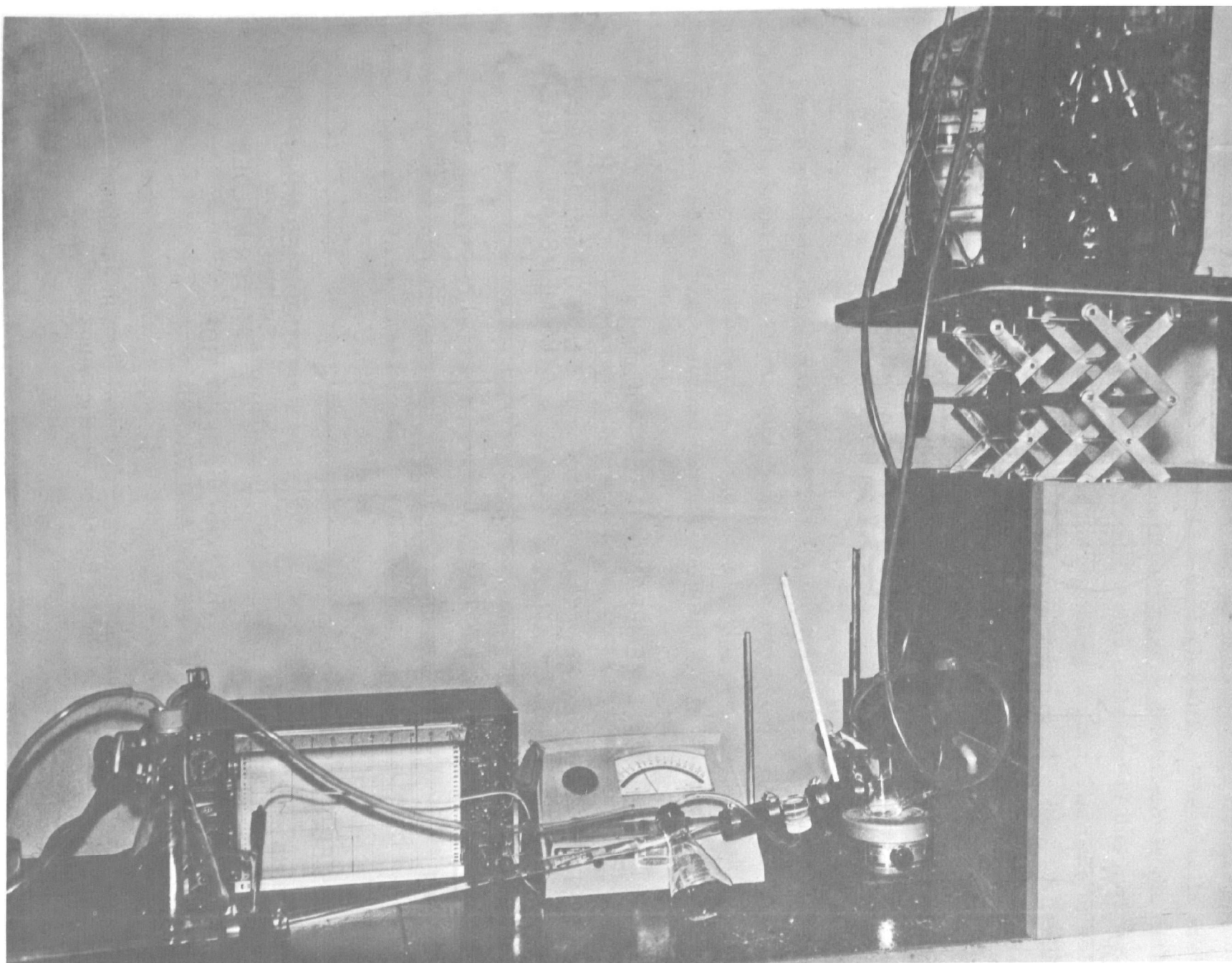


Figure 3. Reaction Kinetics Apparatus, Modified for Rapid Flow

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all orthophosphate determinations involving wastewater. In the experiments with pure phosphate solutions, the lanthanum analyses were made by an emission spectrographic technique. The method, however, was found to lack the desired sensitivity and precision and the values reported may be somewhat different from the actual concentrations. Of the several sensitive colorimetric and fluorometric methods available for the analysis of lanthanum, none was found to be free from interference from phosphate ion. In one phosphate precipitation experiment with wastewater where the residual phosphate concentration was less than 0.01 mg/l P an extraction-flame photometric method⁽¹¹⁾ was used to determine the residual lanthanum concentration. The method was found to be sensitive to lanthanum concentrations as low as 0.5 mg/l La. No interference was encountered from other residual ionic and nonionic species in the wastewater since an identical calibration curve was obtained when the wastewater (phosphate content less than 0.01 mg/l P) was substituted for distilled water in the preparation of the lanthanum standards.

Test Procedures

Jar Test Experiments

Many of the studies were carried out in batch type ("jar test") experiments. The usual procedure in these tests was as follows. Five hundred ml of the test phosphate solution was placed in a 1 l beaker. While stirring at 90 rpm, 5 ml of a lanthanum or aluminum nitrate solution of appropriate concentration was added to the beaker to establish cation-to-phosphate equivalence ratios of 2:1, 1:1, or 0.5:1. After 2 min of rapid mixing at 90 rpm, the stirring rate was slowed down to 20 rpm and the mixing was continued at this rate for 10 min. Following 20 min of quiescent settling the samples were filtered through Whatman No. 42 filter paper and the filtrates analyzed. Prior to filtration, a portion of the sample supernatant was removed by decanting and its turbidity was determined. All precipitation experiments were conducted at ambient temperature ($25 \pm 2^\circ\text{C}$).

In experiments with condensed phosphates and secondary sewage effluent, and in some experiments with orthophosphate, pH adjustments were made by prior addition of NaOH or HCl to the phosphate test solution. In most orthophosphate precipitation experiments, a Radiometer automatic titrator was used

to maintain desired reaction pH through automatic addition of NaOH while the lanthanum or aluminum solution (1-10 ml) was added slowly from a separate burette. In phosphate removal studies on secondary effluent where the desired final pH was in excess of 8, the addition of the NaOH to the wastewater prior to addition of lanthanum was found to result in precipitate formation (possibly calcium carbonate and/or calcium phosphate). In performing these phosphate removal experiment, therefore, the base and the lanthanum were added to the sample concurrently.

Experiments with the Reaction Kinetics Apparatus

The phosphate solutions used in reaction rate studies in the kinetics apparatus, described above, were prepared to contain 24 mg/l P Na_2HPO_4 (7.72×10^{-4} M). Upon mixing with the metal salt solutions at nearly equal flow rate, a final phosphate concentration of about 12 mg/l P (3.86×10^{-4} M) resulted. The aluminum and lanthanum salt solutions were prepared fresh in concentrated forms and were diluted to the necessary volume of 18 l immediately prior to start of each experiment. All kinetics experiments were completed within 10 min of the preparation of the dilute metal solution. The final solution pH in each experiment was maintained within the range for optimum phosphate precipitation and good floc formation (6 to 8 for La(III) and 5 to 7 for Al(III)) by prior addition of NaOH to the phosphate solution.

Samples of mixture leaving the kinetics apparatus were collected and flocculated by gentle mixing (20 rpm), settled, and then the supernatants were filtered through 450 m μ membrane filters. These filtrates and those obtained at the sampling ports were analyzed for residual cation and phosphate content.

Thermogravimetric Experiments

To investigate the nature of the precipitates formed in phosphate removal using lanthanum and aluminum salts, orthophosphate was precipitated from solutions of 12 mg/l P Na_2HPO_4 (3.86×10^{-4} M) using a cation-to-orthophosphate molar ratio of 1:1. The precipitation experiments were conducted at a constant pH of 6.0 for aluminum and 7.0 for lanthanum using a Radiometer automatic titrator. Following flocculation and settling, the supernatant was decanted and the precipitate slurry was centrifuged and washed into a preweighed Gooch crucible containing a glass fiber filter paper (No. 934-AH, Hurlbut Paper Co.). In

the experiment with aluminum, the precipitates from 3-2 liter samples were combined and placed in one Gooch crucible; the lanthanum precipitation experiments were run in triplicate. The fresh precipitates were dried in a desiccator at room temperature and the weight loss with time was determined. The samples were then heated at 104°C for three 2-hr periods. Following each heating, the crucibles were cooled in a desiccator for about 2 hr, weighed, stored in the desiccator for an additional 24 hr and weighed again. After a portion of the dried precipitate was removed for x-ray analysis, the precipitate was weighed and ignited at 600°C for two 2-hr periods. X-ray diffraction analyses were made on all fresh, dried, and ignited precipitates.

RESULTS AND DISCUSSION

The primary objective of the present program was the evaluation of the effectiveness of lanthanum salts for the removal of phosphates by precipitation. As a supplementary objective, lanthanum results were compared with data from similar tests using aluminum. An investigation of the rates of phosphate precipitation with lanthanum and aluminum salts, and studies aimed at the characterization of the precipitates formed were also done in the present study. The results obtained and discussion of them follow.

Lanthanum Precipitation of Orthophosphate

A major portion of this program was devoted to determining the effect of pH and reactant concentration on the precipitation of orthophosphate with lanthanum salts. These experiments were performed at ambient temperature ($\sim 25^{\circ}\text{C}$). The data obtained are presented in Figures 4, 5, and 6.

Figure 4 shows that, at a 0.5:1 lanthanum-to-orthophosphate molar ratio, the residual phosphate concentration was between 4.8 and 6.0 mg/l P in the pH range from 4 to 9, with the minimum value obtained at a pH of 5.0. The removal of phosphate in this pH range was accompanied by near complete precipitation of lanthanum. No appreciable removal of phosphate or lanthanum was observed at pH 2, 10, and 11. Lanthanum was also quantitatively precipitated at a pH of 12, accompanied by a 25% removal of phosphate.

As shown in Figure 5, at a 1:1 lanthanum-to-phosphate ratio, the phosphate removal was greatest within the pH range from 5 to 9. The concentration of

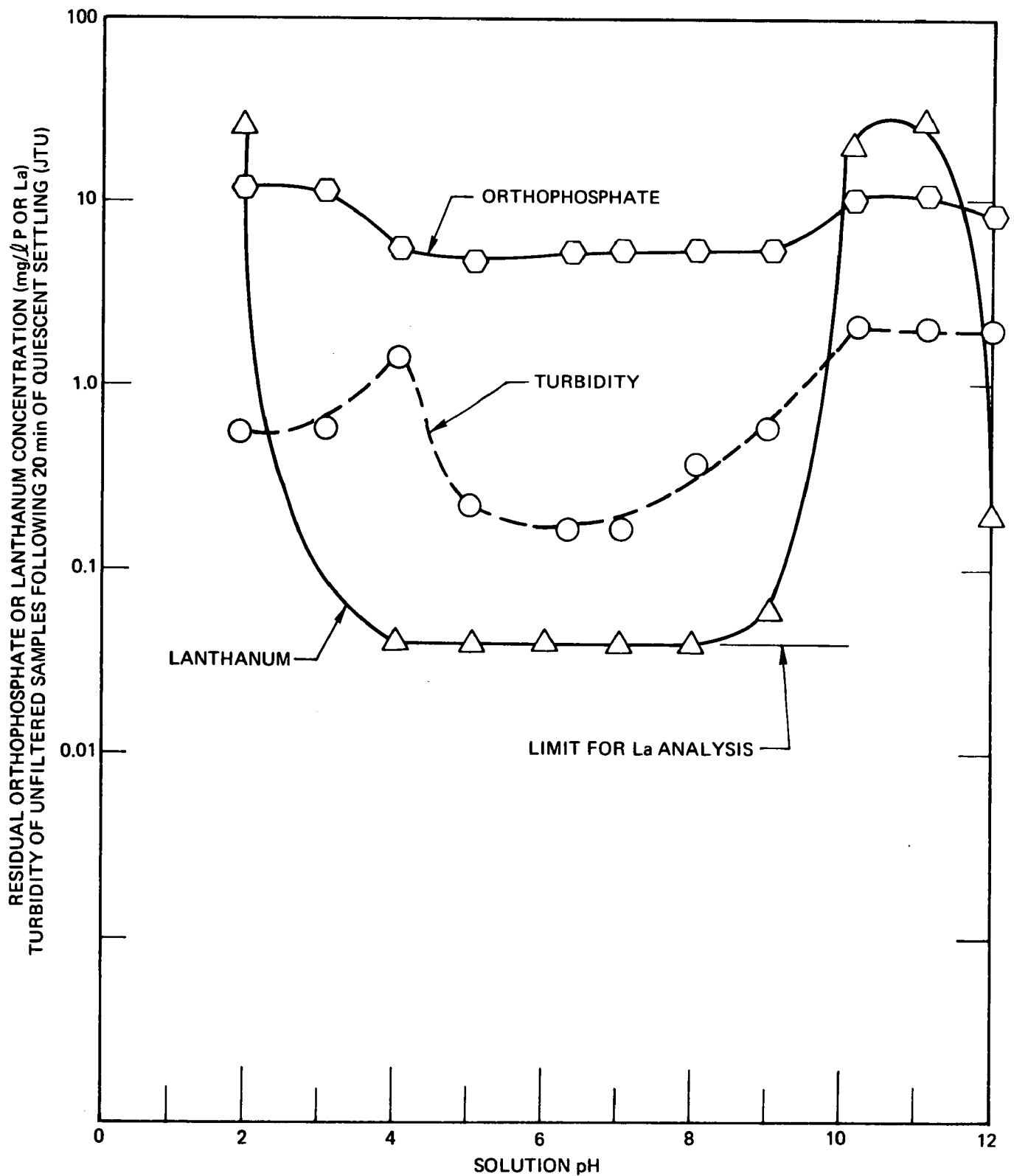


Figure 4. Precipitation of Orthophosphate with Lanthanum at a 0.5:1 Lanthanum-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

