THE REMOVAL OF PHOSPHORUS FROM DOMESTIC SEWAGE

by

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Submitted in Partial Fulfillment of the Requirements
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ABSTRACT

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Youngstown State University, 1985

This investigation was concerned with the removal of phosphorus to the level of 1.0 mg/L total phosphorus, which is the Federally mandated level. Evaluations were performed using aluminum sulfate, iron(III) chloride, iron(II) chloride, and zirconium sulfate, and combinations thereof, to reach the desired level. Secondly, an anionic polyelectrolyte (polymer) was added to each metallic ion system to increase the total phosphorus removal rate.

Various concentrations for each metallic ion system were used in order to determined the best concentration for phosphorus removal that would not overdose the system. Zirconium sulfate, iron(III) chloride, aluminum sulfate, and iron(II) chloride, in descending order of effectiveness, removed the most total phosphorus using the least amount of chemicals.

Next, various concentrations of Nalco 7766 (Polymer) were added to each metallic ion separately, while the concentration of the ion was kept constant.

Results indicated that the addition of this polymer increased the total phosphorus removed and dramatically lowered the zirconium, iron(III), aluminum, and iron(II) ions required for phosphorus removal.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

SYMBOL	DEFINITION
mL	milliliter
mg	milligram
lbs.	pounds
△	difference
Å	Angstrom
mgd	million gallons per day
ICP	Inductively Coupled Plasma
NPDES	National Pollution Discharge Elimination System
mv	millivolt
rpm	revolutions per minute
gal.	gallon
°F.	Fahrenheit -Degrees
	Liter
Zr	Zirconium
STPP	sodium tripolyphosphate
nm	nanometer
mg	million gallons

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CHAPTER I

INTRODUCTION

Sources of Phosphorus

Domestic wastewater normally has a substantial concentration of phosphorus with the primary source being man's daily activities in the home. Human wastes such as urine, feces, and waste food disposal account for approximately 30 to 50 % of the phosphorus in domestic wastewater.[1] Laundry detergents containing phosphate binders, such as sodium tripolyphosphate (STPP), can account for the remainder of phosphorus, or about 50 to 70 % (Table 1).

TABLE 1

DETERGENT PHOSPHATE SOURCES

Orthophosphates:	
Trisodium phosphate	Na_3PO_4
Disodium phosphate	Na_2HPO_4
Monosodium phosphate	NaH_2PO_4
Polyphosphates:	
Sodium tripolyphosphate	$Na_5P_3O_{10}$
Sodium dipolyphosphate	$Na_4P_2O_5$

Other sources of phosphorus may cause deviation from these percentages.

For example, sodium hexametaphosphate or other phosphorus compounds are used for corrosion and scale control in water supply systems. This source can account for 2 to 20 % of the total phosphorus found in wastewater.

The quantity of phosphorus resulting from human excretions ranges from 0.5 to 2.3 lb. per capita per year.[2] The annual contribution of phosphorus from synthetic detergents with phosphate binders is estimated to be about 2.3 lb. per capita, at present. Exclusive of industrial wastes and other phosphorus sources, the domestic phosphorus contribution to wastewater is approximately 3.5 lb. per capita per year.

Ecological Significance

Eutrophication is a natural geological process involving a body of water such as a lake or river, where organic life develops and multiplies over the years. With time, fish, bacteria, algae, and various aquatic plants appear and flourish. The lake bottom collects the remnants of organic life and other sediment builds up. As the lake bottom becomes more shallow, there is a corresponding character change in the marine life and the aquatic plants. Eventually, the lake becomes so shallow that it can become a marshland or swamp. Finally, the lake may become dry land, Normally this process takes thousands of years for a large body of water.

The present concern is that with the inflow of excess rich nutrients (phosphorus) eutrophication is rapidly accelerated.

Factors Limiting Eutrophication

One of the best indicators of advanced eutrophication is the presence of a great deal of algae. Algae are microorganisms which live suspended and free-floating in water. The most common species are called blue-green algae and about 2500 species of blue-green algae are known to exist. All plant and animal cells contain 3 to 10 % phosphorus in both organic and inorganic forms. However, phosphorus is not the only critical element needed for growth. The ratios of these elements are shown in Figure 1.[3]

The sizes of the circles representing the elements show the relative amounts of the various elements needed. The ratio of the number of atoms of carbon to nitrogen to phosphorus needed is approximately 106:16:1. Most natural waters contain all of these elements to some extent. If a lake contains a low amount of phosphorus as phosphate, algae will no longer grow when all of the phosphate is consumed, regardless of the amounts of other nutrients present. Phosphorus is the limiting element for algal growth in this case. The same can be true for other essential elements.

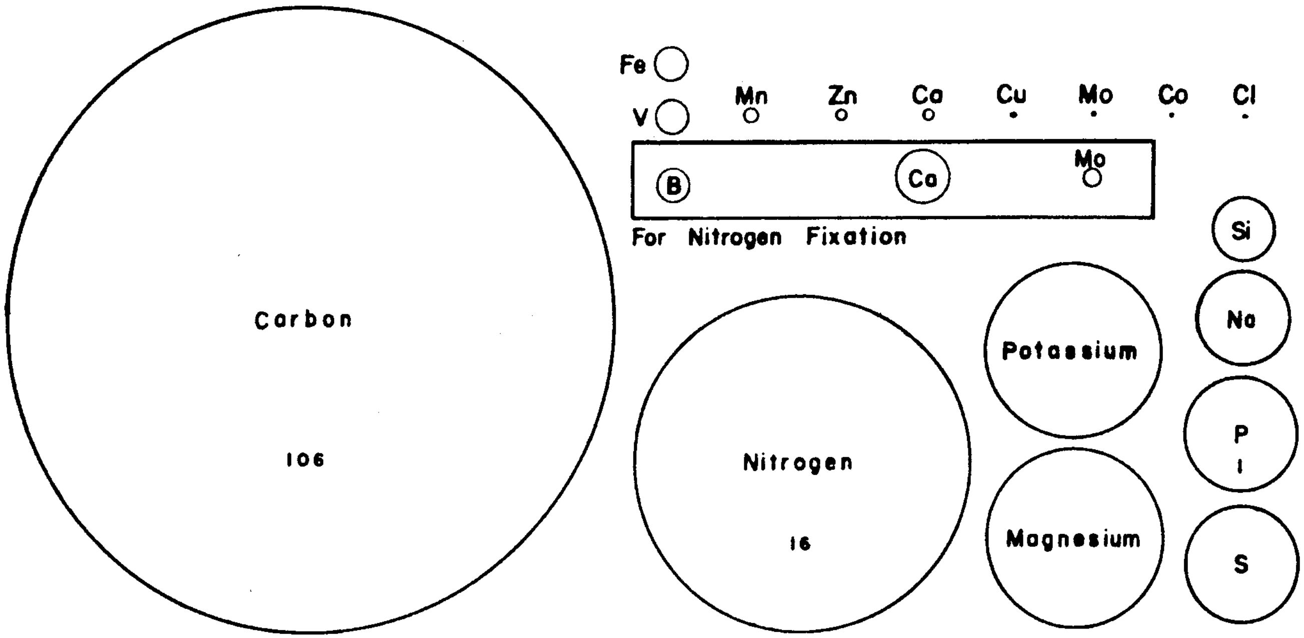


Figure 1 - Ratio of Growth Elements

The element which is present in the amount that is depleted first by the growing algae is the limiting element in that particular lake.

Table 2 considers some of these elements from a treatment standpoint. Oxygen, sulfur, hydrogen, carbon, and nitrogen at a point in the treatment sequence, either in an aerobic or anaerobic environment, can go through oxidation and reduction to a gaseous product. These elements are then lost to the atmosphere. Phosphorus compounds enter a treatment plant in their highest oxidized form and cycle between organic and inorganic phosphorus compounds. No common biological systems reduce phosphate. Phosphorus is conserved in the system. Once in an environmental system, phosphorus will cycle endlessly unless it is completely separated from the system by physical isolation, complete insolubility, or wash-out by dilution. In this context, to fully evaluate the environmental influence of phosphorus, an effort must be made to measure all the phosphorus contributing to the situation. Because of this cyclical pattern only a total phosphorus analytical procedure can indicate the reservoir of phosphorus available.

TABLE 2. ELEMENTS AND BIOLOGICAL TREATMENT

ELEMENT	BIOLOGICAL REACTION	RESULT OF TREATMENT NET LOSS
OXYGEN	OXIDATION AND/OR REDUCTION	CO_2 CH_4
CARBON		
HYDROGEN		H_2 H_2O
NITROGEN		N_2
SULFUR		H_2S
		NO LOSS
PHOSPHORUS	NO OXIDATION NO REDUCTION	ORGANIC PHOSPHORUS $\uparrow\downarrow$ INORGANIC PHOSPHORUS

Distribution of Phosphorus in Sewage

Three major classifications of phosphorus are present in untreated municipal wastewater, and are shown in Figure 2.4 The relative amounts shown are based on extensive laboratory testing of over thirty different wastes and are average values encountered. It can be seen that approximately one-third of phosphorus is in the soluble poly form, and one-third in the suspended form.

Suspended phosphorus originates from human waste, food scraps, and insoluble inorganic materials. Polyphosphorus consists mainly of pyro- and tripolyphosphates which are builders used in detergent formulations. Orthophosphate is derived directly from simple inorganic salts or indirectly as a degradation product of organic phosphorus compounds or soluble condensed phosphates. Poly- and suspended phosphorus can also be degraded by biological means or chemical hydrolysis into the orthophosphate form (Table 3).

TABLE 3

TYPES OF PHOSPHATE IN SEWAGE

Phosphate in solids:	Human wastes and food disposal. All cells contain from 3 to 10 % phosphate.
Polyphosphate:	Detergent binders
Orthophosphate:	Mainly degradation products

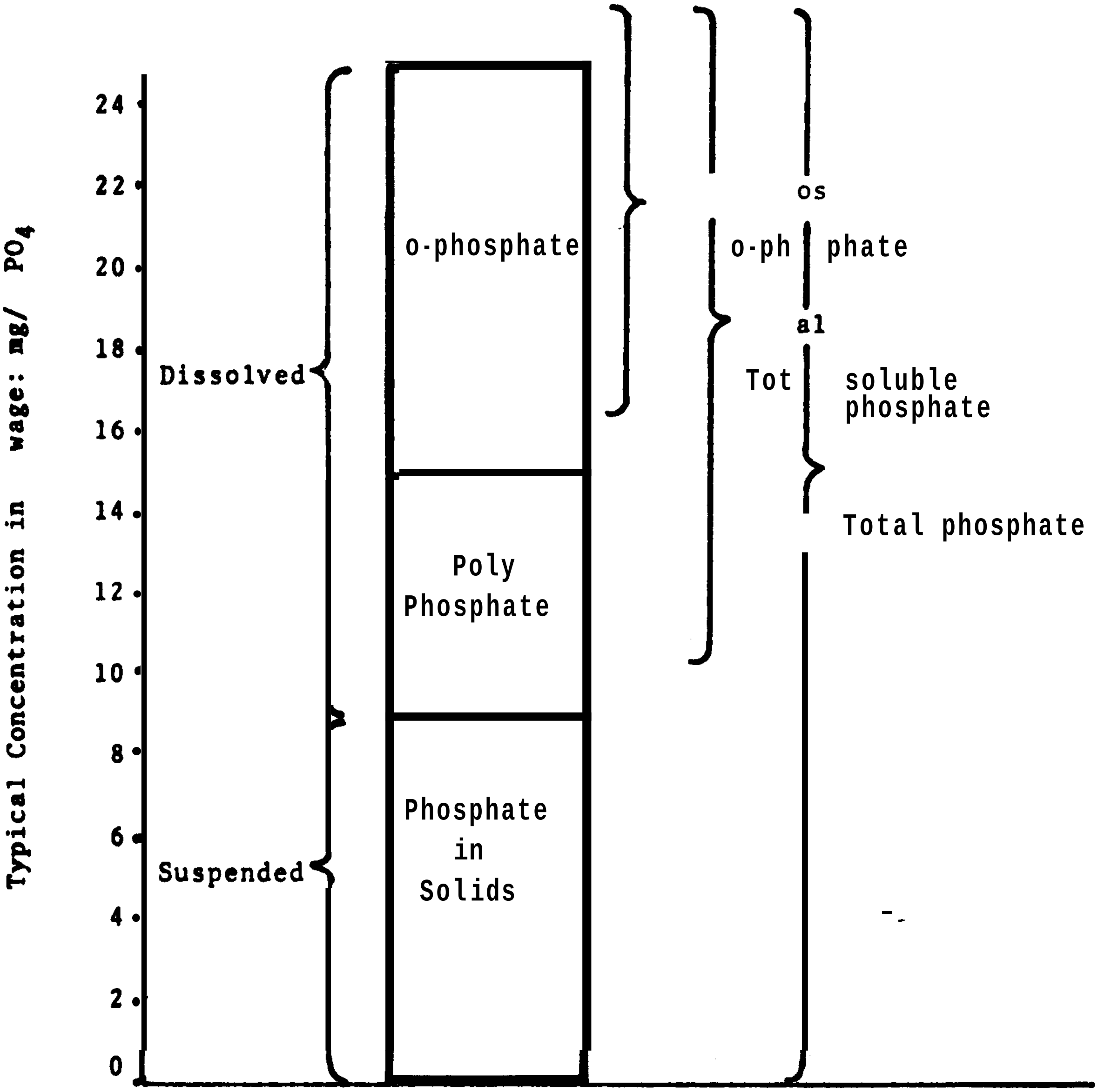


Figure 2 - Classification of PO_4

Significance of Chemical Coagulation

Laboratory studies of chemical coagulation are often required to determine the best chemical or combination of chemicals and quantities needed to accomplish a desired objective in water, sewage, and industrial waste treatment. The results obtained can serve as a basis of design and operation of treatment facilities.