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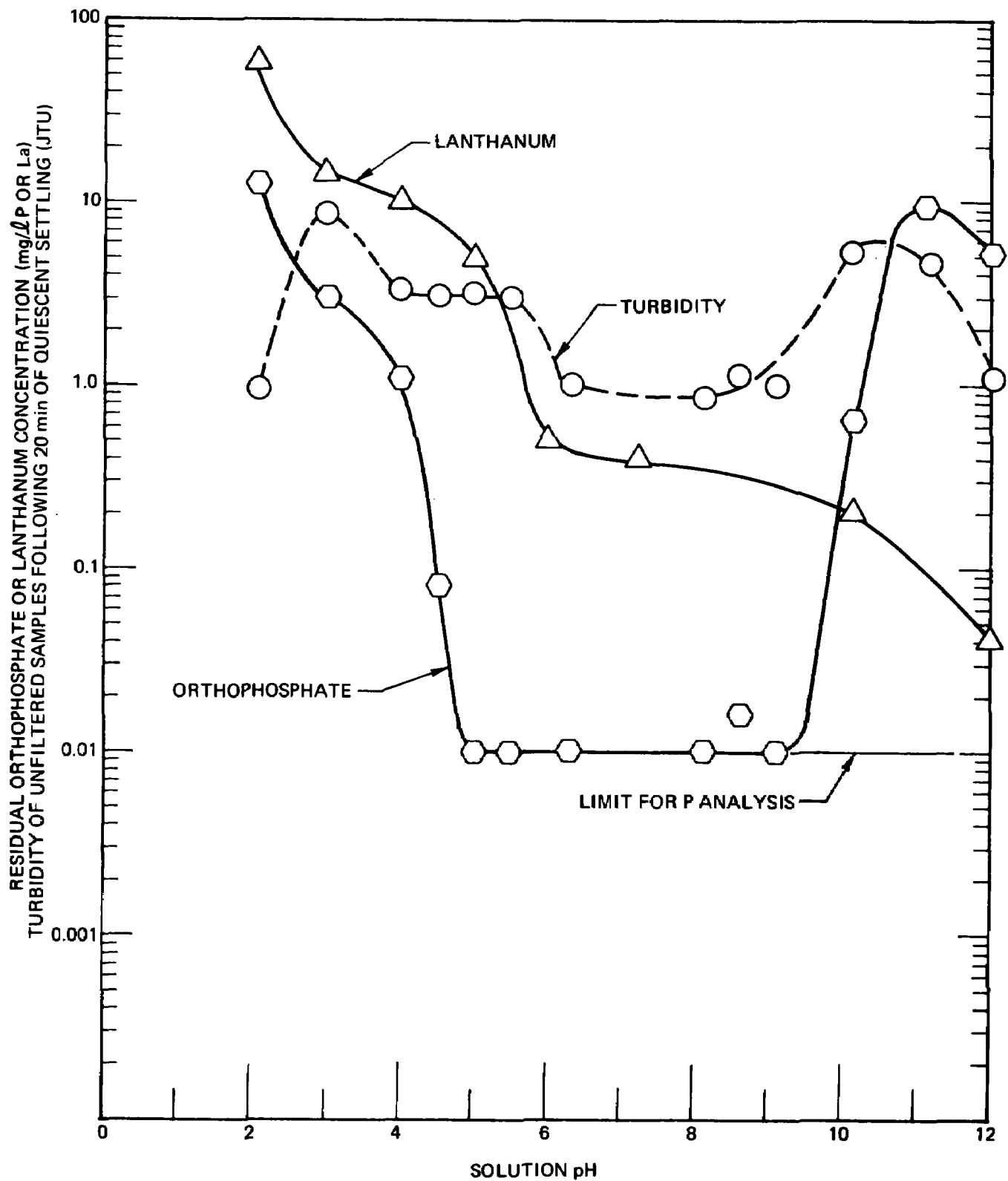


Figure 5. Precipitation of Orthophosphate with Lanthanum at a 1:1 Lanthanum-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

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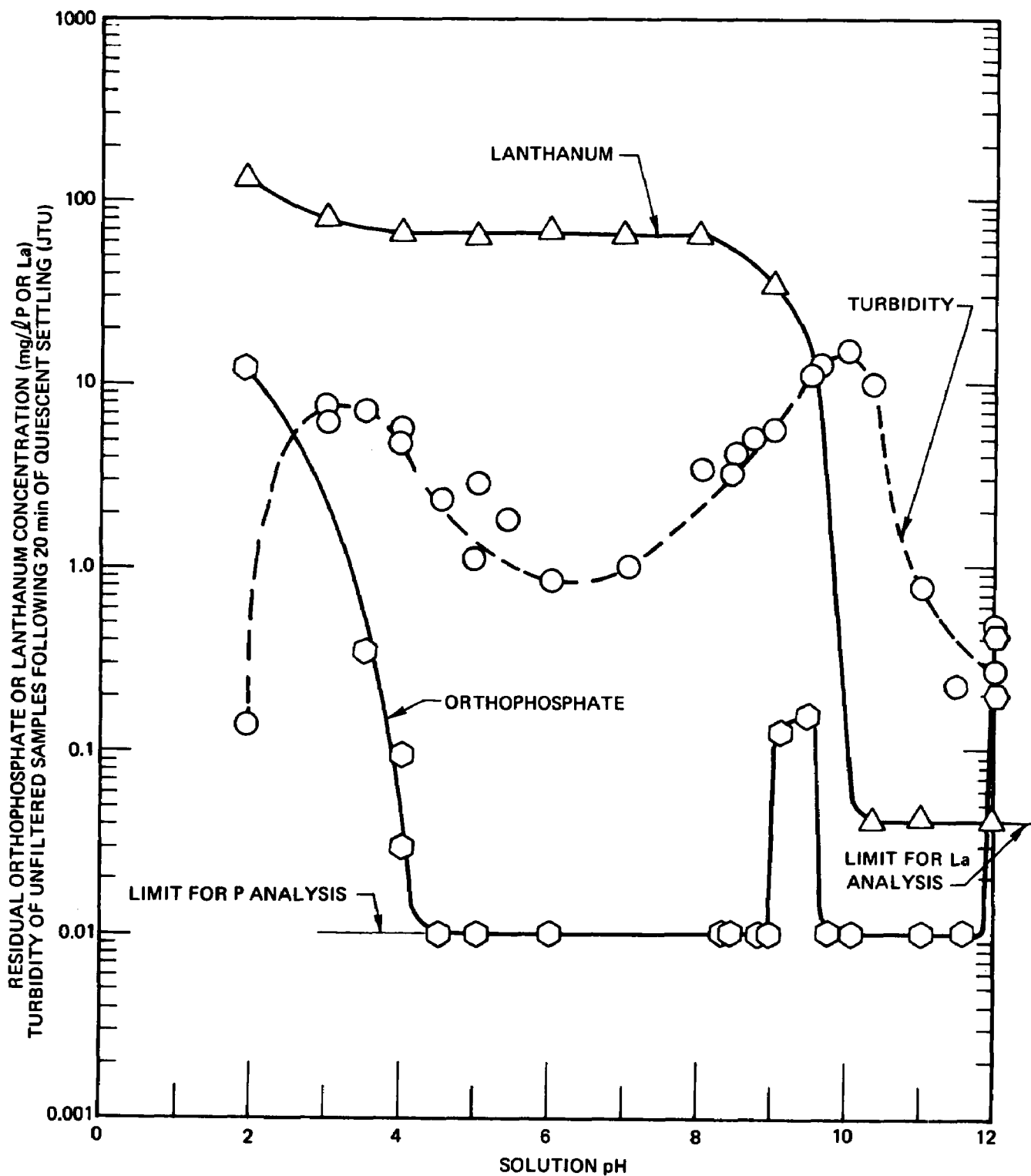


Figure 6. Precipitation of Orthophosphate with Lanthanum at a 2:1 Lanthanum-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

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residual phosphate within this region is given as 0.01 mg/l P. This is the limit of sensitivity and precision of the method and instrument used for phosphate determination. Within the pH range of greatest phosphate removal and also at lower pH levels, the removal of lanthanum closely followed that of phosphate roughly on the basis of a 1:1 reaction stoichiometry. At a pH of 12, the precipitation of lanthanum was accompanied by a greater reduction in phosphate concentration than that observed at a pH of 11.

At a 2:1 lanthanum-to-phosphate ratio (Figure 6) two pH regions of good phosphate removal may be noted, one extending from a pH of about 4 to a pH of about 9, and another in the pH range from 9.7 to 11.5. Near complete precipitation of phosphate was obtained within both these regions. The removal of phosphate at high pH levels, noted here and above at a 1:1 molar ratio, may be due to adsorption of phosphate on precipitating lanthanum hydroxide and/or may result from the formation of a lanthanum-hydroxy-phosphate precipitate.

The turbidity data obtained in these orthophosphate precipitation experiments are also plotted in Figures 4 to 6. The close correlation between phosphate removal and the formation and settling of the precipitate is apparent. At low pH values where no turbidity develops, no removal of phosphate is observed. At higher pH levels in the pH range for optimum phosphate removal, the lanthanum-phosphate reaction results in the formation of precipitates which agglomerate into large readily settleable flocs.

Figure 7 shows the results obtained when phosphate precipitation with lanthanum was carried out at a constant pH of 7.0 using La(III)/PO_4^{-3} molar ratios ranging from 0.1:1 to 1.0:1. Results of similar experiments with aluminum are also shown; these are discussed below where La(III) and Al(III) results are compared. The lanthanum data in this figure indicate that complete removal of phosphate can be achieved at La(III)/PO_4^{-3} molar ratios as low as 0.9. In the 0.1-0.9 molar ratio range, the removal of phosphate is directly proportional to the amount of added lanthanum, and is about 14% higher than that which would be expected from a 1:1 lanthanum-to-phosphate reaction stoichiometry. This suggests that the mono- and dihydrogen orthophosphate ions in addition to the trivalent orthophosphate ion are involved in precipitate formation. The linear relationship between phosphate removal and amount of added lanthanum strongly suggests that a chemical reaction occurs between these species, and physical processes such as adsorption are little, if at all, involved in the removal.