The initial in-plant operation of the coagulation process is a rapid mix in which chemicals are added and distributed throughout the waste. The next stage consists of flocculation, a slow mix used for the purpose of promoting collisions between destabilized particles resulting in the formation of highly settling aggregates. The final operation in the process consists of separation of the destabilized aggregates from the suspending liquid by sedimentation as shown in Figure 3.[5]

Statement of Problem

The control of phosphorus in wastewater effluents centers around three major approaches. The biological approach operates on the principle that because phosphorus is such a key element in metabolism, organisms can be induced to take up more than their normal share of phosphorus. The inducements are in the form of the control of aeration rates, dissolved oxygen, food/microorganism ratios, residence or retention times of the active sludge in the various unit processes.

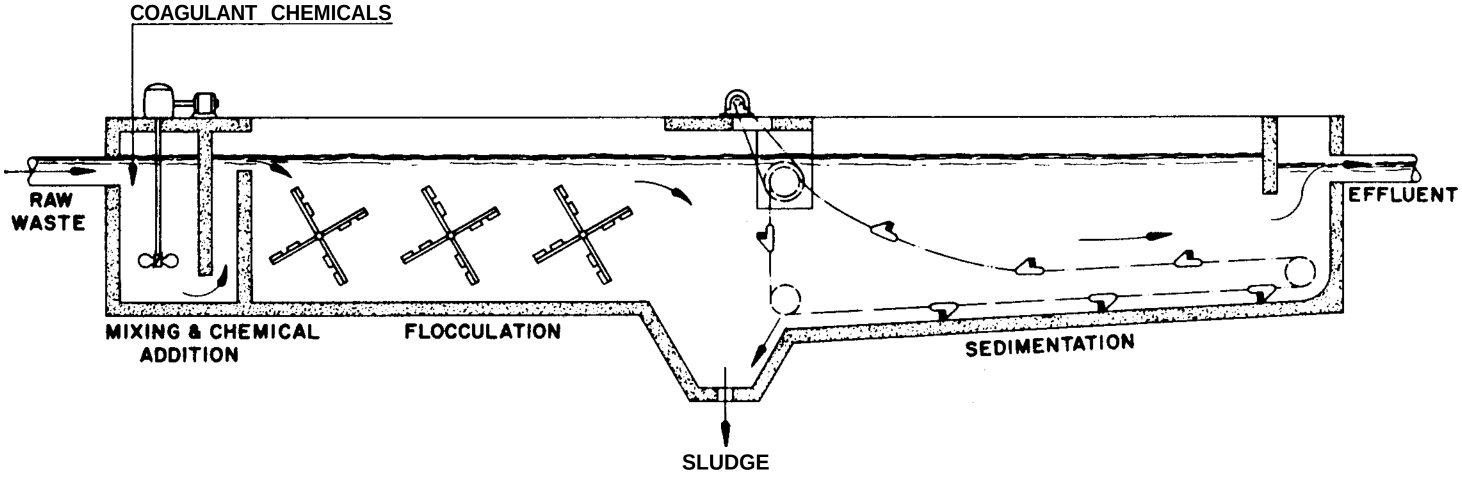


Figure 3 - In Plant Coagulation Process

The chemical approach carries out chemical operation on the effluent from a biological process or any of the input streams to the treatment plant. The objective here is to form a separable sludge containing slightly soluble phosphorus compounds. Because of the clarifying and adsorptive capacities of the compounds used in this method, highly efficient biological treatment is not of great importance.

The third approach combines both the biological and chemical control methods. Materials that form slightly soluble phosphorus compounds are introduced directly to the active microorganisms of the mixed liquor. Additives such as aluminum salts cause no interference in the biological activity, and the mixing and detention times provided an the aeration tank automatically allow for the efficient formation of precipitates. There is no increase in the volume of sludge produced because the chemical additive improves the settling characteristics of the mixed liquor. Overall, the chemical process stabilized the biological process.

The Clean Water Act of 1972 placed restrictions on point source phosphorus discharges to a maximum of 1.0 mg/L total phosphorus for most receiving waters. At present the City of Youngstown Wastewater Treatment Plant doesn't have to meet this criterion to discharge into the Mahoning River. This investigation concentrates on the chemical approach to phosphorus removal. In this study, various metallic salts are independently compared. Secondly, these are compared with the addition of an anionic organic polymer to each in an attempt to reduce the total phosphorus concentration of the City of Youngstown's wastewater to less than 1.0 mg/L as Federally mandated.

CHAPTER II

HISTORICAL REVIEW

Alum as a Coagulant

Alum (aluminum sulfate), the coagulant most widely used today, has an ancient background, being known to the early Egyptians of 2000 B.C. Its use, however, as a coagulant was first mentioned by Pliny (77 A. D.), who described the use of both lime (Chalk of Rhodes) and alum (Argilla of Italy) as useful for rendering bitter water potable.

Its use in large industrial plants seems to have begun in the early part of the nineteenth century. The earliest use of coagulation for the treatment of municipal water supplies occurred at Bolton, England, in 1881.

In the years 1895 to 1897 at Louisville, Kentucky, George Warren Fuller and his associates conducted a series of important experiments on turbid Ohio River water in which a series of coagulants was tried: alum or basic sulfate of alumina, potash alum, and lime. Of these alum was found most suitable.

By 1934, wastewater treatment: plants in 34 U.S. cities were using chemical coagulation and precipitation. Chemical use in wastewater declined in this country during World War II, and for some years thereafter, because of varying costs and limited availability of chemicals. With higher soluble organic removal requirements for secondary wastewater treatment, biological treatment gained favor, since chemicals were of limited use in the removal of soluble organics. Research over the past ten years in the area of physical-chemical treatment processes and widespread recognition of the need for nutrient (phosphorus) removal from effluents have resulted in a resurgence in the use of chemicals in wastewater treatment. Today. numerous treatment plants are being designed and operated using chemical for nutrient removal, as well as sludge conditioning, and as an aid to the sedimentation process.

CHAPTER III

PRESENT METHODS OF PHOSPHORUS ANALYSIS

Inductively Coupled Plasma - ICP

A number of publications have demonstrated that ICP analysis gives accurate results for a variety of 'samples, but there are few reports that describe applications where the ICP has been used as a tool for the evaluation of an environmental problem such as eutrophication.6

Wastewater samples deserve special attention, even though their analysis is apparently simple. One reason is that, depending upon the source, wastewater samples will have varying degrees of suspended solids. Samples to be analyzed on the ICP require filtration through a 0.45u millipore filter. In the event that filtration is omitted deliberately or unknowingly, such suspended particulates are incorporated into the plasma, dissociated, and excited in the intenseheat source. Solids in the ICP nebulizer can be a problem because the nebulizer is easily clogged by excessive amounts of undissolved solids such as those found in wastewater samples.

Colorimetric Methods

Phosphorus analyses encompass two general procedural steps (1). conversion of the phosphorus form of interest to dissolved orthophosphate, and (2). colorimetric determination of dissolved orthophosphate.

Because phosphorus may occur in combination with organic matter, a digestion method to determine total phosphorus must be able to oxidize organic matter effectively to release phosphorus as orthophosphate. Three digestion methods are commonly used. The perchloric acid method, the most drastic and time consuming, is recommended only for difficult samples such as sediments. The nitric acid - sulfuric acid method is recommended for most samples, and the simplest method is the persulfate oxidation technique.

Three colorimetric methods of orthophosphate determination are available for use. Selection will depend on the concentration and range of orthophosphate. The vanadomolybdic acid method is most useful for routine analysis in the range of 1 to 20 mg P/L. The stannous chloride method or the ascorbic acid method is more suited for the range of 0.01 to 6 mg P/L.

For the purposes of this thesis, all total phosphorus analysis were conducted by approved analytical methods cited in regulations contained in Title 40 of the Code of Federal Regulations (C.F.R., July 1, 1980), primarily Part 136 (the NPDES regulations approving water methods) and Part 141 (the safe drinking water regulations).

At this time, the only EPA approved test procedure for total phosphorus is the persulfate digestion method followed by manual or automated ascorbic acid reduction. The results acquired from these methods were periodically checked by performing an ICP determination of phosphorus on the previously-analyzed samples.

CHAPTER IV

THEORY OF PHOSPHORUS REMOVAL

Coagulation

In wastewater terminology, coagulation refers to the addition of chemicals to a wastewater influent to combine small dispersed particles into larger agglomerates which may be removed by some other method such as filtration, air flotation, or sedimentation. Most coagulation operations are intended to lower the soluble phosphate level in wastewater by precipitation, but additional benefits are often obtained by lowering the level of suspended solids found in wastewater which also contain phosphates.

Properties of Suspended Particles

The sizes of the various components which are involved in coagulation can vary by many orders of magnitude as seen in Table 4.7 Analysis of the total solids in wastewater would include all sizes, from individual ions up to visible particles, all giving wastewater its turbidity. The soluble fraction usually has a size < 10Å while the colloidal particals can lie between 10 - 10,000Å in diameter with the suspended solids being between the soluble and settleable size (10 - 1,000,000Å).

TABLE 4

DISTANCES INVOLVED IN COAGULATION

Colloidal Systems:	
Color bodies	50-1000Å
Inert bodies	1000-30,000Å
Emulsions	2000-100,000Å
Bacteria	5000-100,000Å
Algae	50,000-8,000,000Å
Cations:	1-2Å
Polyelectrolytes:	250,000-40,000,000Å
Electrical Double Layer:	5-100Å
Water:	4Å

The stability of the colloids to remain suspended in water is related to the electrical charges carried by the individual particles causing their mutual repulsion. In most wastewater situations, the charge on organic, inorganic, and biocolloids is negative when suspended in water and is possibly caused by lattice imperfections, ionizable groups (amino, carboxyl, and hydroxyl), or ionic materials adsorbed from the water. The destabilization of a suspension by chemical treatment is directed toward neutralization or reducing the electrical charge so that mutual repulsion is reduced and the particles will approach each other close enough to agglomerate.

The negatively charged colloid attracts a group of positive ions due to electrostatic forces. These positive ions are considered to be grouped into two broad layers: an inner layer, including adsorbed ions, and a diffuse layer, where the ions are randomly distributed due to electrical forces and fluid motion. Stern[8] proposed a model as shown in Figure 4.[9] about the thickness of a hydrated ion radius from the surface. Adsorbed ions are attached to the surface by electrostatic or van der Waals forces. Within the second diffuse layer is a shear plane which represents the limit to which counter ions can be swept from the surface by fluid motion. The ions within the shear plane move with the particle and those outside of it move independently of the particle and are subject to fluid and thermal motions.

Electrokinetic potentials are related to the mobile part of the particle. The electrical potential difference can be found between the surface of the shear plane and the bulk of the solution. This can be measured and is called the Zeta Potential (ZP). In the ZP measurement procedure, a sample of wastewater is placed in a cell under a microscope. When a voltage is applied to the electrodes at each end of the cell, the charged particles will move to the electrode having the opposite polarity. The velocity of the particle motion is measured and related by calibration to the charge on the particle at the shear plane.