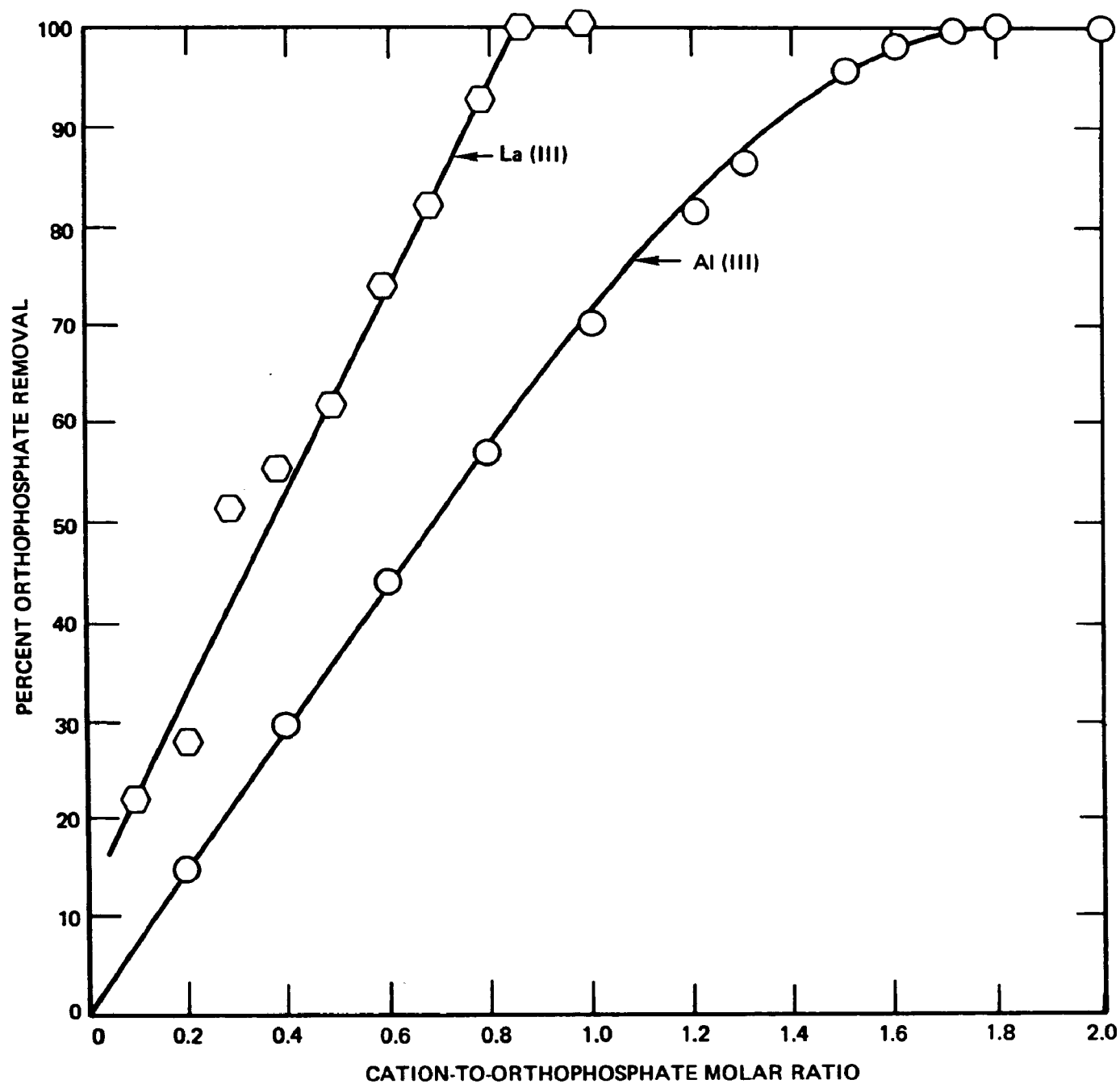


Figure 7. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Orthophosphate; La (III) at pH = 7.0, Al (III) at pH = 6.0 (Initial Orthophosphate Concentration, 12 mg/l P)

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In these studies of the lanthanum-orthophosphate reaction and in the polyphosphate precipitation experiments (to be described later) no quantitative assessment was made of the nature and the extent of colloidal surface charges and their role in agglomeration and dispersion of the precipitates. In qualitative terms, it was found that the changes in pH can result in a dispersion of the phosphate precipitate. The dispersion at higher pH levels can probably be explained in terms of a net negative surface charge on the colloid particles arising from increased dissociation of the surface phosphate groups of the precipitates and/or adsorption of phosphate and hydroxide ions from solution onto the particle surfaces. The dispersion of the precipitates at low pH may be attributed to the adsorption of excess cations onto the surface of the precipitates resulting in a net positive surface charge.

Effect of Sulfate on Lanthanum Precipitation of Orthophosphate

The lanthanum-orthophosphate reaction data, presented in Figures 4-7, were obtained using pure phosphate solutions. Before the effectiveness of lanthanum for the removal of phosphate from actual wastewaters was evaluated, the effects of sulfate and calcium, two common wastewater constituents, on the precipitation of phosphate were investigated. These ions with their divalent charge might be expected to affect the results significantly. The 12 mg/l P Na_2HPO_4 phosphate solution was made 0.0025 M in sodium sulfate (240 mg/l SO_4^{-2}) and the experiments were conducted at ambient temperature.

Figure 8 contains data on the precipitation of orthophosphate in the presence of sulfate using a 1:1 lanthanum-to-phosphate molar ratio. For the purpose of comparison, the phosphate precipitation data in the absence of sulfate (data on Figure 5) are also reproduced in Figure 8. These data indicate that the overall effect of sulfate on the phosphate precipitation curve was a slight narrowing of the pH range of effective phosphate removal and a shift toward higher pH levels. The pH shift was about 0.5 unit for pH levels above 9 and generally close to 1.0 for pH values less than 6.0. Figure 8 also shows data, obtained in the tests on sulfate containing solutions, on the turbidity of the unfiltered samples following 20 min of quiescent settling. As was observed in other cases, a good correlation exists between the development and settling of turbidity and the removal of phosphate.

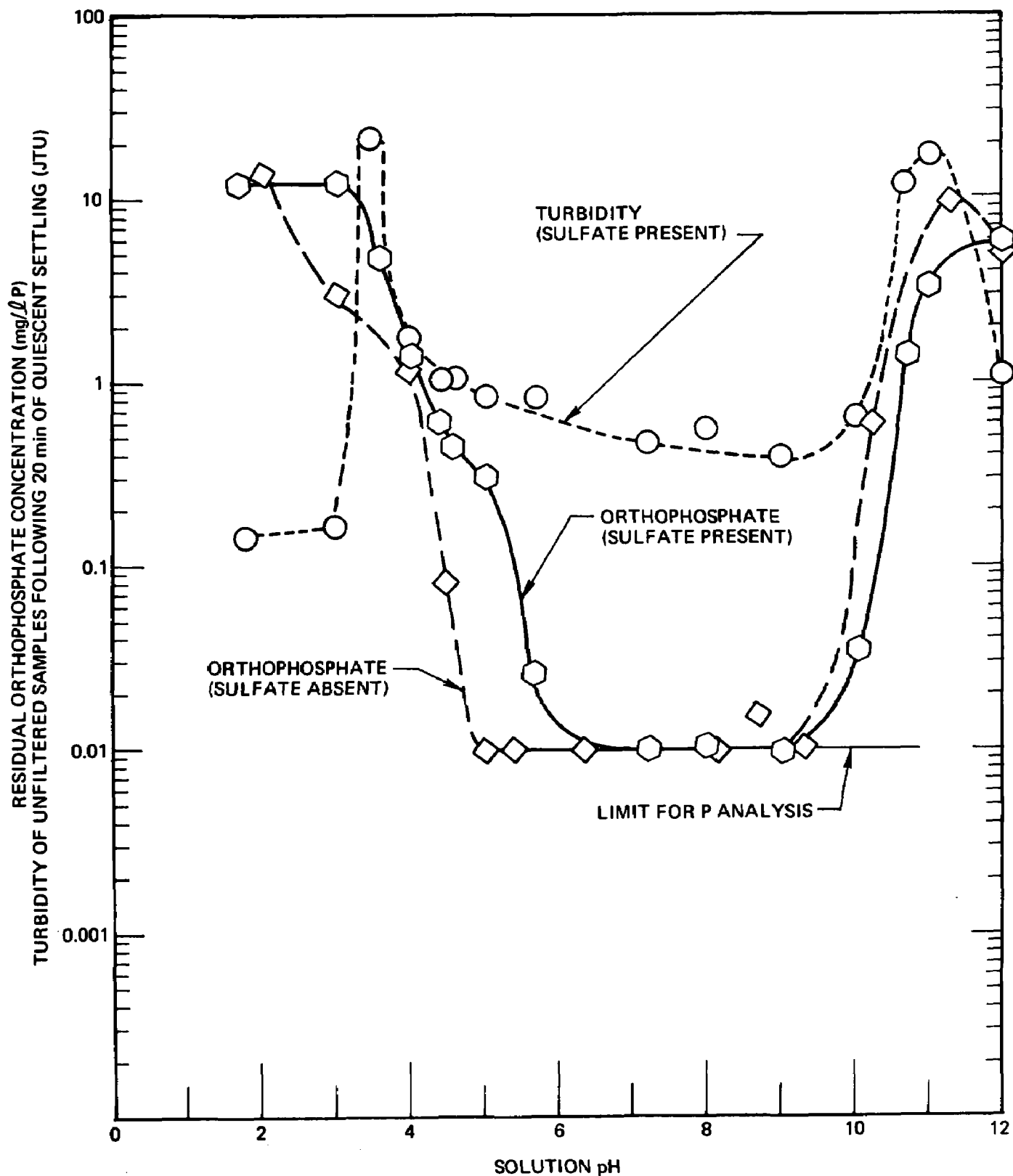


Figure 8. Precipitation of Orthophosphate with Lanthanum at a 1:1 Lanthanum-to-Orthophosphate Molar Ratio in the Presence and Absence of Sulfate. (Initial Orthophosphate Concentration 12 mg/L P; Sulfate Concentration = 0.0025 M (240 mg/L SO_4^{2-}))

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Another common divalent constituent of wastewater is calcium ion. Despite the relative insolubility of calcium phosphate, wastewaters usually contain both calcium and phosphate ions at concentrations above those which would be expected from solubility considerations. No explanation is yet available for this apparent anomaly. An evaluation of the effect of calcium ion on phosphate precipitation with lanthanum could not be made, since the addition of calcium to a phosphate solution resulted in the development of turbidity and formation of a precipitate, probably calcium phosphate.

Lanthanum Precipitation of Condensed Phosphates

The effects of pH and lanthanum concentration on the precipitation of pyro- and tripolyphosphates from pure solutions by lanthanum were investigated. The results obtained are summarized in Figures 9 through 12. In these figures, residual phosphate and turbidity of test samples following settling are plotted as functions of solution pH for lanthanum-to-phosphate equivalence ratios of 1:1 and 2:1.

As with the precipitation of orthophosphate, the extent of polyphosphate removal with lanthanum is a function of solution pH and reactant ratios. The optimum precipitation pH range for both pyrophosphate and for tripolyphosphate is 5.5 to 6.0 at a 1:1 lanthanum-to-phosphate equivalence ratio, and 7 to 9 at a 2:1 ratio. Minimum pyrophosphate residuals of 0.06 and 0.002 mg/l P and minimum tripolyphosphate residuals of 0.18 and 0.007 mg/l P were observed for 1:1 and 2:1 lanthanum-to-phosphate ratios, respectively. It should be noted that the phosphate data reported in Figures 10 and 12 were obtained using a Cary Model 14 recording spectrophotometer, whose 10 cm light path permitted phosphate residual concentrations as low as about 0.002 mg/l P to be determined.

At a 0.5:1 lanthanum-to-tripolyphosphate ratio, no phosphate removal was observed at any of the pH levels examined. Table 1 contains data on the turbidity produced under these conditions. These data indicate that some reaction probably takes place in the pH 4 to 6 region, but that particles produced are very fine since no phosphate was removed by filtration through Whatman No. 42 filter paper.

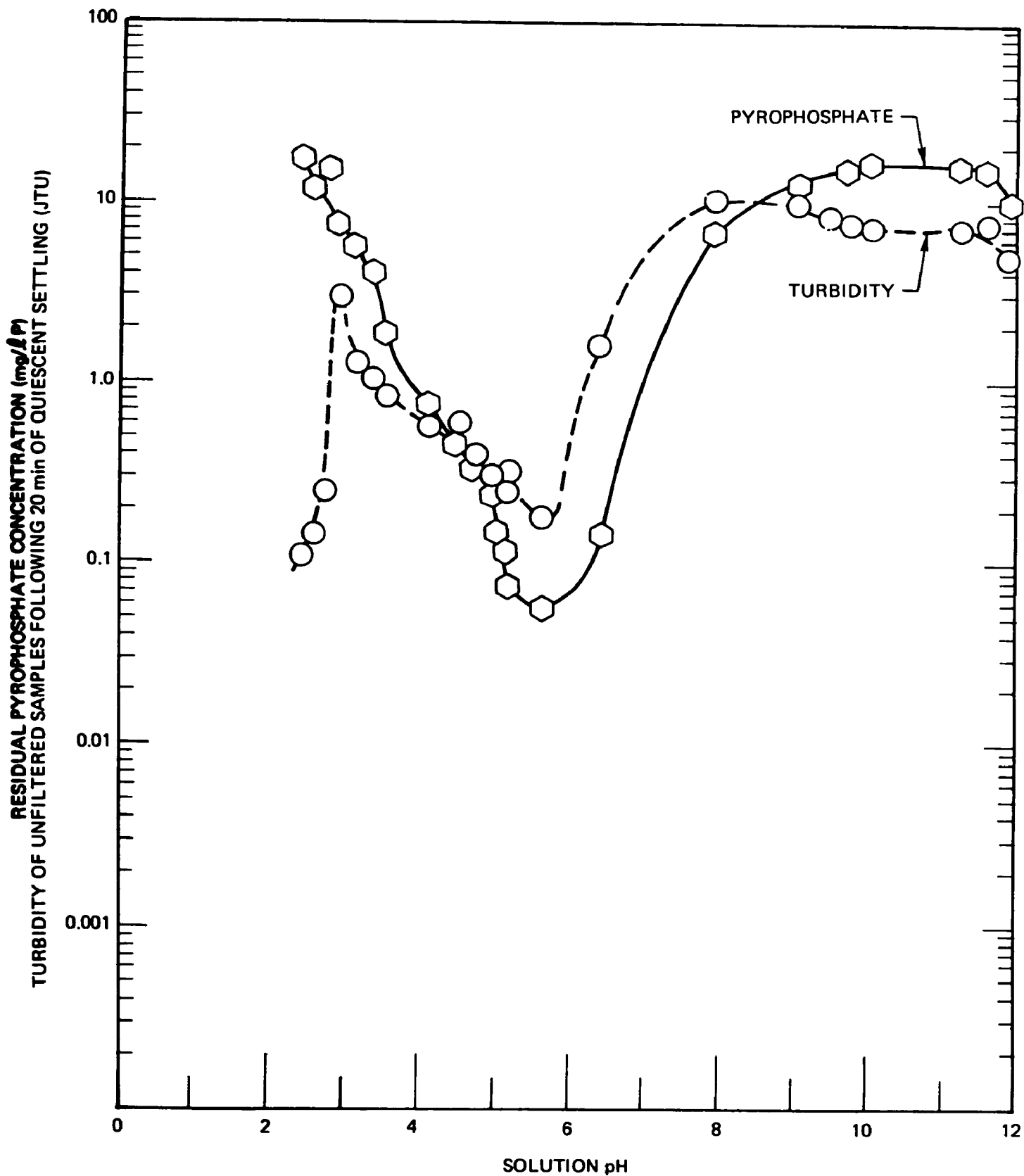


Figure 9. Precipitation of Pyrophosphate with Lanthanum at a 1:1 Lanthanum-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/l P)

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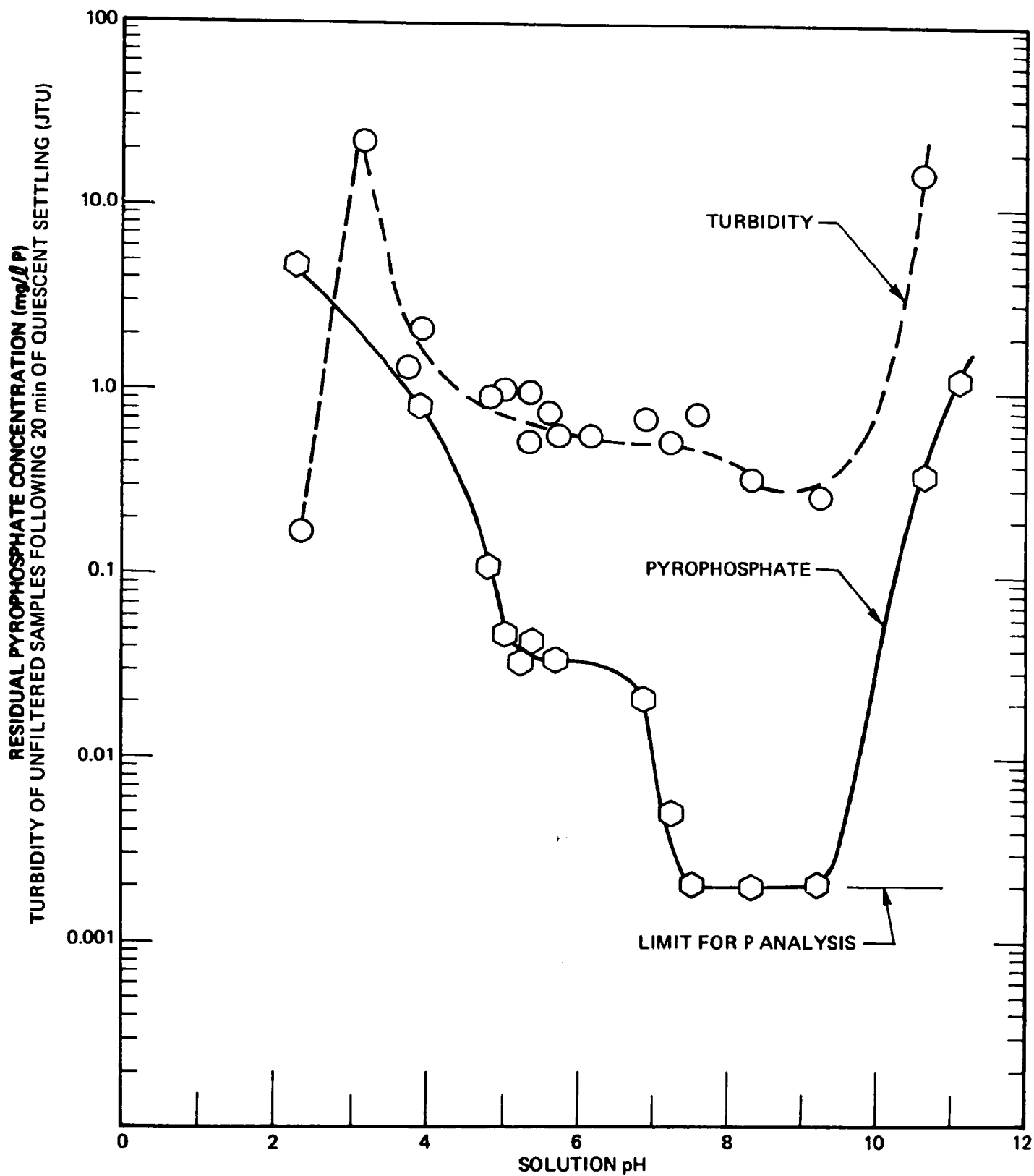


Figure 10. Precipitation of Pyrophosphate with Lanthanum at a 2:1 Lanthanum-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/l P)

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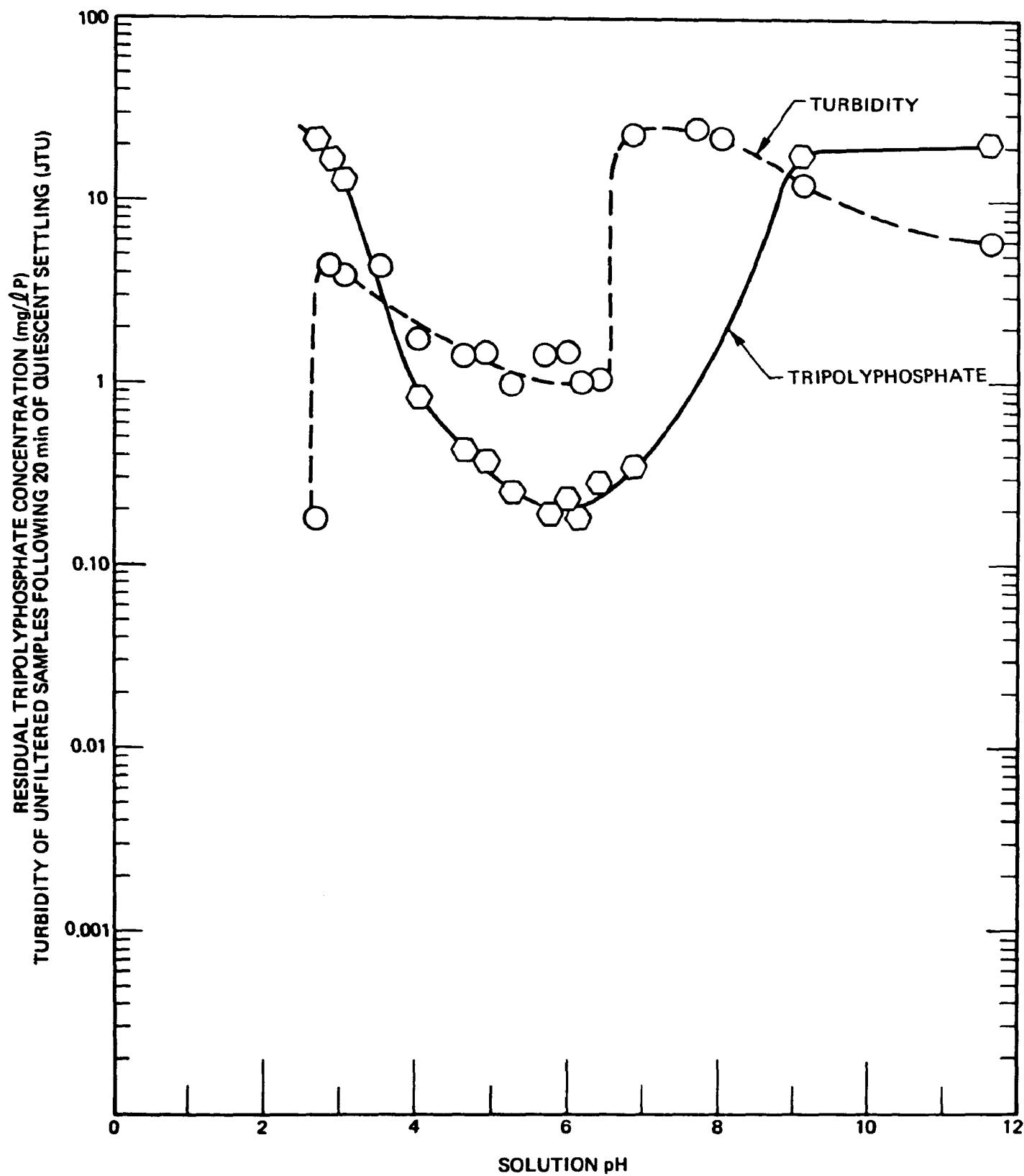


Figure 11. Precipitation of Tripolyphosphate with Lanthanum at a 1:1 Lanthanum-to-Tripolyphosphate Equivalence Ratio (Initial Tripolyphosphate Concentration, 21.6 mg/L P)

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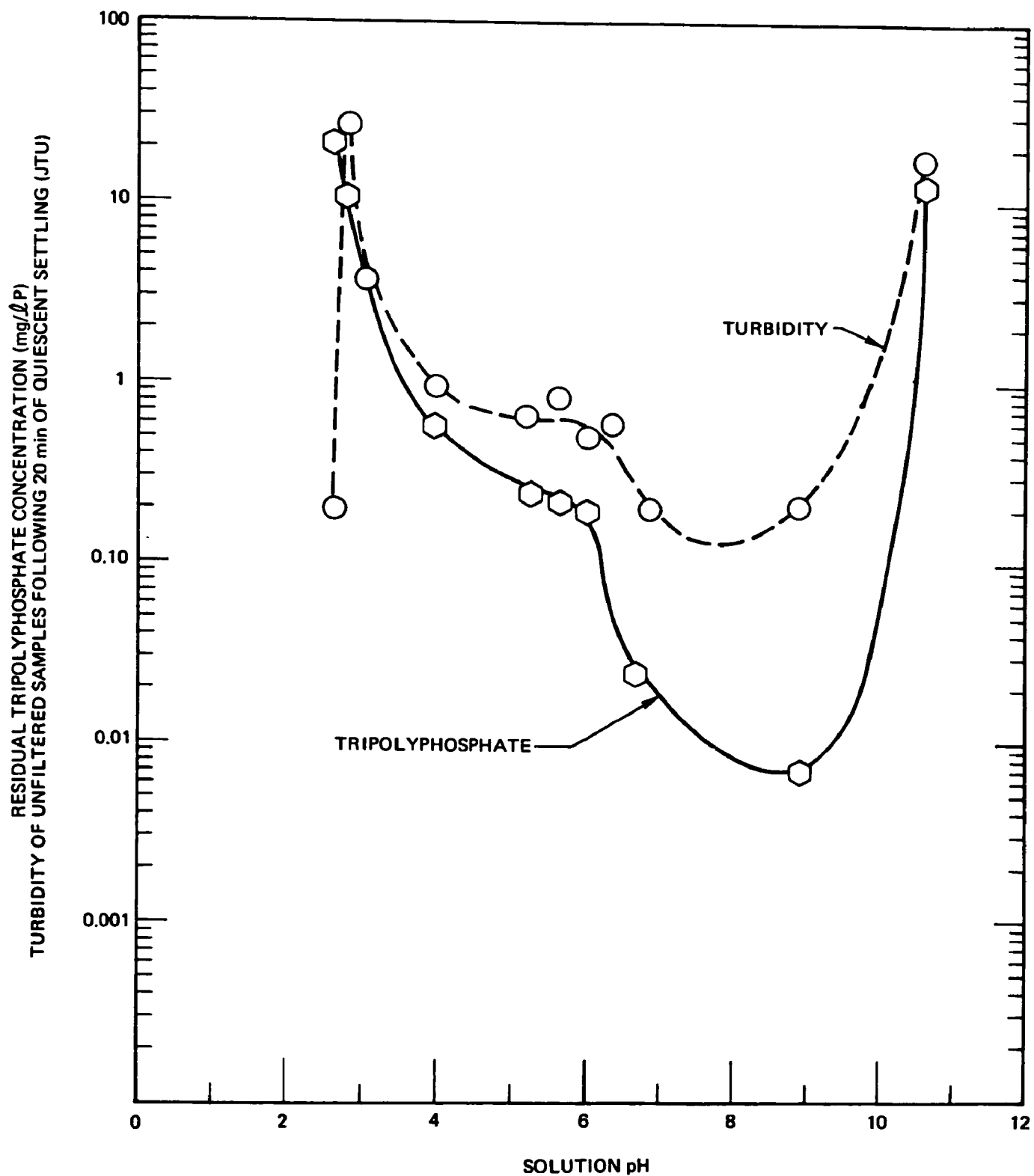