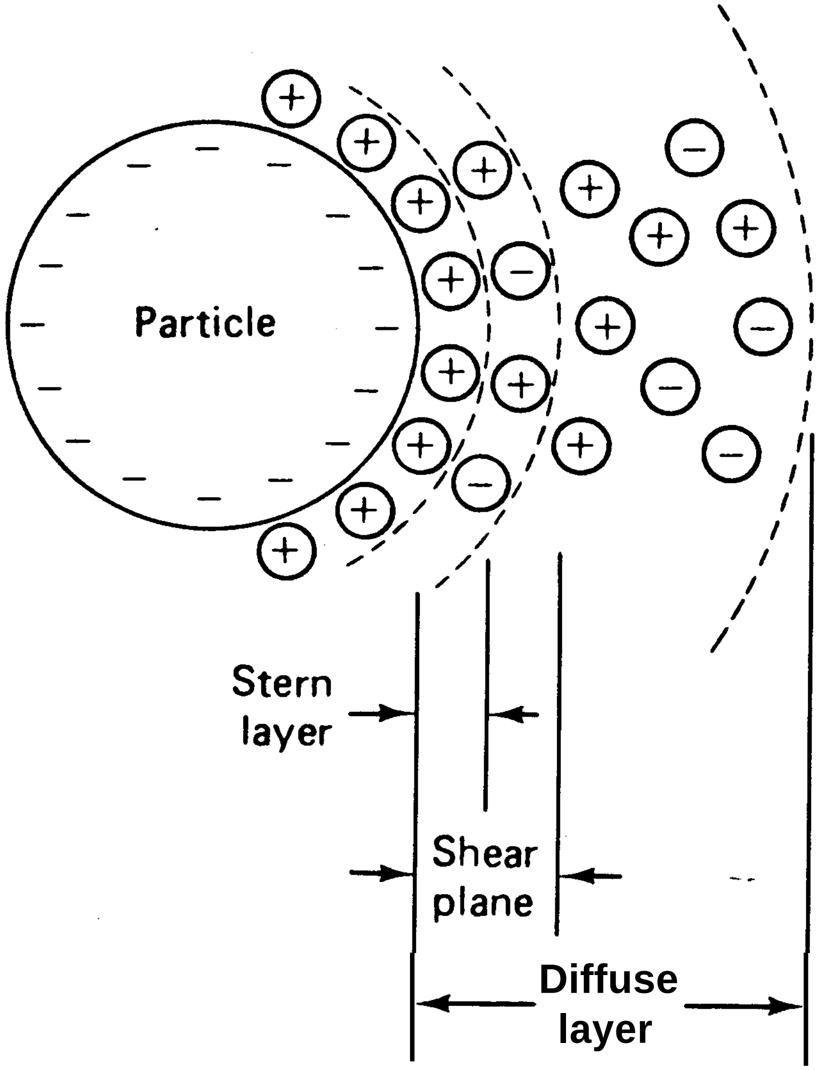


Figure 4 - Electric Double Layer

The ZP is used as a qualitative tool to predict the potential for coagulation. In natural water systems, colloidal suspensions are commonly found to possess ZPs of 20 to 30 mV and are negatively charged. In contrast, some wastewaters are found to have negative ZPs on the order of 40 or 50 mV. In order to achieve coagulation in most wastewater systems, the ZP must be reduced in value to less than 5 mV.[10]

The total potential energy between the colloidal particles is proportional to the sum of an attractive force and a repulsive force (Figure 5).[11] The attractive force is due to the London--van der Waals forces caused by dipoles set up between the nucleus and its surrounding electrons. These attractive forces drop with the distance proportional to 1/z (z=thickness of double-layer, cm). The repulsive forces are caused by coulombic repulsion of the charged particles and drop off with distance proportional to e $^{-2}$ (e=dielectric constant). The total potential energy required for separation of the colloids is characterized by a maximum potential energy which functions as an activation energy. If the maximum potential energy is much larger than the thermal energy, few colloidal particles will have enough energy to cross the potential barrier and no coagulation will occur. It is the purpose of coagulation chemicals to lower the energy barrier so that colloidal particles can approach each other close enough to allow the attractive forces to dominate.

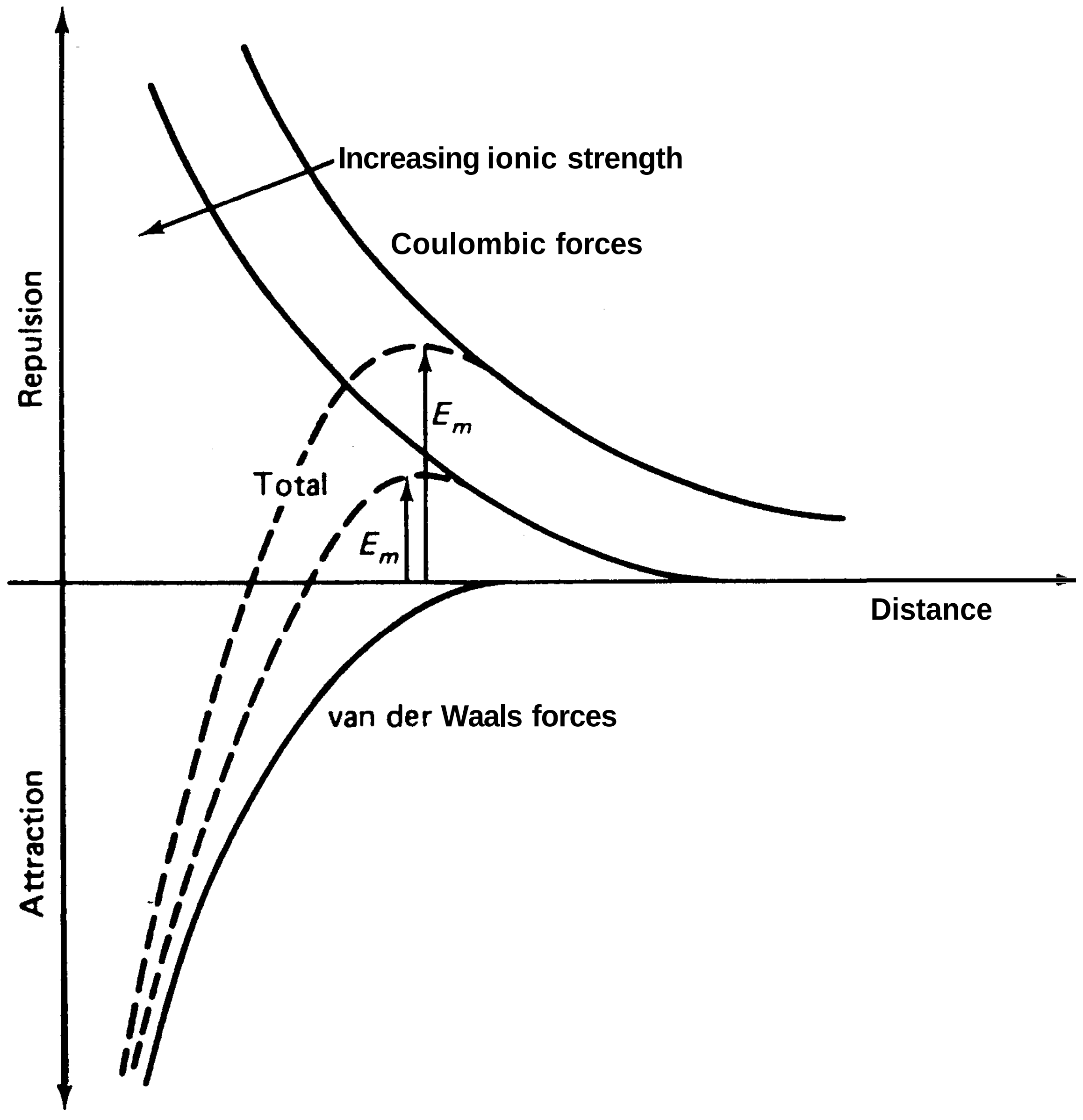


Figure 5 – Energy Forces Between Colloidal Particles

Destabilization Mechanisms

In order to get suspended particles to cluster into a large mass, the electrostatic repulsive forces must be overcome or suppressed. In wastewater terminology, this procedure is known as destabilization and may involve any of the following mechanisms: reduction of the surface charge by repression of the double-charge layer, charge neutralization by adsorption of counter-ions, bridging between particles by polymers, entrapment by formation of a sweeping floc.

Double-Layer Repression

The atmosphere of counter-ions in the wastewater surrounding the particle and the surface charges on it are known as the electrical double-layer. The distribution of counter-ions in the diffuse layer (Figure 4) functions in the same manner as the Debye-Huckel ionic theory predicts for strong electrolytes. The thickness of the double layer is arbitrarily taken as the distance from the surface at which the potential falls to 37 % of its surface value.

As ions are added to the wastewater, increasing the ionic strength, the repulsive forces are dissipated over shorter distances shifting the repulsive curve (Figure 5) to the left. For water and monovalent electrolytes, the thickness of the double-layer is approximately 10Å at 0.1 molar and 100Å for a 0.001 molar solution.

Some salt concentration may eventually be reached where the thickness of the double-layer is small enough to allow van der Waals forces to cause clumping. In the double-layer repression theory, the quantity of colloidal charges is not significantly reduced, but just the extent to which the charge extends from the surface, Since the ionic strength depends upon the square of the ionic charge the concentration of salts to achieve destabilization by charge dissipation decreases as the cation changes from Na^+ to Ca^{2+} to Al^{3+} to Zr^{4+}.

Charge Neutralization

This theory involves the attachment of the destabilizing chemical containing oppositely-charged ions to the suspended particle within the Stern layer such that the effective charge outside of the shear plane is reduced. In contrast to the double-layer repression, which alters the charge distribution within the diffuse layer, charge neutralization acts primarily within the mano-layer around the colloidal particle. Charge neutralization can result in charge reversal when excesses of a coagulant are added to wastewater.

Bridging

There has been a rapid increase in the use of organic polymers as destabilizing agents in the treatment of wastewater. Polymers contain many active sites along the chain where colloids can interact and become adsorbed. Under ideal conditions, suspended particles become attached to several sites along the polymer chain. Although the attractive adsorptive force between the colloid and organic polymer may be the same as in charge neutralization, destabilization results primarily by the slowing of the particle motion due to the bridges formed between the colloid particles. However, restabilization can occur when polyelectrolytes (polymers) are added in excess, because each suspended particle has its own organic polymer molecule, with few sharing a polymer chain and forming a bridge. Since the colloids retain most of their original charge after they are attached to the polymer, restabilization occurs due to coulombic repulsion.

Entrapment

If massive amounts of coagulants are added to the wastewater, they will form various hydrous polymers which will precipitate from solution. As these large, three-dimensional polymers form, the solids are trapped within the floc. The solids remain trapped within the settling floc and appear to be swept from the wastewater. Disadvantages to this procedure are the large amounts of metallic sludges which are produced. These metallic sludges are extremely difficult to dewater and are difficult to incinerate.

Flocculation

Sometimes flocculation and coagulation are used interchangeably, although a distinction should be made. Generally speaking, coagulation refers to the process of destabilization of colloidal particles by the addition of some material to the wastewater. Flocculation refers to the collision and aggregation of the destabilized solids into large flocs. Flocculation only describes the steps involving collision frequency and hydrodynamics of floc formation after the particles have been destabilized.

The coagulation-flocculation process is shown qualitatively in Figure 6.[12] The coagulant is added to the wastewater influent with rapid mixing and high turbulence. This is initially involved in destabilizing the particles and in precipitate formation of the dissolved phosphorus. The rapid mixing continues to promote the initial flocculation by collision of the primary particles. Once these particles have combined together to give larger aggregates to grow into a sufficiently large size that permits rapid removal by sedimentation, dissolved air floatation, or filtration. The flocculation process involves both a rapid mixing step that allows dispersion and initial aggregation of the particles and precipitates, and a slow mixing step where the aggregates can grow without high shear forces which can break up the flocs.

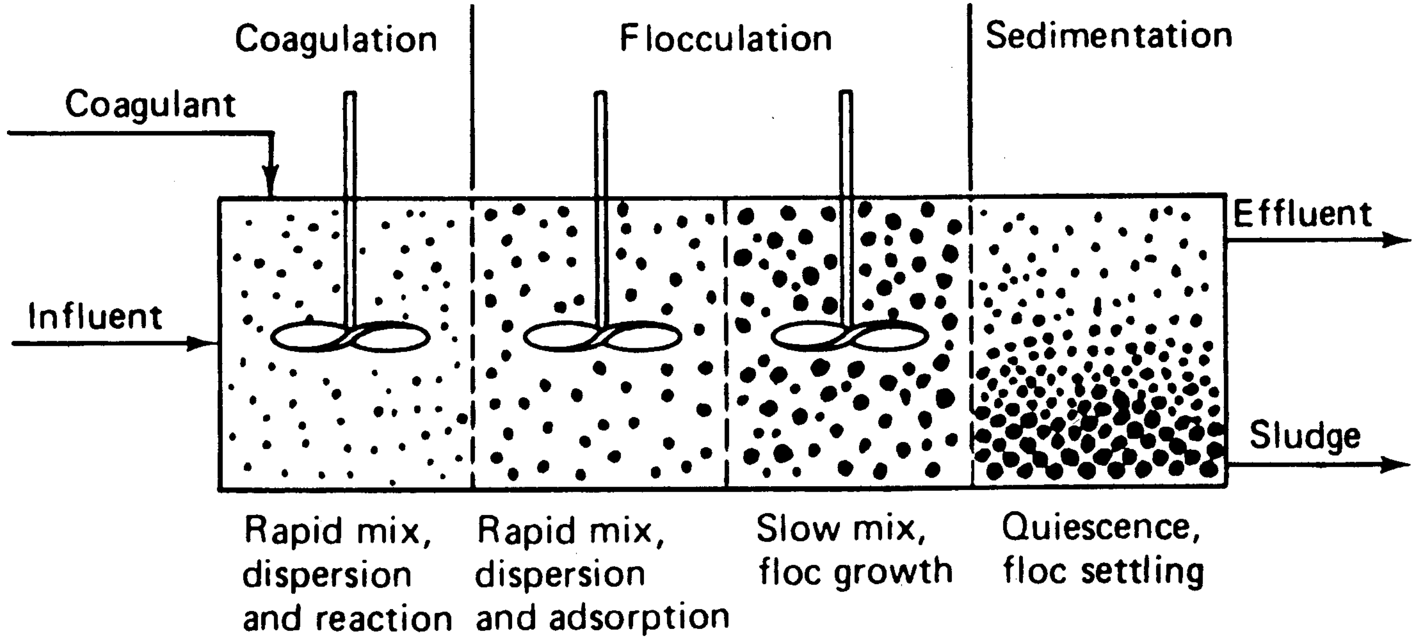


Figure 6 - Coagulation-Flocculation Process

Flocculation Model

Flocculation tanks are intended to promote contact between suspended particles. These collisions can occur either by random Brownian motion or by the forced collision of the colloidal particles due to the velocity gradients set up in fluid mixing. The latter method, known as orthokinetic flocculation, is the dominant mechanism used in wastewater to promote particle contact in the rapid mixing tanks. O'Melia[13] has derived a first-order model for batch flocculation treatment involving a collision frequency factor, n, the volume of colloidal particles per unit volume of suspension, ^, and a mean velocity gradient, Vg. If Np' is the number of separate particles initially, then the number of separate particles remaining, Np, after time t becomes

$$Ln[Np/Np'] = -4/-n\hat{}Vgt. \tag{1}$$

The mean velocity gradient given by Camp and Stein[14] is

$$Vg = [P/Vu]1/2, \tag{2}$$

where P is the power input to the fluid in the tank, V is the liquid volume in the tank, and u is the viscosity of the wastewater.

The slow mixing step is usually done with paddle type mixers for up to 60 minutes to allow the small flocs to combine into larger ones. Fiedler and Willus[15] have modeled this process with a second-order expression containing a delay time (detention time) to give

$$1/Np - 1/Np' = Kf(t-t0)U(t-td), \qquad (3)$$

where Kf is an empirical rate constant, U is a step function ($U=0$ for $t<td$ and $U=1$ for $t>td$), and td is the delay time. The delay time is inversely proportional to the initial colloidal concentration, Np', and must be experimentally determined for any wastewater. The rate constant Kf is usually independent of colloid concentration, but is influenced by both the time of mixing and the speed of the paddle type mixer.

The latter equation implies that in domestic wastewater treatment practice, with hydraulic detention times, td, generally in the range between 0.5 and 2.0 minutes, caution must be exercised to prevent either undermixing or overmixing. Undermixing will result in inadequate dispersal of coagulants causing uneven dosing. Overmixing may result in the rupture of wastewater solids already present in the water or cause excessive dispersal or break-up of newly-formed flocs.

Application to Phosphorus Removal

For the purposes of this investigation, the type of coagulant and its optimum concentration was evaluated in the laboratory using jars containing various doses of coagulants. The coagulants were tested in parallel using a variable speed, paddle type, gang stirrer. The efficiency of the coagulant (aluminum sulfate, iron(III) chloride, iron(II) chloride, and zirconium sulfate), with regard to phosphorus removal, was determined by measuring the total phosphorus before and after the addition of coagulant {with mixing) for each coagulant used.

Ascorbic Acid Method

The principal reaction is that of ammonium molybdate and potassium antimonyl tartrate reacted in an acid medium with orthophosphate to form a heteropoly acid phosphomolybdic acid. This is reduced to a molybdenum blue color by ascorbic acid.

Interferences to the reaction are arsenates which react with the molybdate reagent to produce a blue color similar to that formed with orthophosphate Concentrations as low as 0.1 mg arsenate/L interfere with the orthophosphate analysis. Hexavalent chromium and nitrite interfere to give results about 3 % low at concentrations of 1 mg/L and 10 to 15 % low at 10 mg/L.

Procedure

To 50 mL of previously digested sample 8.0 mL of combined reagent (50 mL of 5 N sulfuric acid, 5 mL potassium antimonyl tartrate, 15 mL ammonium molybdate, and 30 mL ascorbic acid) is added and mixed thoroughly. After 1.0 minutes, but in no longer than 30 minutes, the absorbance of the sample is measured at 880 nm. The total phosphorus is calculated from an individually-prepared calibration curve from a series of six standards with total phosphorus ranges of 0.50 ml/L to 5.0 mg/I. Absorbances vs. total phosphorus is then plotted in accordance to Beer's Law [16]

Jar Test Method

In wastewater treatment, there are so many different process methods for using coagulation and sedimentation that it is impossible to write a single standard procedure that will fit all possible applications. For this investigation, a standardized, recommended procedure for jar testing of water is used as a guideline as presented in the 1974 Annual Book of ASTM Standards (Part 31, titled "Standard Recommended Practice for Coagulation-Flocculation Jar Testing of Water" (Designation: D2035-74)).[17] Since wastewater treatment requires a special emphasis on parameters such as sludge volume, sludge age, and variations in hydraulic and solids loadings to the system, a slightly modified procedure is used for this investigation.

Procedure

A series of six 1-liter beakers is used, each containing 500 mL of sample (raw domestic sewage). The desired amount of metallic cation is added to each sample (ranging from 20 mg/L to 129 mg/L cation) while stirring the samples vigorously. One minute after cation addition the anionic polyelectrolyte is added. This flash mixing is done at 100 rpm and lasts for two minutes. The samples are flocculated for 25 minutes while being mixed gently at a paddle speed of 45 rpm. The six samples are allowed to settle for a period of 25 minutes.

At the end of the 25-minute settling period, 20 mL of the clarified wastewater is drawn off with a glass hypodermic syringe and analyzed for total phosphorus by the method indicated previously. Total suspended solids and pH are also determined on each sample by approved EPA methods.[18]

During the jar test procedure, flocculation and sedimentation are reported on a subjective scale of relative floc size and relative rates of floc settling. The floc sizes are VS = very small, S = small, M = medium, L = large, and VL = very large. The floc settling rates are P = poor, F = fair, G = good, and E = excellent.

Summary of Methods

In this investigation, aluminum sulfate, iron(II) chloride, iron(III) chloride, and zirconium sulfate are compared separately in various concentrations to determine which metallic cation removes phosphorus most effectively. Secondly, a carboxyl-containing anionic polyelectrolyte is used in conjunction with the optimum concentration of each metallic cation to aid in floc formation and to possibly lower the optimum metallic anion concentration.

CHAPTER VI

MATERIALS & APPARATUS

Materials

The grade, formula, and manufacturer of the various reagents used are given in Table 5. The pH meter is standardized using Sargent-Welch standard buffer solutions in accordance with the meter manufacturer's two-buffer standardization recommendation.

Apparatus

Spectrophotometer

All absorption readings are taken on a Pye Unicam UV/VIS single beam spectrophotometer PU8600 series. Cuvets used are 10 mm silica and are a matched set.

Six Paddle Stirrer

Mixing is accomplished using a Phipps and Bird gang stirrer with flat paddles capable of mixing up to six samples simultaneously over a range of 10 to 100 rpm using a variable speed motor. A fluorescent lamp mounted below a translucent plastic is used as a base to provide diffused light through the floc samples (Figure 7, fluorescent base not shown).[19]

TABLE 5

LIST OF REAGENTS

Material/Formula	Grade	Manufacturer
Sulfuric Acid/H_2SO_4	Analyzed	Baker
Ammonium Persulfate/ $(NH_4)_2S_2O_8$	Analytical	Mallinckrodt
Sodium Hydroxide/NaOH	Reagent	Ricca
Phenolphthalein Indicator/ $C_{20}H_{14}O_4$	Certified	Fisher Scientific
Potassium Antimonyl Tartrate/$K(SbO)C_4H_4O \cdot 4H_2O$	Certified	Fisher Scientific
Ammonium Molybdate/ $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Certified	Fisher Scientific
L-(+)-Ascorbic Acid/$C_6H_8O_6$	Reagent	Eastman Kodak
Potassium Dihydrogen Phosphate/KH_2PO_4	Certified	Fisher Scientific
Ferric Chloride/$FeCl_3$	Purified	Fisher Scientific
Aluminum Sulfate/ $Al_2(SO_4)_3 \cdot 18H_2O$	Analyzed	Baker
Ferrous Chloride/ $FeCl_2 \cdot 4H_2O$	Analyzed	Baker
Zirconium Sulfate/ $Zr(SO_4)_2 \cdot 4H_2O$	Laboratory	Al-Don Chemicals
Liquid Anionic Flocculant/ Unknown	Practical	Nalco

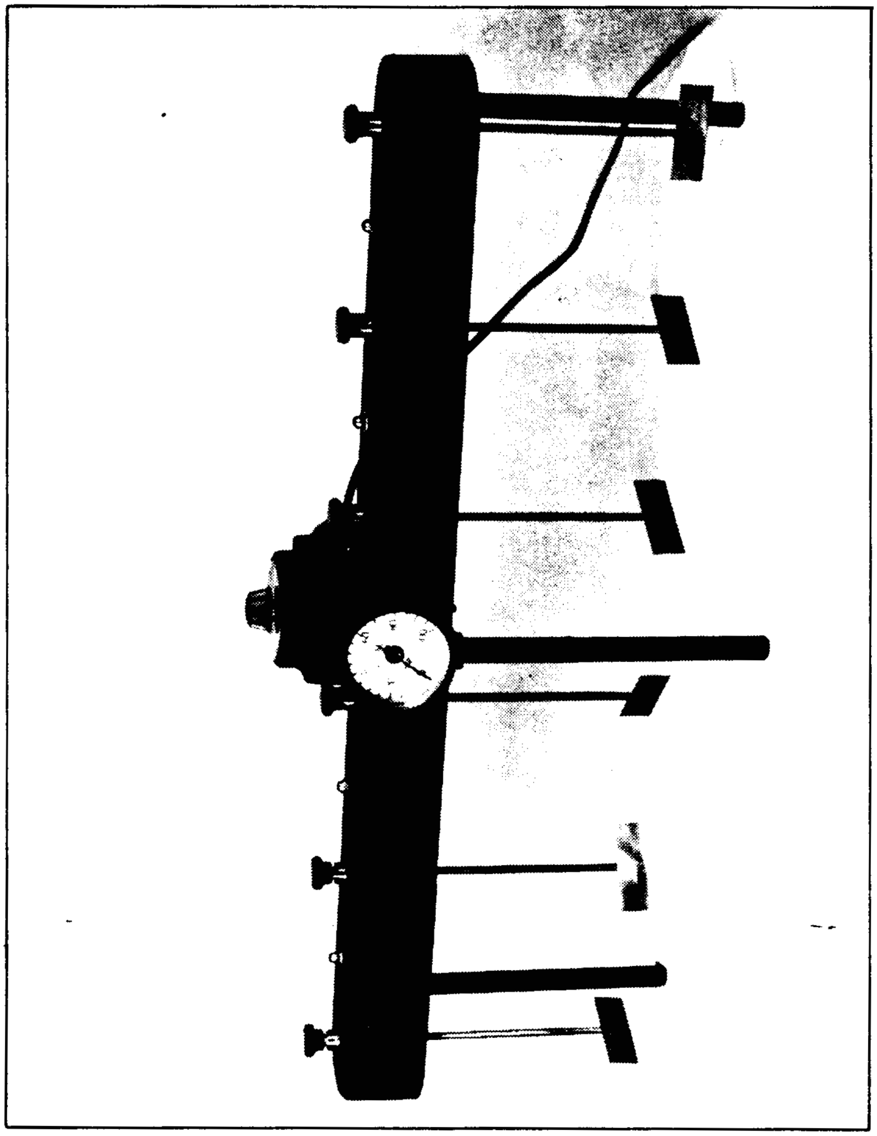


Figure 7 - Six Paddle Stirrer

Miscellaneous Apparatus

A Mettler EA 163 analytical balance is used for all suspended solids determinations and to weigh out reagents. An Orion 407L pH meter is used for all pH measurements.

Nalco 7766 Flocculant

Nalco 7766 is a liquid polymer of high molecular weight. It has a moderate anionic charge in solution and a typical density of 8.7 lb/gal. The pH of a 1 % solution can range between 7-8 and the polymer has a freezing point of 17 degrees F. Nalco 7766 has been approved by the United States EPA for use in systems when the dosages do not exceed 1 mg/L of the water flow.

CHAPTER VII

DISCUSSION, RESULTS, and CONCLUSIONS

Introduction

The precipitation and flocculation studies were evaluated on grab samples collected at the head of the trash rake at Youngstown's Wastewater Treatment Plant. The grab samples were taken on different days and at different times of the day to represent the changing conditions of influent wastewater. The systems were evaluated on the basis of three criteria: (1) concentration of metallic ion that meets discharge limits of less than 3.00 ml/L total phosphates, (2) ion/P weight ratio, and (3) per cent removal of total phosphates. The polymer was evaluated on whether it was an aid to phosphorus removal and the concentration that exhibited best phosphorus removal.

Aluminum Sulfate System

Aluminum sulfate (alum) is an acidic salt containing considerable water of hydration. In aqueous solutions it forms various hydrolyzed cationic species, reduces the pH, and forms insoluble precipitates with soluble phosphorus species. This system generally produces a lighter floc than the iron(III) system, to be mentioned later, and has a narrower effective concentration range.

It produces very clear supernates in combination with the proper flocculant (polymer). Increased amounts of alum result in increased insolubilization of soluble phosphorus following its solubility product. [illegible] of total suspended solids is also increased up to a point where hindrance can occur by the formation of excess aluminum hydroxide floc. Alum's role in phosphorus removal includes precipitation of phosphates as aluminum phosphate, as well as phosphate absorption in the floc mass produced in the hydrolysis reaction. Alum's function in illustrated as follows:

$$Al_2(SO4)_3 + 2PO_4 \dashrightarrow 2AlPO_4 + 3SO_4. \qquad (4)$$

The hydrolysis reaction with natural alkalinity is represented as follows:

$$Al_2(SO4)_3 + 3CaCO_5 \dashrightarrow 2Al(OH)_3 + 3CaSO_4 + 3CO_2, \qquad (5)$$

As the above reaction indicates, the addition of alum will lower the pH of the wastewater because of the neutralization of alkalinity and release of carbon dioxide. The extent of the decrease in pH depends on the initial alkalinity of the wastewater. The higher the alkalinity the less is the pH decrease for a given alum dose. Since the wastewater used for this investigation contained sufficient alkalinity, the alum doses used did not lower the pH enough to require the addition of an alkaline substance (sodium hydroxide, soda ash, or lime) to raise the pH to the

Federally mandated minimum of 6.0 (see Tables 7 through 11).