Figure 12. Precipitation of Tripolyphosphate with Lanthanum at a 2:1 Lanthanum-to-Tripolyphosphate Equivalence Ratio (Initial Tripolyphosphate Concentration, 21.6 mg/L P)

70-A15-032-30

TABLE 1
LANTHANUM-TRIPOLYPHOSPHATE REACTION AT
0.5:1 EQUIVALENCE RATIO
(Phosphate Solution Used: 21.6 mg/l P $\text{Na}_5\text{P}_3\text{O}_{10}$)

pH	Turbidity (JTU)	pH	Turbidity (JTU)
3.45	0.17	6.70	0.13
4.10	2.20	7.50	0.20
4.35	1.80	9.05	0.18
5.25	3.50	10.00	0.15
5.95	0.70		

Comparison of the lanthanum-polyphosphate reactions at 1:1 and at 2:1 lanthanum-to-phosphate ratios, reveals several interesting points. The two residual phosphate curves for the 2:1 ratio (Figures 10 and 12) exhibit relatively constant low values in the pH 5-6 range. This pH range also corresponds to the region of maximum phosphate removal at the 1:1 ratio. At the 2:1 ratio, up to a pH of about 6, essentially no additional removal of phosphate is effected by the presence of this excess lanthanum. At a 1:1 lanthanum-to-phosphate ratio, substantial amounts of residual turbidity are observed in the pH 6.5-9 region (Figures 9 and 11). This pH region also corresponds to the region of maximum phosphate precipitation when a 2:1 ratio of reactants is used.

The results of a similar study of the aluminum-tripolyphosphate reaction⁽⁵⁾ has shown that a significant amount of residual phosphate remains in the pH regions immediately outside the range of good floc formation. This phosphate is presumably in the form of colloidal particles which cannot be effectively removed by filtration through Whatman No. 42 filter paper; the range of good phosphate removal is somewhat broadened when these solutions are filtered through fine membranes (e.g., 100 m μ). It is possible, therefore, that the rise in residual phosphate observed in the pH 6.5 to 9.0 region at a 1:1 lanthanum-to-phosphate ratio is due, at least in part, to the formation of a highly dispersed, fine precipitate which is not removable by filtration through Whatman No. 42 filter paper. The addition of excess lanthanum (use of a 2:1 La/phosphate ratio) would bring about a destabilization of this dispersed colloidal turbidity and therefore result in a

broadening of pH range for good phosphate removal. The possibility should be considered that the lanthanum-polyphosphate reactions which take place in the pH 6.5 to 9 range lead to different products than those occurring at lower pH levels (pH 5 to 6), since the precipitates formed in the high pH region at the 2:1 ratio were noted to be more bulky and gelatinous than those observed at lower pH levels.

Within the pH range of optimum phosphate removal, the lanthanum-polyphosphate reactions resulted in the formation of large settleable flocs. Immediately outside this pH region, colloidal suspensions were formed. At very low pH levels where no turbidity was formed, the lanthanum-polyphosphate reactions either do not occur or they result in the formation of soluble products.

Lanthanum Precipitation of Phosphate from Secondary Effluent

The effectiveness of lanthanum in precipitating phosphates from actual wastewater, a secondary effluent, was evaluated in a series of batch type precipitation experiments. The experiments were conducted as a function of pH using a 2:1 lanthanum-to-phosphate molar ratio. The residual concentrations of phosphate following precipitation with lanthanum are plotted in Figure 13 as a function of final solution pH. (Results obtained using aluminum salts on the same effluent are also shown; these will be discussed later when results with La(III) and Al(III) are compared.)

It may be seen, comparing the lanthanum results in Figure 13 with those shown in Figure 6, that the phosphate removal from wastewater exhibits a dependence on pH similar to the phosphate removal from pure solutions. With the secondary effluent, a minimum residual phosphate concentration of 0.01 mg/l P or less was obtained in the pH 5.6 to 7.6 range. Also, the residual phosphate concentration was less than 0.1 mg/l P in the pH 4.4 to 8.8 range. The corresponding range with a somewhat more concentrated pure orthophosphate solution was from pH 4 to 9. As with pure phosphate solutions, the optimum pH for phosphate removal from wastewater with lanthanum is fairly broad and includes those pH levels normally encountered in the effluents from biological wastewater treatment plants. It is apparent, therefore, that in the treatment of wastewater with lanthanum there would not be any need for costly pH adjustments, e.g., through addition of acid.

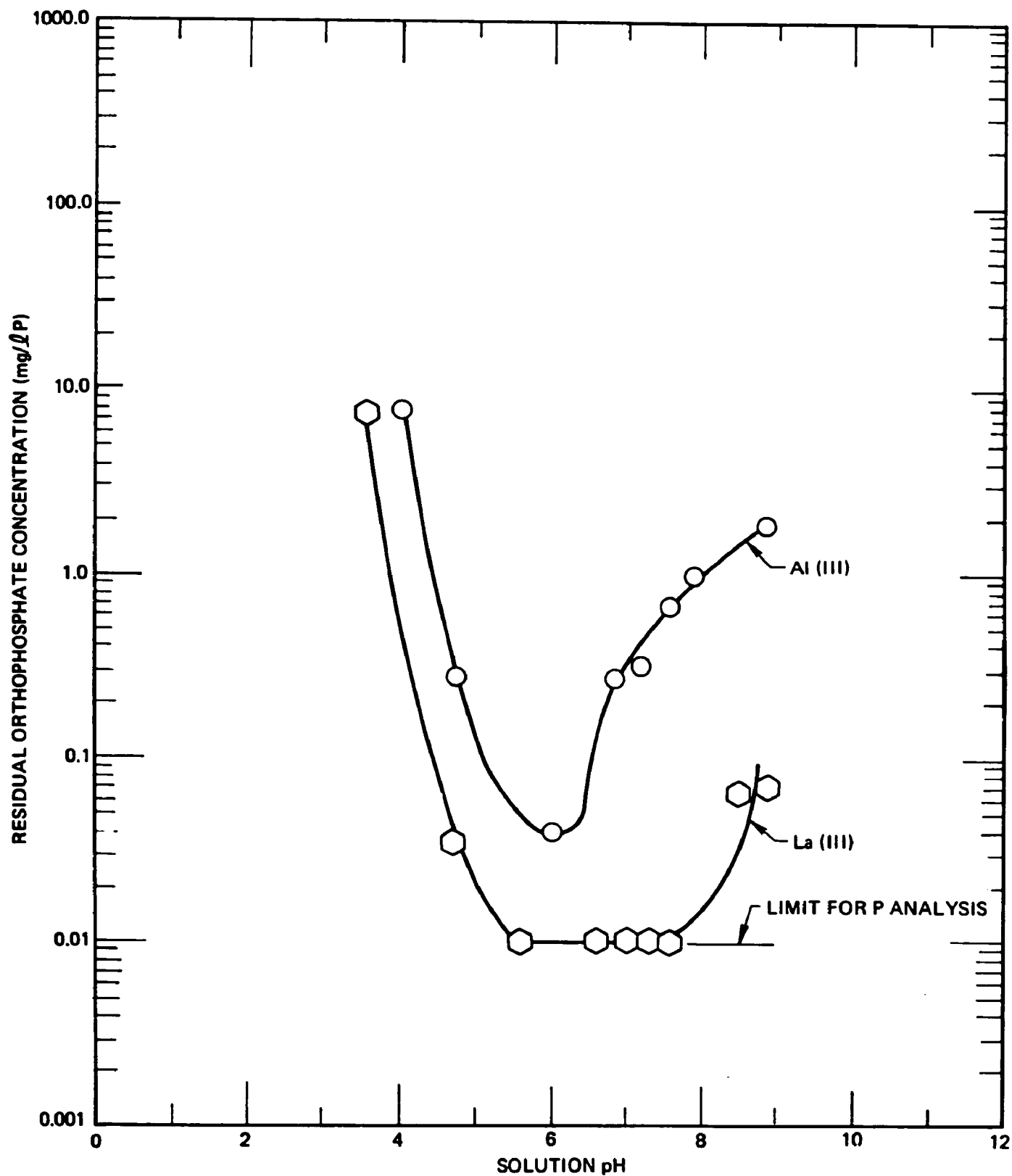


Figure 13. Comparison of the Effectiveness of Lanthanum and Aluminum for the Removal of Orthophosphate from Secondary Effluent at a 2:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 7.75 mg/L P; Initial pH = 7.8)

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In the experiments with lanthanum and secondary effluent, the filtrate from the sample at pH 7.0 (phosphate residual less than 0.01 mg/l P) was analyzed for residual lanthanum using an extraction flame photometric technique.⁽¹¹⁾ Despite the use of excess lanthanum in the precipitation experiment (use of 2:1 La/PO₄⁻³ molar ratio), no lanthanum was detected in the pH 7.0 filtrate in contrast to the high lanthanum residuals found in the comparable experiment with pure solutions. The fact that this excess lanthanum is precipitated is of significant importance since in practice an excess amount of lanthanum could be used to ensure complete removal of phosphate without encountering any significant loss of the lanthanum in the effluent wastewater.

Comparison Between Lanthanum and Aluminum Salts for Precipitating Phosphates

As stated earlier, the principal objective of the present study was to evaluate the effectiveness of lanthanum for the removal of phosphates with a supplementary objective to compare the lanthanum precipitation results with similar data obtained using aluminum. The data on the lanthanum precipitation of phosphate from pure solutions and from secondary effluent were presented and discussed in the previous sections. In this section the lanthanum data are compared with the data obtained using aluminum. The data on the precipitation of phosphate with aluminum will not be discussed in detail but only cited for comparison purposes. The mechanism, rate and stoichiometry of phosphate precipitation with both aluminum and ferric salts have been studied in detail in a separate investigation;⁽⁵⁾ the data presented herein on the aluminum-phosphate reactions have been directly taken from that study. Since the behavior of aluminum-phosphate and ferric-phosphate systems have been shown to be similar in many respects,⁽⁵⁾ most of the conclusions drawn from the comparison of lanthanum with aluminum may also be applied to the comparison of lanthanum with ferric iron.

Studies of the aluminum-orthophosphate reaction⁽⁵⁾ have indicated a slight broadening of phosphate residual - pH curve on the basic side when the pH adjustments are concurrent with the addition of the cation, rather than by prior addition of acid or base. However, the difference is not of sufficient magnitude to be considered in the present discussion; for all practical purposes the data on aluminum-orthophosphate and lanthanum-orthophosphate reaction are directly comparable.

The relative effectiveness of lanthanum and of aluminum in precipitating ortho- and polyphosphates may be seen in the results shown in Figures 13 through 18. Lanthanum may be seen to give superior performance in the following ways. The pH range for optimum removal of phosphate with lanthanum is considerably broader than that for aluminum; this is especially pronounced in the precipitation of condensed phosphates. For example, at a 2:1 aluminum-to-polyphosphate equivalence ratio (Figures 17 and 18) practically no phosphate is removed at pH levels ± 1 unit from that for maximum phosphate removal; with lanthanum, on the other hand, the corresponding polyphosphate residual is less than 0.01 mg/l P in the pH 7 to 9 range and is less than 1.0 mg/l P from about pH 4 to approximately pH 10.

On an equivalence basis, lanthanum is far more effective than aluminum for the precipitation of phosphates. At a pH of 7.0 (Figure 7), complete removal of orthophosphate was obtained with a lanthanum-to-orthophosphate molar ratio of slightly less than 0.9:1.0 (i.e., at this ratio of the reactants, the phosphate residual was 0.01 mg/l P or less). On the other hand, the minimum residual phosphate concentrations observed with aluminum at 1:1 and at 2:1 cation-to-orthophosphate molar ratios were 3.5 mg/l P and 0.10 mg/l P, respectively (see Figures 15 and 16). Furthermore, as indicated in Figure 7, the efficiency of phosphate removal with aluminum (at the optimum pH of 6) decreases as the aluminum-to-phosphate molar ratio exceeds 1.0. With lanthanum, on the other hand, up to the point of complete phosphate removal, the phosphate removal efficiency remains independent of the cation-to-phosphate molar ratio used.

The reaction of aluminum with tripolyphosphate (Figure 18), using a 21.6 mg/l P solution of $\text{Na}_5\text{P}_3\text{O}_{10}$, gave at a 2:1 ratio, a minimum residual phosphate concentration of 3.8 mg/l P at a pH of 5.3. At a 1:1 ratio, no removal of phosphate was observed at several pH levels examined within the pH 4.8 to 6.5 region. The minimum residual tripolyphosphate concentrations obtained under the same conditions with lanthanum-to-phosphate ratios of 1:1 and 2:1 were 0.2 mg/l P and 0.01 mg/l P, respectively. As indicated in Figure 17, lanthanum is similarly far more effective than aluminum in the precipitation of pyrophosphate.

With aluminum and secondary effluent as shown in Figure 13, a minimum residual phosphate concentration of 0.04 mg/l P was observed at pH 6.0; however,

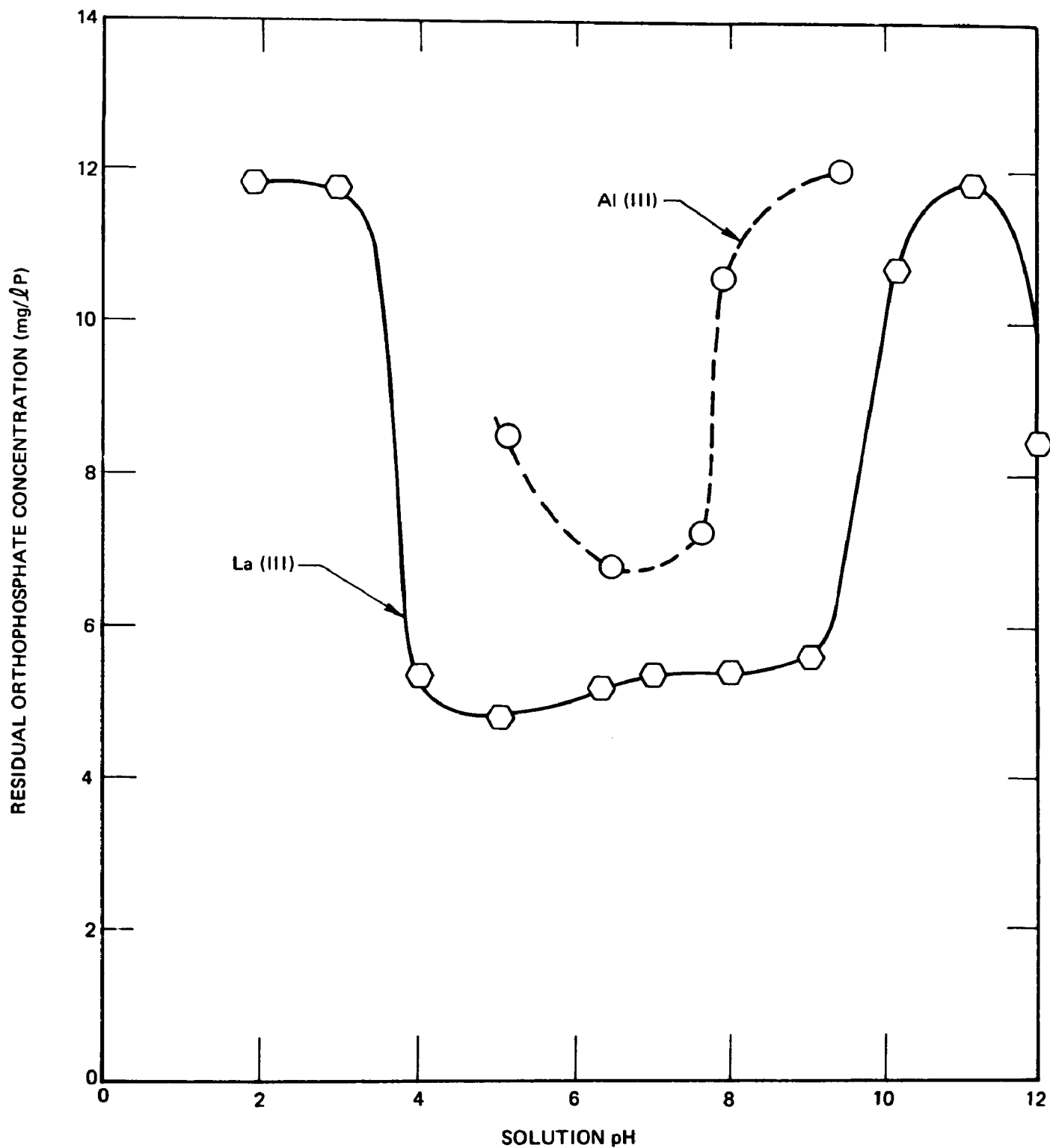


Figure 14. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Orthophosphate at a 0.5:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

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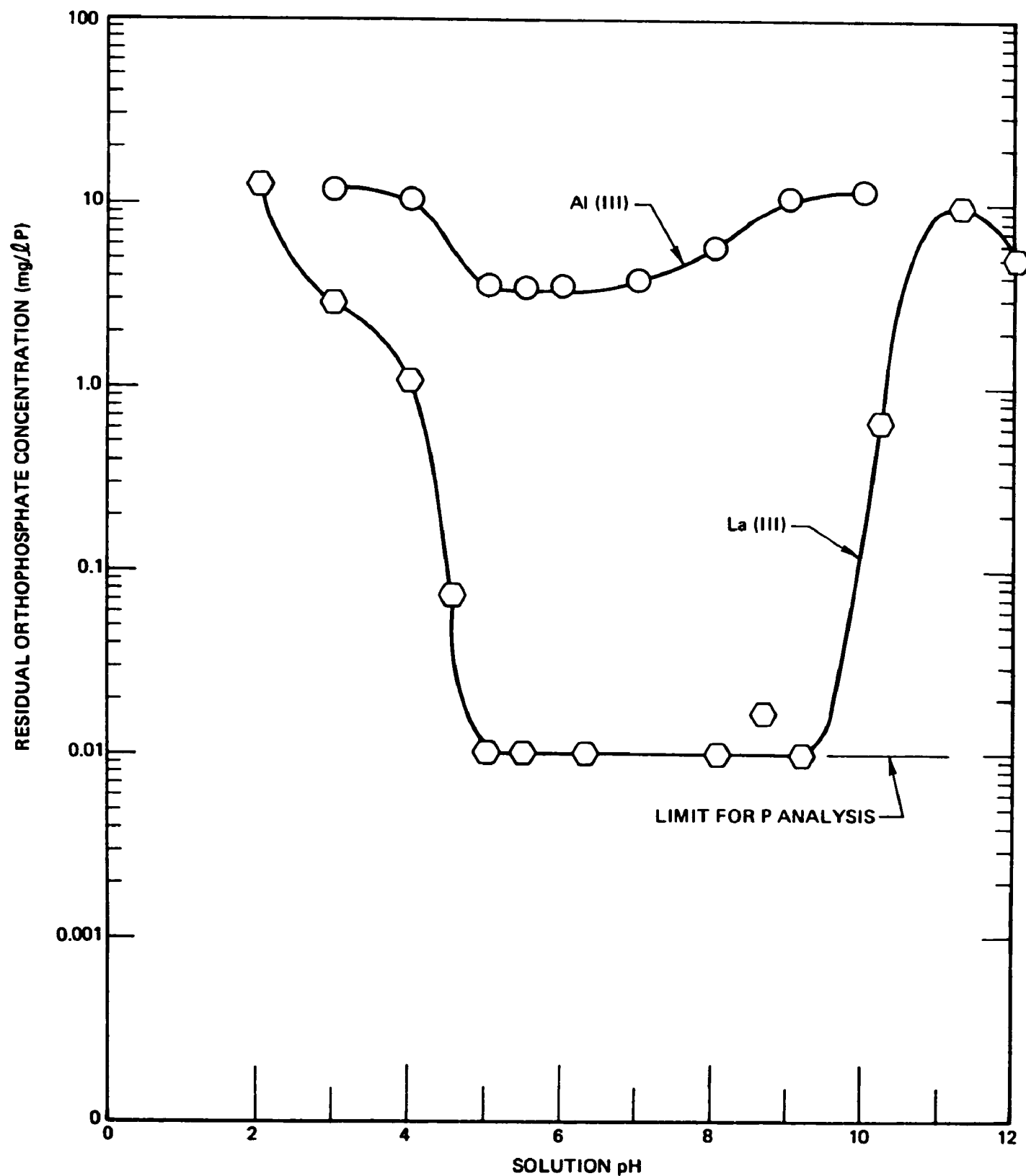


Figure 15. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Orthophosphate at a 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

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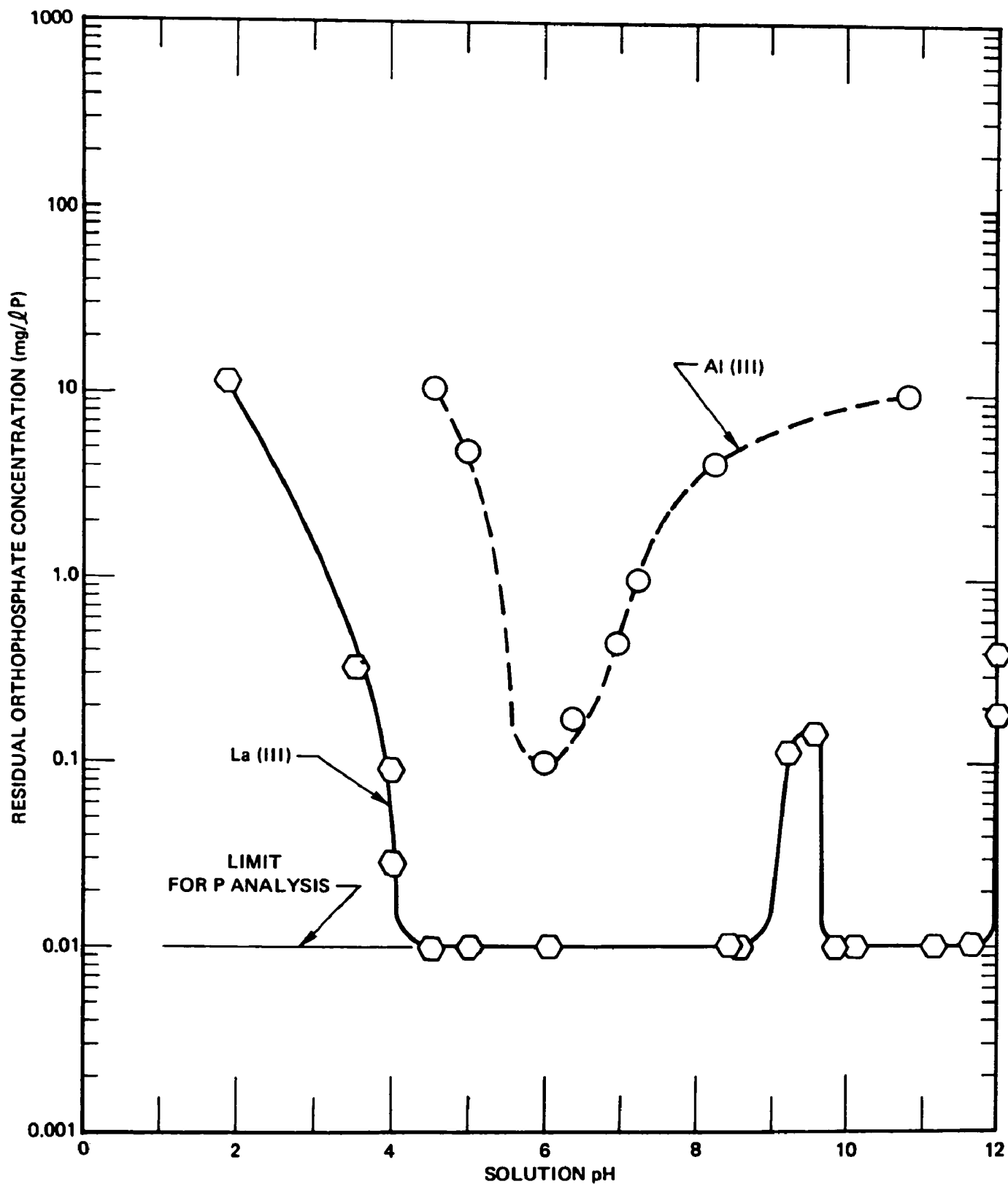


Figure 16. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Orthophosphate at a 2:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/L P)