Stoichiometry of The Aluminum Sulfate System

Aluminum ions can combine with phosphate to form aluminum phosphate as follows:

$$Al^{+3} + PO_4^{-3} \longrightarrow AlPO_4. \qquad (6)$$

The mole ratio for Al:P is 1:1 or Al/P=1 when both aluminum and phosphorus are expressed in terms of gram-moles or pound-moles. Using a weight basis this means that 27 pounds of Al can react with 95 pounds of phosphates to form 122 pounds of aluminum phosphate. Therefore each 95 pounds of phosphates contains 31 pounds P. The weight relationship between Al and P is 27 pounds to 31 pounds of P or 0.87 for this reaction (Table 6).

TABLE 6

STOICHIOMETRY FOR Al COMPOUNDS AND P PRECIPITATION

Mole ratio Al:P = 1:1
Weight ratio Al:P = 27:31 = 0.87:1
Alum, $Al_2(SO_4)_3 \cdot 18H_2O$, contains 8.1 % Al
Alum required per lb. of P = 0.87/0.08 = 10.7 lb.

Phosphate Removal With Variable Alum Concentrations

Tables 7, 8 and 9 illustrate the data obtained with the alum concentration ranging from 0 to 70 mg/L.

Figures 8, 9, and 10 are graphic representations of the total phosphate concentration after precipitation and sedimentation for a given alum concentration The graphs show that at about 70 mg/L the curve . to flatten indicating overdosing with aluminum sulfate. The Al:P weight ratios at 70 mg/L alum concentration are 2.7:1 (Table 7), 1.8:1 (Table 8), and 1.3:1 (Table 9). These ratios are higher because of the hydrolysis of alum. An average of 79 % removal of total phosphates was achieved meeting the discharge limit of 3.0 mg/L total phosphates only when the initial total phosphates concentration was less than 12.5 mg/L.

Aluminum Sulfate and 0.5 mg/L Polymer

Table 10 and Figure 11 show the data obtained when a polymer concentration of 0.5 mg/L is used in conjunction with variable alum concentrations. The addition of the polymer reduced the Al:P weight ratio to 1.0:1 at a 50 mg/L alum dosage with 88 % of the total phosphates removed. The bridging effects of the polymer were responsible for the increased removal of phosphorus and the lower amount of alum that had to be added.

Aluminum Sulfate and Variable Polymer Concentration

The alum dosage for this investigation was held constant at 50 mg/L. As the data suggests from Table 11 and Figure 12, an alum concentration of 50 mg/L and a polymer level of 0.5 mg/L are optimum values for this wastewater system to meet discharge limits. Restabilization of the wastewater occurs as the polymer concentration increases above 0.6 mg/L. The polymer range was 0 to 1.0 mg/L.

Data Summary

Aluminum sulfate can meet EPA guidelines of 1.0 mg/L total phosphorus more consistently with the aid of an anionic polyelectrolyte. Of course larger amounts of alum can be added to wastewater, but this 'swept floc' method produces large amount of metallic sludges which are difficult to dewater.

TABLE 7

ALUMINUM SULFATE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
ALUM., mg/L	0	30	40	50	60	70
Al^{+3}, mg/L	0.0	2.43	3.24	4.05	4.86	5.67
FLOCCULATION	–	VS	S	M	M	M
SEDIMENTATION	–	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	144	103	76	44	39	37
% TOTAL SS REMOVED	–	28	47	69	73	74
TOTAL P mg/L	2.83	1.79	1.49	1.09	0.84	0.69
TOTAL PO_4, mg/L	8.59	5.43	4.50	3.31	2.55	2.09
ΔPO_4, mg/L	-	3.16	3.09	5.28	5.04	6.50
ΔP, mg/L	-	1.03	1.33	1.72	1.97	2.12
A1:P RATIO	–	2.4	2.5	2.4	2.5	2.7
% REMOVAL, TOTAL P	–	37	48	61	70	76
pH	7.1	7.0	7.0	6.9	6.9	6.9

TABLE 8

ALUMINUM SULFATE, VARIABLE CONCENTRATION

BEAKER #	**1**	**2**	**3**	**4**	**5**	**6**
ALUM., mg/L	**0**	**30**	**40**	**50**	**60**	**70**
Al^{+3}, mg/L	0.0	2.43	3.24	4.05	5.46	5.67
FLOCCULATION	–	**VS**	**S**	**S-M**	**M**	**M**
SEDIMENTATION	–	**P**	**F**	**F-G**	**G**	**G**
TOTAL, SUSPENDED SOLIDS, mg/L	**181**	**135**	**103**	**60**	**49**	**41**
% **TOTAL SS REMOVED**	–	**25**	**43**	**67**	**73**	**77**
TOTAL P mg/L	**4.03**	**2.56**	**2.22**	**1.68**	**1.11**	**0.84**
TOTAL PO_4, mg/L	12.24	7.76	6.72	5.09	3.37	2.57
ΔPO_4, mg/L	-	4.48	5.52	7.15	8.87	9.67
ΔP, mg/L	-	1.46	1.80	2.33	2.89	3.15
A1:P **RATIO**	–	**1.6**	**1.8**	**1.7**	**1.7**	**1.8**
% **REMOVAL, TOTAL P**	-	37	45	58	72	79
	7.0	7.0	6.9	6.9	6.9	6.9

TABLE 9

ALUMINUM SULFATE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
ALUM., mg/L	0	30	40	50	60	70
Al^{+3}, mg/L	0.0	2.43	3.24	4.05	5.46	5.67
FLOCCULATION	–	S	S	M	M	M-L
SEDIMENTATION	–	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	154	119	87	56	45	32
% TOTAL SS REMOVED	–	23	44	64	71	a9
TOTAL P mg/L	5.66	3.36	2.84	1.78	1.80	1.05
TOTAL PO_4, mg/L	17.15	10.18	8.62	5.40	5.46	3.19
ΔPO_4, mg/L	-	6.97	8.53	11.75	11.69	13.95
ΔP, mg/L	-	2.27	2.78	3.83	3.81	4.55
Al:P RATIO	–	1.1	1.2	1.4	3.4	1.3
% REMOVAL, TOTAL P	–	41	50	69	68	81
pH	6.9	6.9	6.8	6.7	6.7	6.6

TABLE 10

ALUMINUM SULFATE AND 0.5 mg/L POLYMER

BEAKER #	1	2	3	4	5	6
ALUM., mg/L	0	30	40	50	60	70
Al^{+3}, mg/L	0.0	2.43	3.24	4.05	4.86	5.67
NALCO 7766 mg/L	0.5	0.5	0.5	0.5	0.5	0.5
FLOCCULATION	–	S	M	M-L	S	S
SEDIMENTATION	–	P	F	G	P	P
TOTAL, SUSPENDED SOLIDS, mg/L	2.08	110	62	49	33	29
% TOTAL SS REMOVED	–	47	70	76	84	86
TOTAL P mg/L	4.44	3.47	2.17	0.53	1.10	1.06
TOTAL PO_4, mg/L	13.46	10.53	6.58	1.63	3.36	3.20
ΔPO_4, mg/L	-	2.93	6.88	11.83	10.10	10.26
ΔP, mg/L	-	0.97	2.27	3.90	3.33	3.39
Al:P RATIO	–	2.5	1.42	1.01	1.5	1.7
% REMOVAL, TOTAL P	-	22	51	88	75	76
	7.3	7.1	7.0	7.0	6.8	6.7

TABLE 11

ALUMINUM SULFATE AND VARIABLE POLYMER CONCENTRATION

BEAKER #	1	2	3	4	5	6
ALUM., mg/L	0	50	50	50	50	50
Al^{+3}, mg/L	0.0	4.05	4.05	4.05	4.05	4.05
NALCO 7766 mg/L	0.0	0.10	0.30	0.50	0.70	1.00
FLOCCULATION	–	S	S	M	M	L
SEDIMENTATION		P	P	F	F	G
TOTAL, SUSPENDED SOLIDS, mg/L	------------------------------------					
% TOTAL SS REMOVED	------------------------------------					
TOTAL P mg/L	5.24	2.27	1.42	0.37	0.46	0.51
TOTAL PO_4, mg/L	15.89	8.24	4.29	1.11	1.39	1.55
$\triangle PO_4$, mg/L	–	7.65	11.60	14.78	14.50	14.34
$\triangle P$, mg/L	–	2.52	3.83	4.87	4.79	4.73
Al:P RATIO		1.61	1.06	0.83	0.85	0.86
% REMOVAL, TOTAL P		48	73	93	91	90
pH	7.1	7.2	7.1	7.0	7.0	7.0

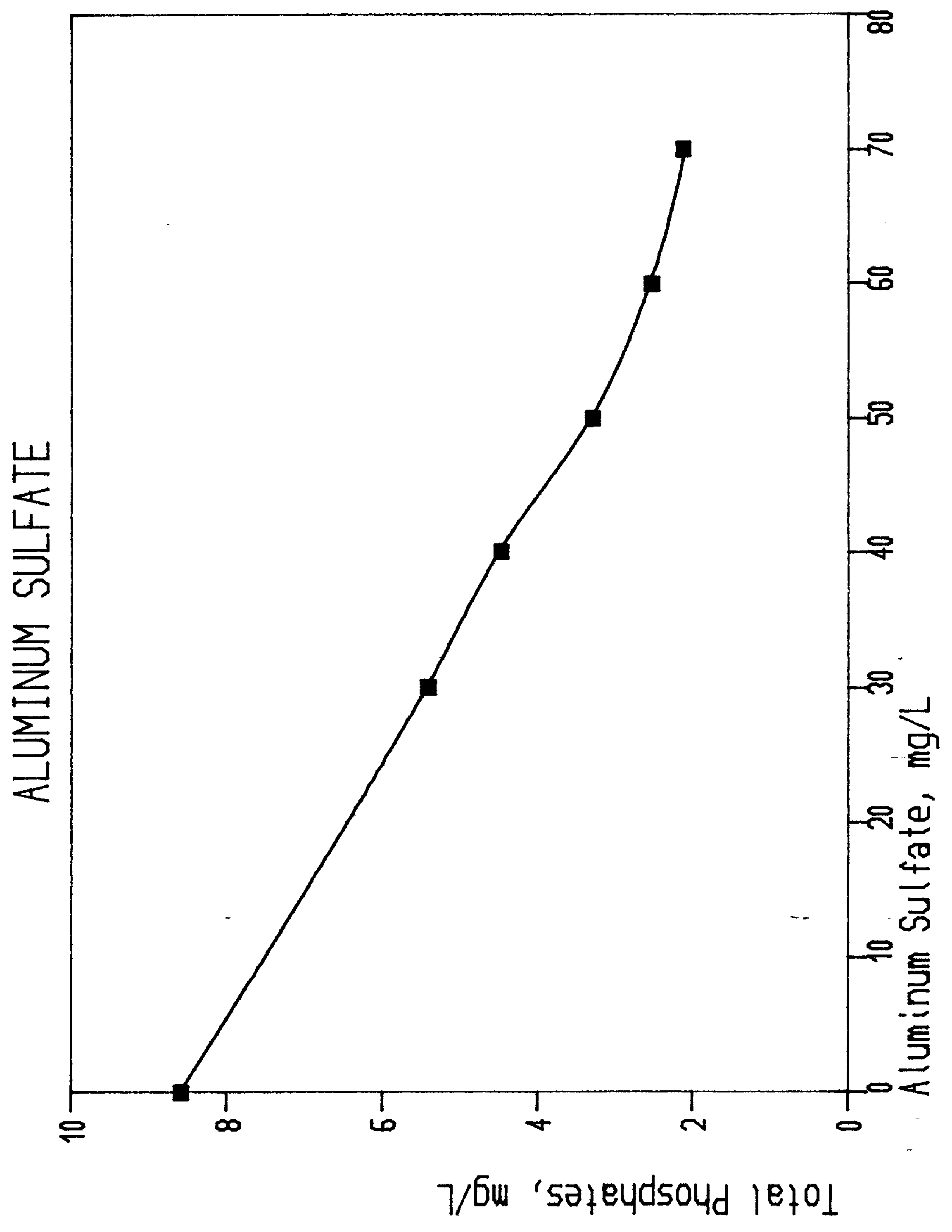
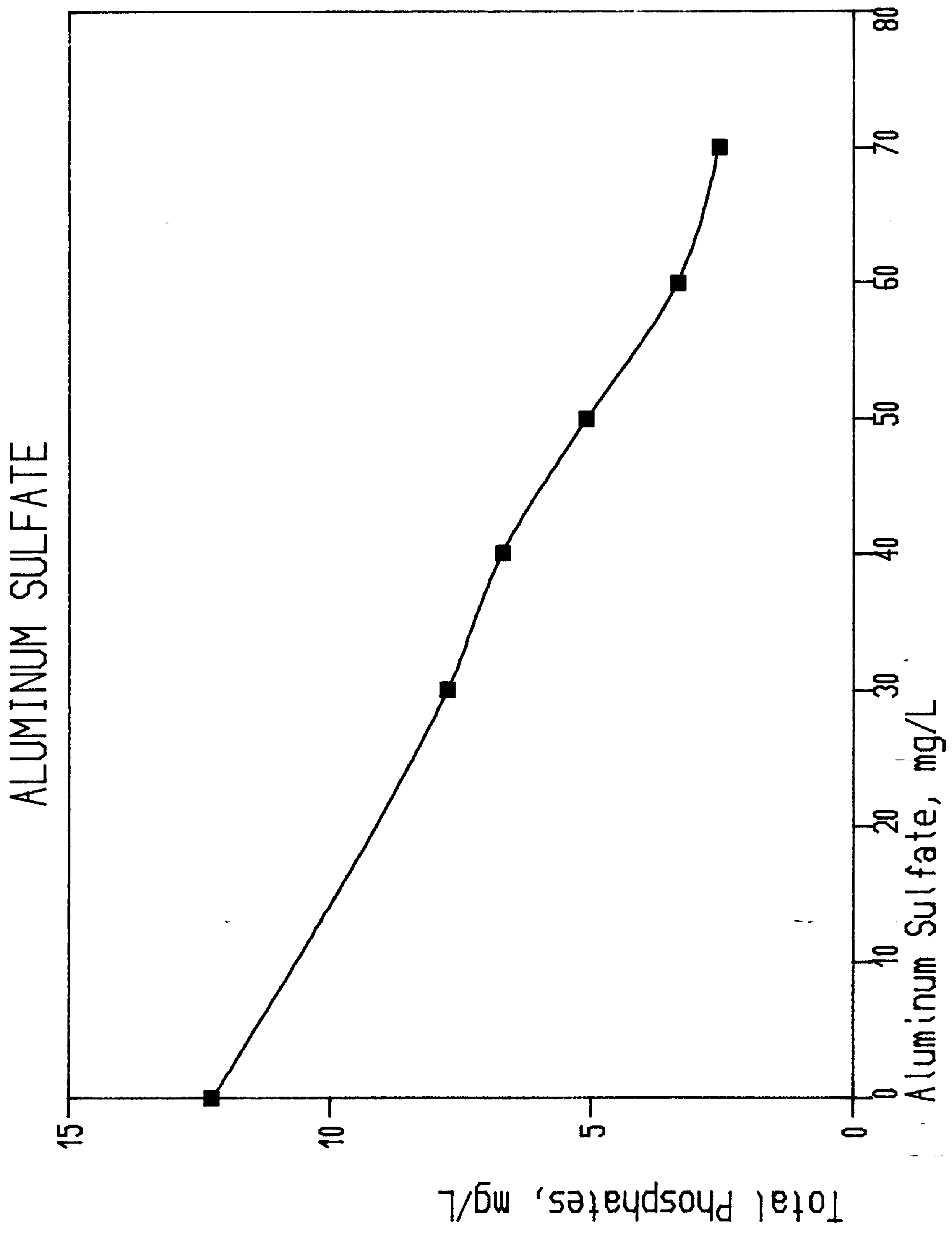