70-A15-032-36

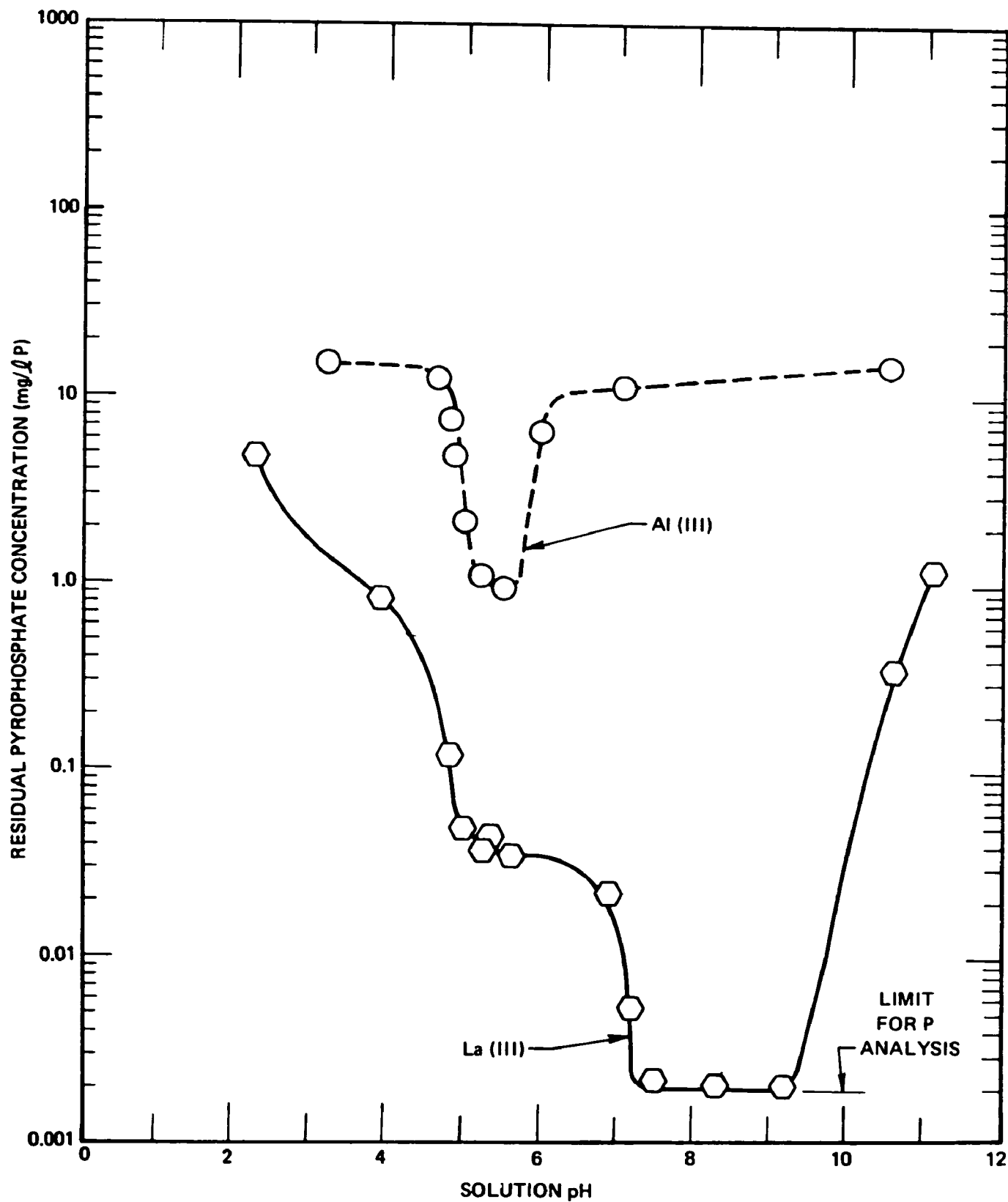


Figure 17. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Pyrophosphate at a 2:1 Cation-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/L P)

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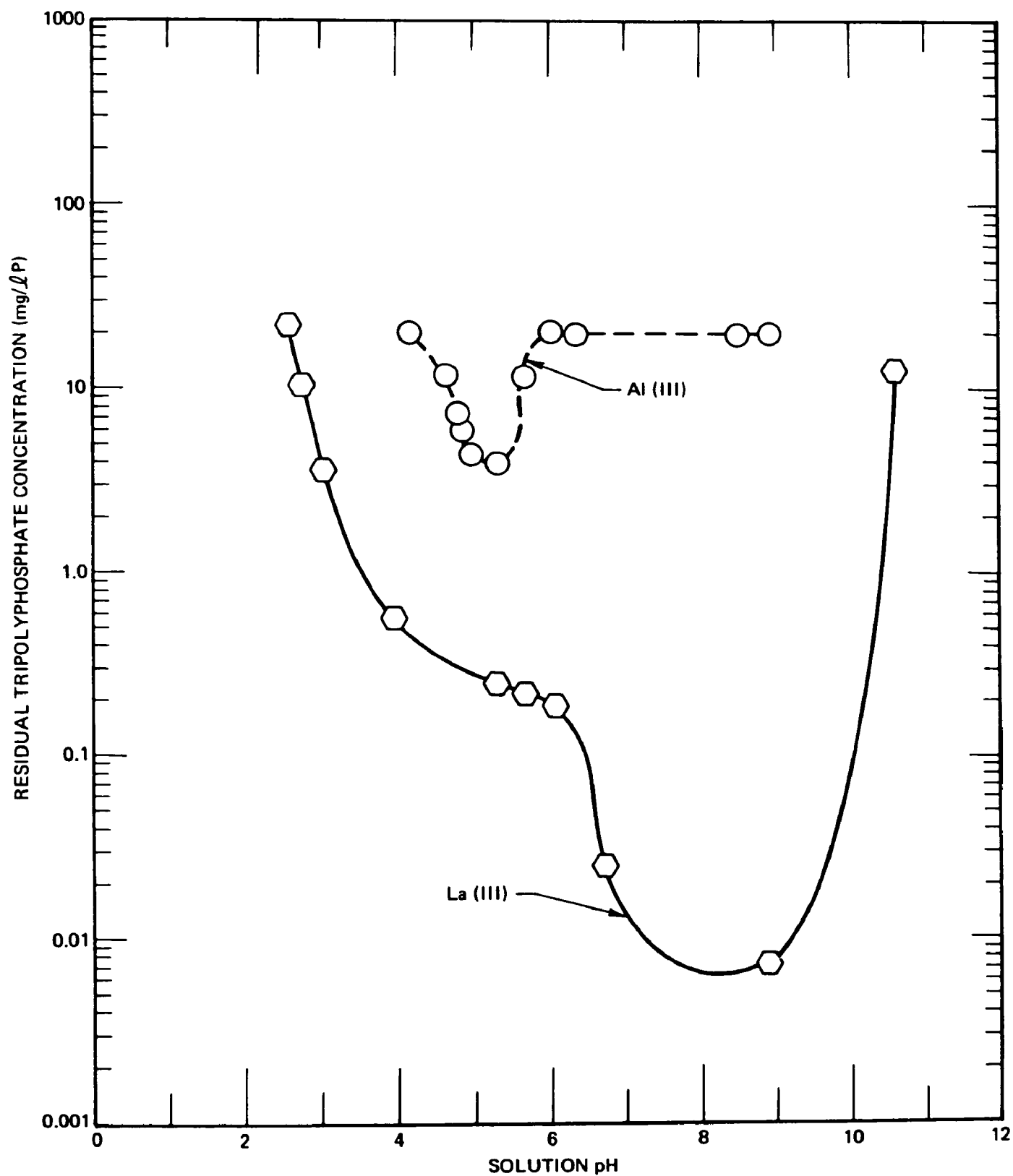


Figure 18. Comparison of the Effectiveness of Lanthanum and Aluminum for the Precipitation of Tripolyphosphate at a 2:1 Cation-to-Tripolyphosphate Equivalence Ratio (Initial Tripolyphosphate Concentration, 21.6 mg/L P)

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the residual phosphate concentration was above 0.3 mg/l P at all pH levels outside the pH 4.6 to 6.8 range. Thus, it is seen that the pH range for optimum phosphate precipitation with aluminum lies below pH = 7. The effectiveness of lanthanum for phosphate removal, on the other hand, extends well above pH 7 into the alkaline range and includes those pH levels normally encountered in domestic wastewater (7.0 to 8.0). This is a very desirable feature for application of lanthanum to wastewater treatment since it eliminates the necessity for costly pH adjustment by addition of acid or excess aluminum salt. A loss of buffer capacity will occur with pH adjustment. This may in itself be undesirable since it necessitates careful control of chemical addition to avoid wide pH fluctuations. Furthermore, it has been demonstrated in other studies⁽⁵⁾ that the addition of excess aluminum can result in the formation of poorly settleable flocs which cannot be effectively removed by plain sedimentation or by ordinary filtration methods. Also, if the discharge of acidic effluents is to be avoided, the pH of the wastewater must be readjusted with lime or soda ash following the treatment with aluminum.

The pH dependence of phosphate removal efficiency for both lanthanum and aluminum can be explained in terms of two competing reactions, hydrolysis and precipitate solubility. Hydrolytic products of both Al(III) and La(III) with their smaller ionic charge would be less effective in precipitating phosphates than the trivalent cation species. Since the extent of cation hydrolysis increases with the rise in the concentration of OH⁻ ions, the efficiency of the cations for phosphate removal tends to decrease as the pH is raised. At lower pH levels where La(III) and Al(III) are less hydrolyzed, an increased solubility of the precipitates is brought about by a decrease in the concentration of the orthophosphate ion. The extent of the pH-dependence of the two reactions (cation hydrolysis and precipitate solubility) determines the extent of the pH range of phosphate removal. Since La(III) hydrolyzes to a lesser extent than Al(III), and has a lower phosphate solubility, it is more effective than Al(III) for phosphate removal.

Jar Test Reaction Rate Studies with La(III) and Al(III)

Preliminary tests were made using the "jar test" procedure to determine the rate at which La(III) and Al(III) reacted with ortho- and pyrophosphates to form a precipitate and thus remove the phosphate from the system. Changes in

pH and conductivity were used to measure the course of the precipitation reactions. In all cases examined, the recorded changes in pH and conductivity all took place within 10 to 60 sec after the addition of the lanthanum or aluminum salt solution. In one experiment with Al(III), aliquots of solution were removed from the reaction beaker at selected intervals following addition of aluminum nitrate, vacuum filtered, and the filtrates analyzed for residual phosphate. The results indicated that the initial drop in pH and conductivity which took place within 30 to 60 sec following additions of aluminum nitrate was accompanied by a drop in phosphate concentration from 12 mg/l P to 0.10 mg/l P. No further removal of phosphate was observed after this period despite the very noticeable gradual growth and agglomeration of the flocs.

An HCl-NaOH neutralization experiment, conducted under identical mixing conditions, gave patterns of pH and conductivity change identical to those observed in the phosphate precipitation experiments. Since this type of acid-base reaction is known to be practically instantaneous, it was postulated that the aluminum-phosphate and the lanthanum-phosphate reactions which result in changes in pH and conductivity might also be instantaneous, and that the measured time delay in attaining constant pH and conductivity levels could in fact be due to the time required for mixing the added reagents.

Reaction Rate Studies Using the Reaction Kinetics Apparatus

As was discussed in the section "Kinetics Apparatus," a reaction kinetics apparatus was designed and built to permit monitoring of pH and residual phosphate concentration within a very short time following mixing of the phosphate and the lanthanum or aluminum salt solutions. In the first tests with this equipment, only the pH of the solution mixture leaving the reaction flask (see Figure 1) was monitored. The pH data collected at several points in the flow line showed essentially constant values for both aluminum (6.4 to 6.6) and lanthanum (8.5 to 8.6). This constancy clearly indicated that within the period of observation the reactions between orthophosphate and aluminum and lanthanum are completed within 1.3 sec.

In experiments where phosphate removal data were collected, the reaction kinetics apparatus was modified so that the time of solution travel to the first sampling port was reduced from 1.3 sec to slightly less than 1 sec. In these experiments, 0.5:1 lanthanum-to-orthophosphate and 1:1 aluminum-to-orthophosphate molar ratios were used.

The pH of the solution mixture was monitored at port B (see Figure 1) during sample collection. A slight gradual increase in pH was observed in almost all cases. It appears, however, that this rise in pH was not real but rather due to instrumental factors (probably brought about by the gradual decrease in the rate of solution flow around the pH probe electrode). In most cases a sample of solution mixture was collected at the discharge point of the kinetics apparatus and flocculated in the Phipps and Bird stirring apparatus. The analyses of filtrates from all the samples showed residual concentrations of 3.90 mg/l P with lanthanum and 4.12 mg/l P with aluminum. No changes occurred in residual phosphate beyond that observed at the first sampling port.

These results indicate that the reactions between La(III) and Al(III) and orthophosphate which results in precipitate formation and removal of phosphate from solution are complete in less than 1 sec and are probably nearly instantaneous. Even when samples of the solution mixture discharged from the kinetics apparatus were flocculated by gentle mixing, the growth and agglomeration of the flocs was not accompanied by any additional removal of the phosphate relative to that obtained by millipore filtration through the sample ports.

Although no phosphate removal data were collected on the reactions of La(III) and Al(III) with polyphosphates, the constancy of pH observed in the batch pyrophosphate precipitation experiments indicates that, at or near the pH of optimum phosphate removal, the cation-pyrophosphate reactions are also very rapid.

From the results of these kinetic studies, the requirement of addition of a molar excess of the aluminum or other metal salts to obtain essentially complete phosphate removal cannot be attributed to inadequate time allowed for precipitate formation. Instead, as discussed before, this can be satisfactorily explained by the occurrence of competing reactions and the dispersion of the phosphate precipitates into extremely fine, nonsettleable particles.

Nature of La(III) and Al(III) Orthophosphate Precipitates

In order to learn more about the precipitates being formed in the reactions of orthophosphate ion with La(III) and Al(III), thermogravimetric measurements and x-ray diffraction studies were carried out. These were done as described earlier in the section, "Thermogravimetric Experiments."

The aluminum precipitates did not reach a constant weight even after a 9-day storage period in the desiccator. However, the extent of weight loss after the 7th day was very small. Accordingly, the weight of this precipitate after the 9th day was used in calculating the total water loss at room temperature, and the percentage weight loss which resulted on subsequent heating at 104°C. The percentage of total weight loss resulting from room temperature drying is substantially lower for the lanthanum precipitates (0.73%) than for the aluminum precipitate (9.72%). If these values of total weight loss, based on the weight change of the precipitate in the desiccator after one day of drying, represent approximately the initial unbound water contents of the precipitates, the lanthanum phosphate precipitate is seen to have a lower unbound water content. This constitutes a desirable feature for large-scale application of lanthanum salts to the removal of phosphates from wastewater.

The precipitates, on heating at 104°C, were found to be somewhat hygroscopic and slight increases in weight were observed following the first weighing after each heating. Accordingly, the smallest weights observed were used in calculating the weight losses resulting from heating at 104°C. Essentially no further change in weight was observed following the first 2 hr of ignition at 600°C.

To summarize these thermogravimetric results, lanthanum and aluminum-orthophosphate precipitates, obtained under the particular precipitation conditions used, gradually lose weight when heated at 104°C. The total percent weight loss resulting from 6 hr of heating at 104°C, based on the dry weight at room temperature, was 9.9% for the aluminum precipitate and 2.3, 2.4, and 2.5% for the three lanthanum precipitates, one of which had undergone only 4 hr of heating. Correcting for the small portion of the precipitate removed for x-ray analysis from one lanthanum sample, the total weight losses on heating at 104°C and at 600°C were 17.5% for the aluminum and 9.8%, 10.3%, and 10.3% for the lanthanum precipitates. If the assumption is made that the total loss in weight on heating represents water bound in $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, the value of n is approximately 1.5.

Fresh, desiccator-dried and ignited precipitates of aluminum and the fresh precipitate of lanthanum were found to be amorphous on examination by x-ray diffraction. The lanthanum precipitate dried at 104°C and the residue resulting from ignition at 600°C were found to be crystalline with the latter exhibiting a much sharper diffraction pattern. The material was identified as LaPO_4 on the basis of its x-ray diffraction pattern.

Recommendations for Future Work

The basic objectives of the study described in this report have been to assess the potential use of lanthanum salts for the removal of phosphates from aqueous systems and to compare the results with the phosphate precipitation data obtained using aluminum salts. A pure lanthanum salt was used in this preliminary study to represent the lanthanide family. Except for a few precipitation experiments in which actual wastewater was used as the phosphate-containing solution, most of the precipitation studies were conducted on pure phosphate solutions. Lanthanum has been found to be so effective in precipitating phosphates and so superior to aluminum that further experimental work is recommended in order that the lanthanum process be developed for large-scale application to the treatment of wastewater for the removal of phosphates.

The following areas of research and development are recommended as logical extensions of the present study:

- 1) Laboratory evaluation of the effectiveness of lanthanum and mixed lanthanides for removing phosphates from secondary effluent obtained from several different sources and comparison of the results with similar data obtained using Al(III) or Fe(III) salts.
- 2) Characterization of the lanthanum (and mixed lanthanide) precipitates obtained in the treatment of secondary effluent for phosphate removal. Parameters to be evaluated should include: settleability, filterability, and strength (resistance to shear) of the flocs; compaction and dewaterability of the sludge; and means of improving and effecting the solid-liquid separation. For the purpose of comparison, some limited data should also be obtained using Al(III) or Fe(III) salts.
- 3) Evaluation of lanthanide recovery methods using both pure phosphate solutions and secondary effluent. Criteria to be defined should include optimum regeneration conditions, extent of chemical losses and the effectiveness of the recovered lanthanides for precipitating phosphates.
- 4) Laboratory-scale pilot plant evaluation of the lanthanide treatment method for the removal of phosphates from secondary effluent.

- 5) Bioassay studies of the possible effects of lanthanides on living organisms.
- 6) Application of the lanthanide treatment process to a small scale wastewater treatment operation and collection of field data on the basis of which the economics of the treatment process could be assessed with reasonable accuracy.

SUMMARY

Atomics International has conducted a parametric investigation of phosphate removal from aqueous systems using lanthanum precipitation in which the effect of pH and reagent concentration on the rate and the efficiency of phosphate removal were specifically evaluated. The phosphate precipitation data obtained with lanthanum are compared with similar data obtained using aluminum.

Pure solutions of orthophosphate at concentrations representative of those in wastewater, and of pyrophosphate and tripolyphosphates as well as effluent from an activated sludge wastewater treatment plant were used in this investigation. Reaction rate studies were conducted using both batch precipitation and steady-state reagent flow in a specially-designed reaction kinetics apparatus which permitted rapid mixing of the reactant solutions and subsequent monitoring of pH and residual reactant concentrations of the mixed stream. The effects of pH and reactant concentrations on the efficiency of phosphate removal were evaluated in batch precipitation experiments. The precipitates obtained in the reactions of orthophosphate with lanthanum and aluminum were examined by x-ray diffraction and were characterized by weight loss in thermogravimetric experiments.

Reaction rate studies showed that the precipitation of orthophosphate with both aluminum and lanthanum, which results in the removal of phosphate from solution, is very rapid and is completed in less than 1 sec. No further removal of phosphate is effected following the initial drop in the concentration of soluble phosphate.

Orthophosphate removal with lanthanum was found to depend on both pH and the concentration of added lanthanum. The pH range for optimum phosphate removal with lanthanum was found to be quite broad. For an initial orthophosphate

concentration of 12 mg/l P and a lanthanum-to-phosphate molar ratio of 0.5:1, the residual phosphate concentration was between 4.8 and 5.6 mg/l P in the pH 4 to 9 region, with the minimum at pH 5.0. At 1:1 and at 2:1 lanthanum-to-orthophosphate molar ratios, the residual phosphate concentration was less than 0.01 mg/l P in the pH 5 to 9 range.

When the pH was kept constant, the removal of orthophosphate was found to be directly proportional to the concentration of added lanthanum. Nearly complete removal of phosphate was observed at a La(III)/PO_4^{-3} molar ratio of slightly less than 0.9. The existence of such a constant stoichiometric relationship strongly suggests that a chemical reaction is occurring between the lanthanum and the orthophosphate and that the phosphate removal is not occurring by a mechanism involving adsorption (physical or chemical) on a precipitating metal hydroxide.

Precipitates obtained in the reactions of orthophosphate with lanthanum and aluminum were examined by x-ray diffraction and were characterized by weight loss on air drying and heating at 104° and at 600°C. The aluminum precipitate was found to be amorphous under x-ray examination. The lanthanum precipitate heated at 104°C and the residue resulting from its ignition at 600°C were both found to be crystalline with diffraction patterns corresponding to those of lanthanum phosphate (LaPO_4).

Lanthanum was also found to be effective in precipitating condensed inorganic phosphates. For an initial pyrophosphate concentration of 18 mg/l P, minimum phosphate residuals of 0.05 mg/l P (at pH 5.6) and 0.002 mg/l P (at pH 8-9) were obtained with lanthanum-to-pyrophosphate equivalence ratios of 1:1 and 2:1, respectively. For an initial tripolyphosphate concentration of 21.6 mg/l P, minimum residual tripolyphosphate concentrations were 0.18 mg/l P (at pH 6) and 0.007 mg/l P (at pH ~9) at these same ratios of the reactants, respectively.

Within the range of optimum phosphate removal, the reaction of lanthanum with both ortho- and polyphosphates resulted in the formation of large, settleable flocs. Immediately outside this pH range fine turbidity developed which did not settle out very well. At higher pH levels, some residual turbidity was observed in almost all cases. No turbidity or precipitate formation was observed at very low pH levels with either ortho- or polyphosphate.

The effectiveness of lanthanum in precipitating phosphates from actual wastewater (secondary effluent) was evaluated as a function of solution pH using a 2:1 lanthanum-to-orthophosphate molar ratio. The effluent used in the precipitation experiments had a pH of 7.8 and contained 7.75 mg/l P orthophosphate and no condensed phosphates. A minimum residual phosphate concentration of less than 0.01 mg/l P was observed in the pH 5.6 to 7.5 range. Also, the phosphate residual concentration was less than 0.1 mg/l P in the pH 4.4 to 8.8 region. The filtrate from the precipitation experiment at pH = 7.0 was analyzed for residual lanthanum content using an extraction - flame photometric technique which was shown to be capable of detecting lanthanum concentrations as low as 0.5 mg/l P. Despite the addition of excess lanthanum (use of 2:1 La(III)/PO₄⁻³ molar ratio), no lanthanum was detected in the sample filtrate.

Comparison of the lanthanum phosphate removal data with the similar data obtained using aluminum indicates that lanthanum is far superior for the precipitation of phosphates. For the 12 mg/l P orthophosphate solution, the minimum residual phosphate concentrations with aluminum were 6.8, 3.5, and 0.09 mg/l P for the conditions of 0.5:1, 1:1, and 2:1 aluminum-to-orthophosphate molar ratios, respectively. The corresponding values of minimum residual orthophosphate concentrations obtained with lanthanum were 4.8, <0.01, and <0.01 mg/l P, respectively. The superiority of lanthanum to aluminum is especially pronounced in the precipitation of condensed phosphate. For example, at a 1:1 cation-to-phosphate equivalence ratio, no removal of tripolyphosphate was obtained with aluminum at several pH levels examined. Lanthanum, on the other hand, showed good removal of tripolyphosphate over a broad pH range with a minimum residual phosphate concentration of 0.18 mg/l P observed at pH 6. At a 2:1 cation-to-tripolyphosphate ratio, the minimum residual phosphate concentrations with aluminum and lanthanum were 3.8 and 0.007 mg/l P, respectively.

Lanthanum exhibits a considerably broader effective pH range for phosphate removal than observed with aluminum; this is particularly true in the case of polyphosphates. For example, at 2:1 equivalence ratios, practically no removal of pyro- and tripolyphosphates was observed with aluminum at pH levels ± 1 unit from that for optimum phosphate removal (pH ~ 5.5). In the case of tripolyphosphate precipitation with lanthanum, the residual phosphate concentration was less than 0.1 mg/l P between pH's of 6 and 10 and was less than 1.0 mg/l P in the 4 to 10.5 pH range. One very attractive feature of the use of lanthanum for the removal

of phosphates from wastewater is that the pH of almost all domestic wastewaters lies within the pH range where lanthanum is most effective. To reach the optimum precipitation pH of about 6 with aluminum, large quantities of acid, or a considerable excess of aluminum, must be added to the wastewater to overcome its natural buffer capacity.

Based on the results of this investigation, it is evident that lanthanum salts show great potential for removal of phosphates from wastewater, and further studies including pilot plant testing appear warranted.

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1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM

5	Organization
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6	Title
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27	Abstract
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A parametric study was made of the removal of ortho- and polyphosphates from pure solutions and secondary effluent with La(III), and the results compared with those from similar tests with Al(III). The reactions of orthophosphate with both La(III) and Al(III), resulting in precipitate formation and phosphate removal, were complete in less than 1 sec. La(III) showed a broader effective pH range and lower residual phosphate concentration and thus proved to be far superior to Al(III) for phosphate, especially polyphosphate, precipitation. Within the pH range for optimal phosphate removal, the La(III)-phosphate reactions produced large, settleable flocs. Immediately outside this range, poorly settling fine turbidity developed. At pH levels above this region, some residual turbidity was generally observed. No turbidity or precipitation was observed at very low pH levels. At constant pH, orthophosphate removal was directly proportional to the La(III)/PO₄⁻³ molar ratio, with complete removal at a ratio of ~ 0.9. This strongly suggests that orthophosphate removal with La(III) occurs solely through a chemical reaction and not through an adsorption process. With secondary effluent, as with pure solutions, lower residual phosphate resulted over a wider pH range with La(III) than with Al(III); no pH adjustment is needed for effective removal with La(III), while considerable amounts of acid or excess Al(III) are required to achieve the optimum pH of 6 for phosphate removal.

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