ALUMINUM SULFATE
Total Phosphates, mg/L
Aluminum Sulfate, mg/L
0
2
4
6
8
10
0
10
20
30
40
50
60
70
80

Figure 8


ALUMINUM SULFATE
Total Phosphates, mg/L
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10
5
0
Aluminum Sulfate, mg/L
0
10
20
30
40
50
60
70
80

Figure 9

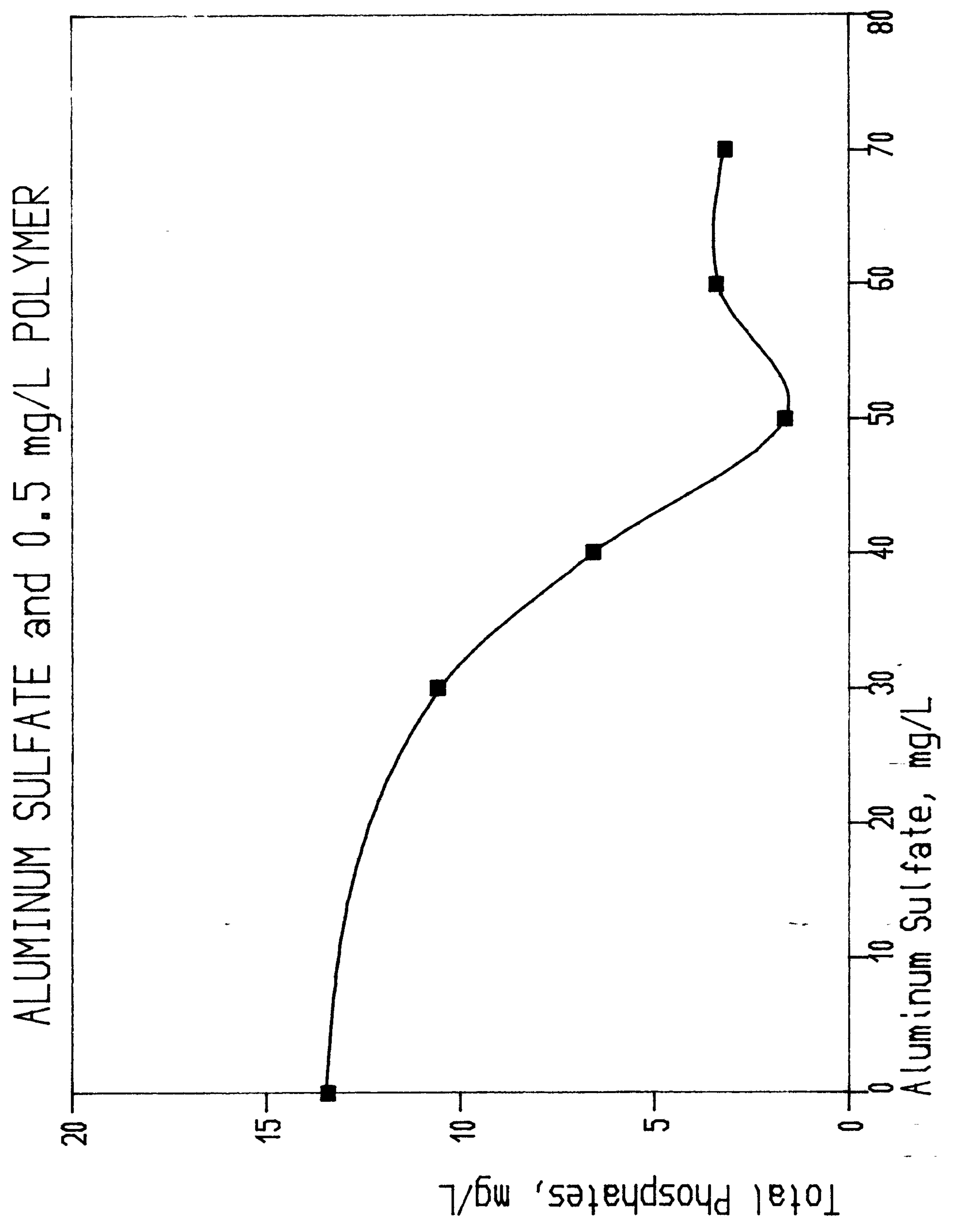

ALUMINUM SULFATE and 0.5 mg/L POLYMER
Total Phosphates, mg/L
0
5
10
15
20
Aluminum Sulfate, mg/L
0
10
20
30
40
50
60
70
80

Figure 11

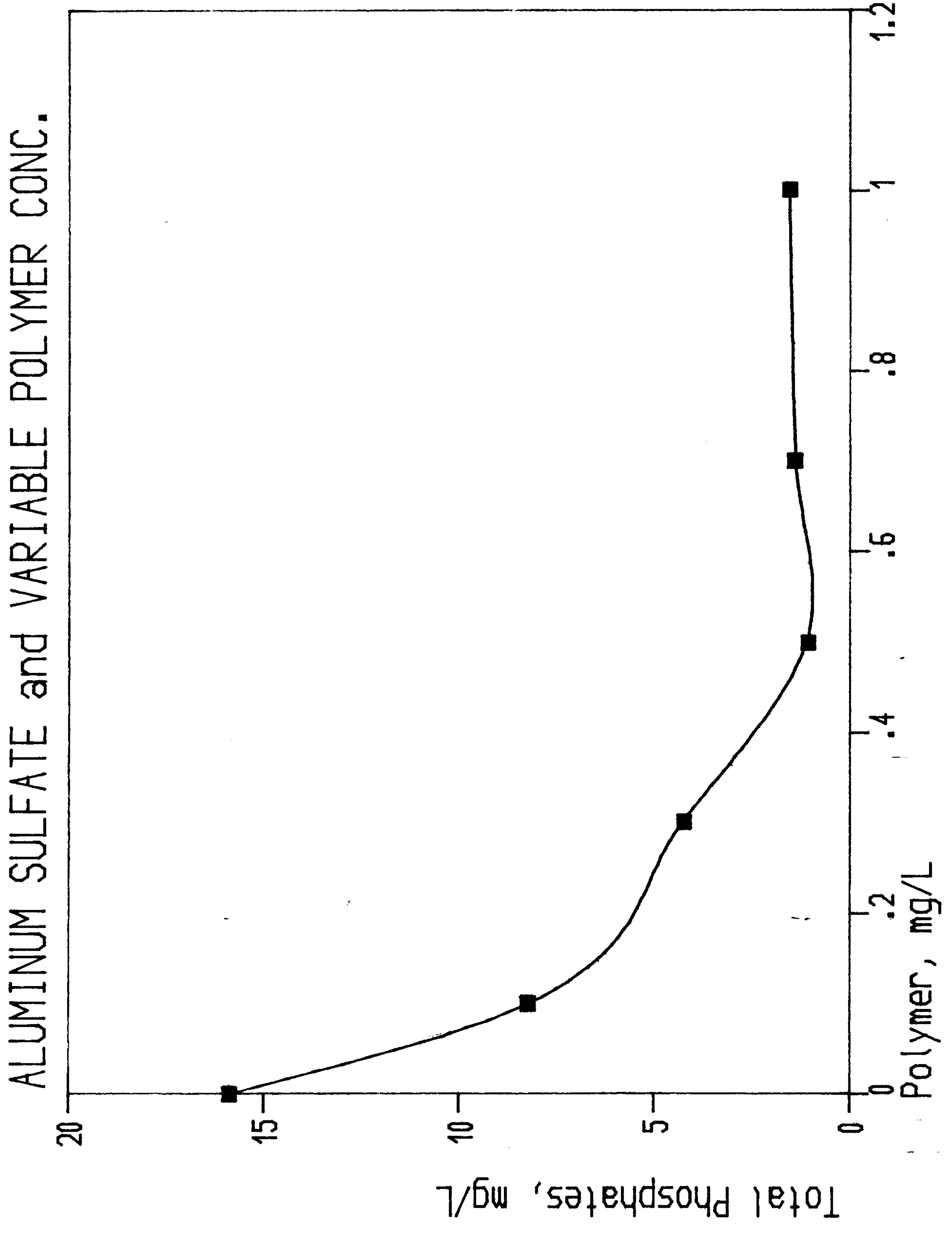

ALUMINUM SULFATE and VARIABLE POLYMER CONC.
Total Phosphates, mg/L
20
15
10
5
0
Polymer, mg/L
0
.2
.4
.6
.8
1
1.2

Figure 12

Iron(III) Chloride System

Iron(III) chloride is an acidic salt which, upon the addition to sewage, will, like alum, reduce the pH. The iron(III) system is generally very amenable to precipitation with a broad effective range. Large, dense flocs are produced which are fairly resistant to the high shear rates produced in pipes and open channels. Iron(III) chloride's action in wastewater is written similar to that shown for the precipitation of aluminum phosphate and will not be shown.

Stoichiometry of The Iron(III) Chloride System

Iron(III) ions can combine with phosphate to form iron(III) phosphate as follows:

$$Fe^{+3} + PO_4^{-3} \dashrightarrow FePO_4. \qquad (7)$$

Again, the mole ratio for Fe:P is 1:1 or Fe/P=1 when both iron(III) and phosphorus are expressed in terms of gram-moles or pound-moles. Using a weight basis this means that 56 pounds of iron(III) can react with 95 pounds of phosphate to form 151 pounds of iron(III) phosphate. Since each 95 pounds of phosphate contains 31 pounds of P, the weight relationship between Fe and P is 56 pounds of Fe to 31 pounds of P or 1.8 for this reaction (Table 12).

TABLE 12

STOICHIOMETRY FOR IRON(III) COMPOUNDS AND P PRECIPITATION

Mole ratio Fe:P = 3:1

Weight ratio Fe:P = 56:31 = 1.8:1

Iron(III) chloride, $FeCl_3$, contains 34.4 % Fe

Iron(III) chloride required per lb. of P = 1.8/.33 = 5.39 lb.

Phosphate Removal: Variable Fe(III) Chloride Concentration

The data obtained from the three grab samples are seen in Tables 13, 14, and 15. The iron(III) chloride range was from 0 to 70 mg/L. Figures 13, 14, and 15 are graphs of the total phosphates concentration after precipitation and sedimentation with each iron(III) chloride dose. The iron(III) curves begin to flatten out and show signs of overdosing in the 45 to 70 mg/L range. The Fe:P weight ratios at 70 mg/L iron(III) chloride concentration are 4.3:1 (Table 13), 5.5:1 (Table 14), and 9.6:1 (Table 15). These values are higher than stoichiometric values because of hydrolysis of iron(III) chloride. The average total phosphate removal percentage was 77 %. But, this system met the EPA requirements of 3.0 mg/L only once, when the initial total phosphate level was less than 10.5 mg/L.

Iron(III) Chloride and 0.5 mg/L Polymer

The data shown in Table 16 and Figure 16 represent a grab sample that was precipitated with variable iron(III) levels and flocculated with 0.5 mg/L of polymer. With the help of the polymer bridging, total phosphate removal was increased to 85 % with a iron(III) chloride concentration of 50 mg/L. This compares to an average total phosphate removal percentage of 50 % at a 50 mg/L iron(III) chloride level without the use of a polymer. The Fe:P weight ratio was also reduced by use of the polymer.

Iron(III) Chloride and Variable Polymer Concentration

For this investigation, the iron(III) level was kept at 50 mg/L and the polymer dosage ranged from 0 to 1.0 mg/L. The data obtained are shown in Figure 17 and Table 17. A polymer dosage of between 0.4 and 0.5 mg/L can meet discharge limits with an initial influent total phosphate concentration of 17.0 mg/L.

Data Summary

Iron(III) chloride produced results similar to those of alum, but with the help of the polymer produced better total phosphate removal rates. Removal rates in excess of 80 % would be needed to meet discharge limits.

TABLE 13

IRON(III) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
Fe Cl_3, mg/L	0	30	40	50	60	70
Fe^{+3}, mg/L	0.0	10.02	13.76	17.20	20.67	24.08
FLOCCULATION	VS	S	S	M	M	M
SEDIMENTATION	P	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	198	152	112	66	48	36
% TOTAL SS REMOVED	-	23	43	67	76	82
TOTAL P mg/L	7.29	4.76	3.92	3.06	2.19	1.67
TOTAL PO_4, mg/L	22.09	14.42	11.89	9.28	6.63	5.08
ΔPO_4, mg/L	-	7.67	10.20	12.81	15.46	17.01
ΔP, mg/L	-	2.53	3.37	4.23	5.10	5.61
Fe:P RATIO	-	4.0	4.1	4.1	6.2	4.3
% **REMOVAL, TOTAL P**	-	35	46	58	70	77
	7.0	7.0	6.9	6.8	6.8	6.7

TABLE 14

IRON(III) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
$FeCl_3$, mg/L	0	30	40	50	60	70
Fe^{+3}, mg/L	0.0	10.02	13.76	17.20	20.67	24.08
FLOCCULATION	VS-S	S	S-M	M	M	M
SEDIMENTATION	P	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	82	61	47	29	18	12
% TOTAL SS REMOVED	–	26	43	65	78	85
TOTAL P mg/L	5.56	3.69	2.84	2.21	1.61	1.18
TOTAL PO_4 mg/L	16.84	11.17	8.62	6.70	4.89	3.57
ΔPO_4, mg/L	–	5.67	8.22	10.14	11.95	13.27
ΔP, mg/L	–	1.87	2.71	3.35	3.94	4.38
Fe:P RATIO	–	5.4	5.1	5.1	5.3	5.5
% REMOVAL, TOTAL P	–	34	49	60	71	79
pH	7.4	7.3	7.0	6.9	6.8	6.7

TABLE 15

IRON(III) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
$FeCl_3$, mg/L	0	30	40	50	60	70
Fe^{+3}, mg/L	0.0	10.02	13.76	17.20	20.67	24.08
FLOCCULATION	S	S	M	M	M	M
SEDIMENTATION	P	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	104	81	64	43	29	19
% TOTAL SS REMOVED	–	22	38	59	72	82
TOTAL P mg/L	3.41	2.15	1.75	1.31	1.03	0.88
TOTAL PO_4, mg/L	10.32	6.51	5.31	3.97	3.13	2.68
ΔPO_4, mg/L		3.81	5.01	6.35	7.19	7.64
ΔP, mg/L	–	1.26	1.65	2.10	2.37	2.52
Fe:P RATIO	–	8.0	8.3	8.2	8.7	9.6
% REMOVAL, TOTAL P	–	37	49	62	70	74
pH	6.8	6.7	6.6	6.5	6.3	6.2

TABLE 16

IRON(III) CHLORIDE AND 0.5 mg/L POLYMER

BEAKER #	1	2	3	4	5	6
Fe Cl_3, mg/L	0	30	40	50	60	70
Fe^{+3}, mg/L	0.0	10.02	13.76	17.20	20.67	24.08
FLOCCULATION	–	S	S	M	M	M
SEDIMENTATION	–	P	F	F	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	170	119	84	49	34	21
% **TOTAL SS REMOVED**	–	30	51	71	80	88
TOTAL P mg/L	6.41	2.82	2.43	0.99	0.64	0.46
TOTAL PO_4, mg/L	19.41	8.54	7.38	2.99	1.94	1.39
ΔPO_4, mg/L	–	10.87	12.03	16.42	17.47	18.02
ΔP, mg/L	–	3.59	3.97	5.42	5.77	5.95
Fe:P **RATIO**	–	2.79	3.47	3.17	3.58	4.05
% REMOVAL, TOTAL P	–	56	62	85	90	93
pH	7.2	7.1	7.1	7.0	7.0	6.9

TABLE 17

IRON(III) CHLORIDE AND VAIABLE POLYMER

BEAKER #	**1**	**2**	**3**	**4**	**5**	**6**
$Fe\ Cl_3$, mg/L	0	50	50	50	50	50
Fe^{+3}, mg/L	0.0	17.20	17.20	17.20	17.20	17.20
NALCO 7766, mg/L	**0.0**	**0.10**	**0.30**	**0.50**	**0.70**	**1.00**
FLOCCULATION	–	**S**	**S**	**S**	**M**	**L**
SEDIMENTATION	–	**P**	**P**	**F**	**G**	**G**
TOTAL P mg/L	**5.66**	**2.38**	**1.13**	**0.97**	**0.79**	**0.51**
TOTAL PO_4, mg/L	17.14	7.21	3.43	2.94	2.39	1.55
ΔPO_4, mg/L	–	9.93	13.71	14.20	14.75	15.59
ΔP, mg/L	–	3.28	4.52	4.69	4.87	5.14
Fe:P **RATIO**	–	**5.24**	**3.81**	**3.67**	**3.53**	**3.35**
% **REMOVAL, TOTAL P**	–	58	80	83	86	91
pH	7.1	7.0	7.0	6.9	6.9	6.8

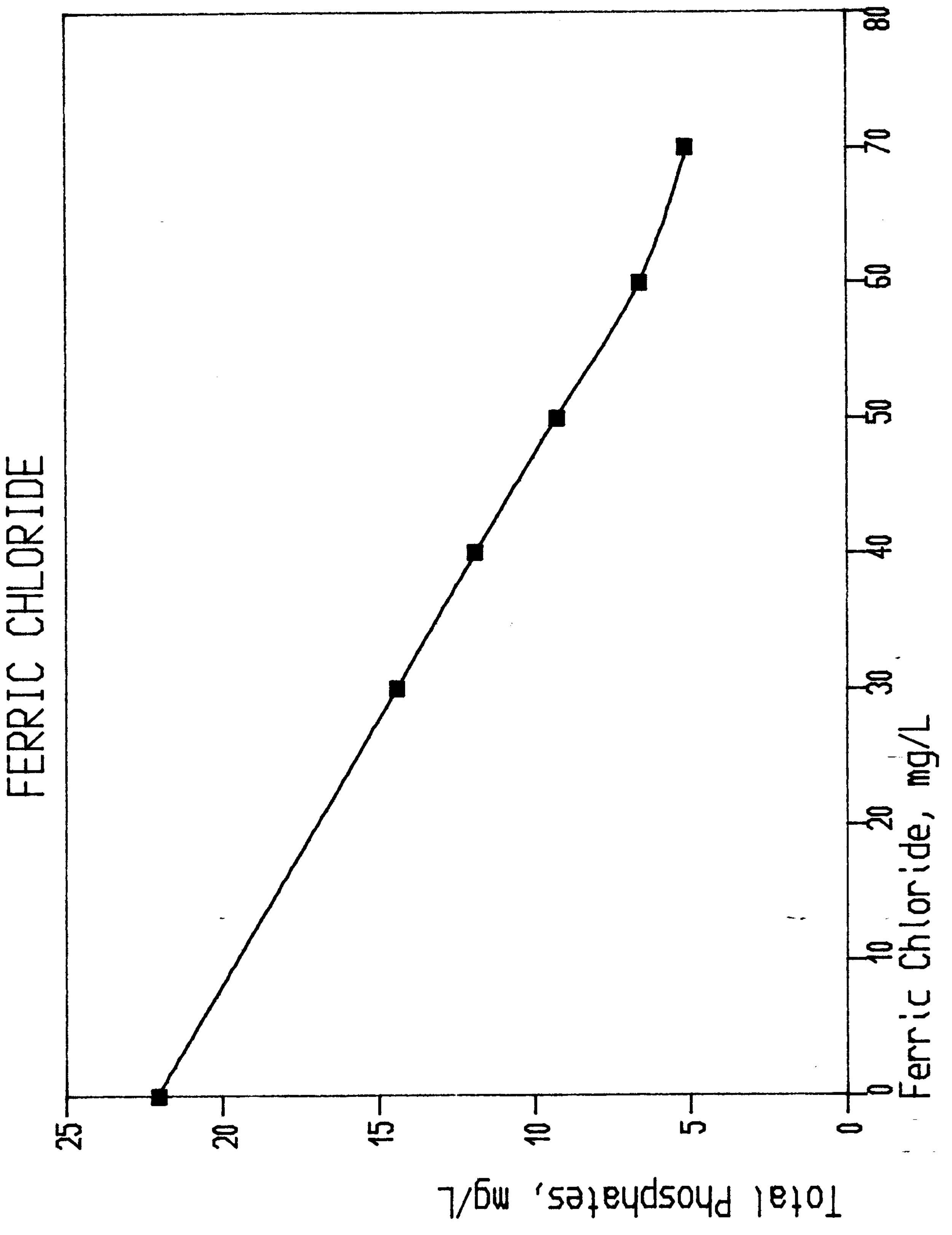

FERRIC CHLORIDE
Total Phosphates, mg/L
0
5
10
15
20
25
Ferric Chloride, mg/L
0
10
20
30
40
50
60
70
80

Figure 13

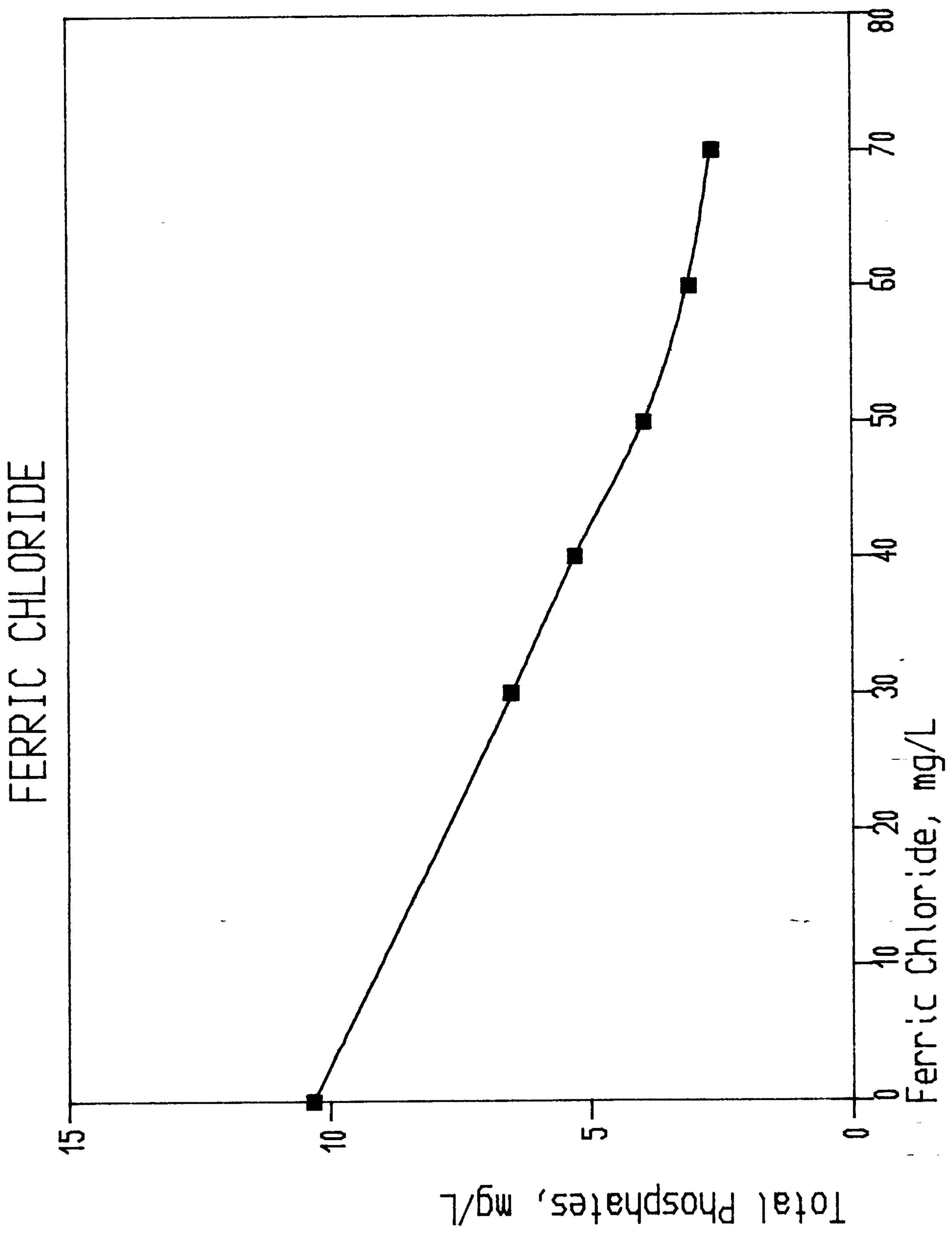

FERRIC CHLORIDE
Total Phosphates, mg/L
0
5
10
15
Ferric Chloride, mg/L
0
10
20
30
40
50
60
70
80

Figure 15

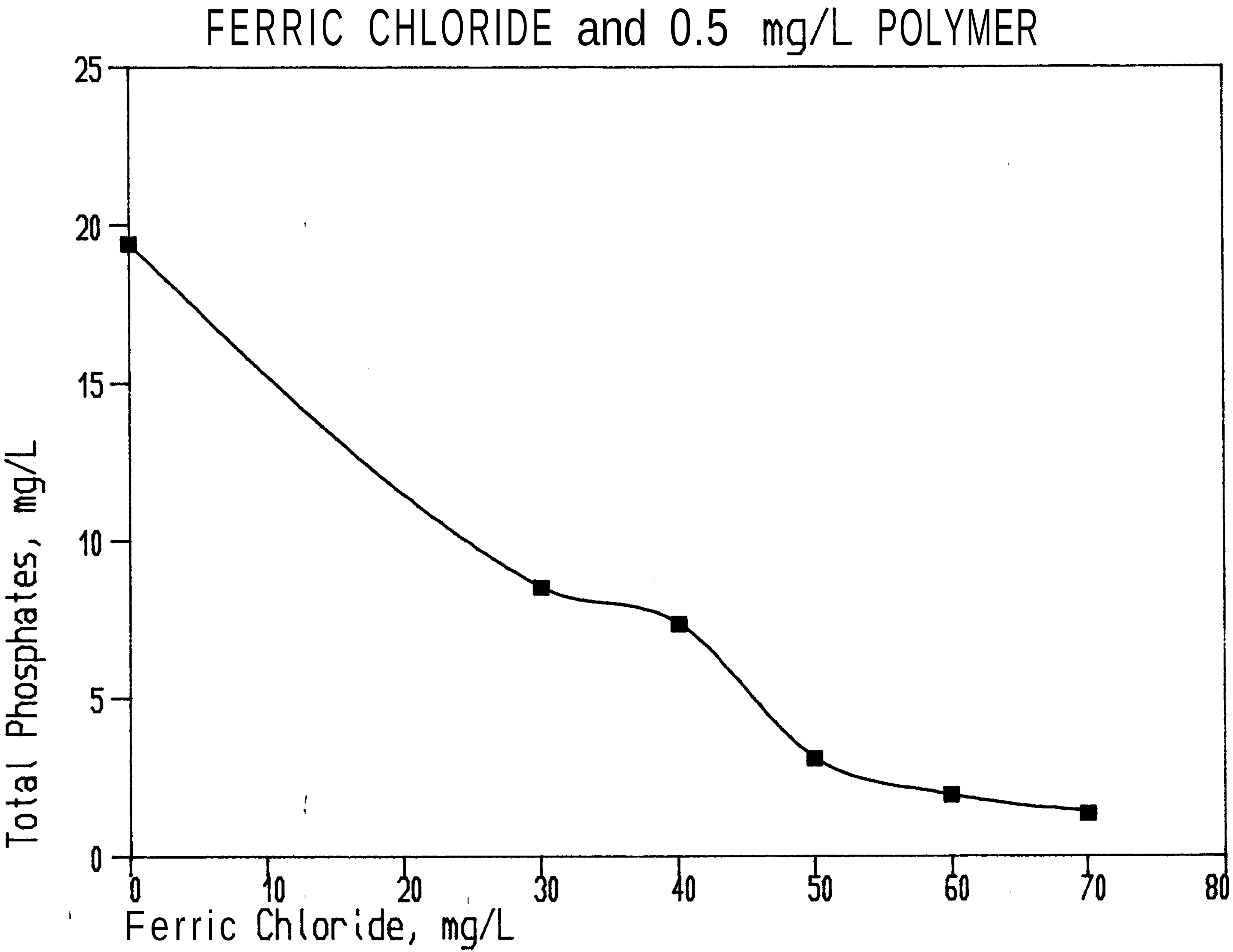

FERRIC CHLORIDE and 0.5 mg/L POLYMER
Total Phosphates, mg/L
25
20
15
10
5
0
0
10
20
30
40
50
60
70
80
Ferric Chloride, mg/L

Figure 16

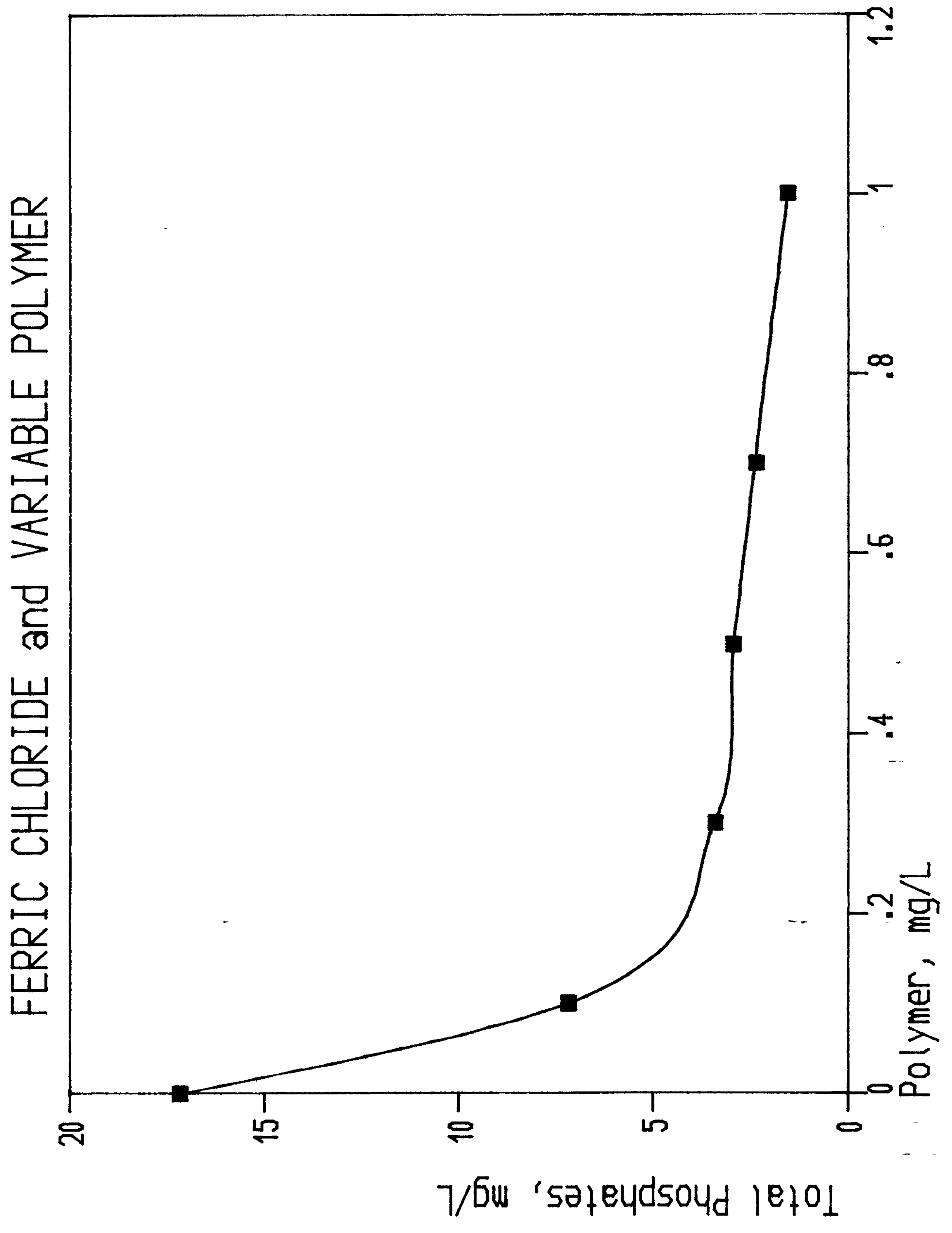

FERRIC CHLORIDE and VARIABLE POLYMER
Total Phosphates, mg/L
0
5
10
15
20
Polymer, mg/L
0
.2
.4
.6
.8
1
1.2

Figure 17

Iron(II) Chloride System

Iron(II) Chloride is another acidic salt. Its chemistry in solution is similar to that of iron(III). Dilute solutions of iron(II) open to air are subject to oxidation to the iron(III) form. Iron(II) chloride's action in the precipitation of phosphorus is similar to aluminum sulfate and will not be shown here.

Stoichiometry of The Iron(II) Chloride System

Iron(II) ion can combine with phosphorus to form iron(II) phosphate as follows:

$$3Fe^{+2} + 2PO_4^{-3} \text{--->} Fe_3(PO4)_2 \ . \qquad (8)$$

The mole ratio for Fe:P is 3:2 or Fe/P=1.5 when both iron(II) and phosphorus are expressed in terms of pound-moles. Using a weight basis this means that 168 pounds of iron(II) can react with 190 pounds of phosphate to form 358 pounds of iron(II) phosphate. Since each 190 pounds of phosphate contains 62 pounds of P, the weight relationship between iron(II) and phosphorus is 168 pounds of Fe and 62 pounds of P or 2.7 for this reaction (Table 18).

TABLE 18

STOICHIOMETRY FOR IRON(II) AND P PRECIPITATION

Mole ratio 3Fe:2P = 1.5

Weight ratio 3Fe:2P = 168:62 = 2.7:1

Iron(II) chloride, $FeCl_2 \cdot 4H_2O$, contains 28.1 % Fe

Iron(II) chloride required per lb. of P = 2.7/.28 = 9.61 lb.

Phosphate Removal: Variable Iron(II) Concentration

The iron(II) chloride concentration ranged from 0 to 120 mg/L. As shown in Tables 19, 20, and 21, doses in excess of 120 mg/L would be required to meet discharge limits when influent total phosphate are above 6.5 mg/L. Overdosing occurs with this system at 110 mg/L (Figures 18, 19, and 20). Fe:P weight at 120 mg/L iron(II) chloride ranged from 8.3:1 to 22.9:1.

Iron(II) Chloride and 0.5 mg/L Polymer

With an influent total phosphate level of 17.8 mg/L, 100 mg/L of iron(II) chloride was needed with the polymer to remove 88 % of the total phosphorus. In cornparision, this system used about twice as much precipitant as the aluminum sulfate or the iron(III) chloride system (Table 22 and Figure 21).

Iron(II) Chloride and Variable Polymer Concentration

The iron(II) chloride concentration was 90 mg/L and the polymer ranged from 0 to 1.0 mg/L. The data are shown in Table 23 and Figure 22. Polymer levels above 0.7 mg/L would be required to meet discharge limits, but with this polymer concentration the system is starting to approach overdosing.

Data Summary

The use of iron(II) chloride to remove phosphorus would also require the addition of a polymer dosage of greater than 0.7 mg/L to be effective. Even though iron(II) chloride was only about half as effective as alum and iron(III) chloride, iron(II) is a by-product of the steel industry (pickling liquor) and may be obtained at such a low cost, that it offsets the fact high quantities are needed to be effective for phosphorus removal. The use of alkalinity in the form of caustic soda or lime can be used to promote the oxidation of iron(II) to iron(III), which would improve the precipitation and removal of phosphorus. One drawback to this method is the high pH levels associated with the use of lime or caustic soda. The pH would have to be lowered to within discharge limits after the precipitation – sedimentation process.

TABLE 19

IRON(II) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
Fe Cl_2, mg/L	0	40	60	80	100	120
Fe^{+2}, mg/L	0.0	11.24	16.86	22.48	28.10	33.72
FLOCCULATION	VS	VS	M	M	M	M
SEDIMENTATION	P	P	F	F	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	190	163	129	95	78	43
% TOTAL SS REMOVED	–	14	32	50	59	77
TOTAL P mg/L	4.09	3.27	2.66	2.18	1.61	1.10
TOTAL PO_4, mg/L	12.39	9.91	7.05	5.61	3.87	3.28
ΔPO_4, mg/L	–	2.48	5.34	6.78	8.52	9.11
ΔP, mg/L	–	0.82	1.76	2.24	2.81	3.01
Fe:P RATIO	–	13.7	9.6	10.0	10	11.2
% REMOVAL, TOTAL P	–	20	43	55	69	74
pH	6.6	6.3	6.2	6.0	5.6	5.2

TABLE 20

IRON(II) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
Fe Cl_2, mg/L	0	40	60	80	100	120
Fe^{+2}, mg/L	0.0	11.24	16.86	22.48	28.10	33.72
FLOCCULATION	VS	S	M	M	M-L	M
SEDIMENTATION	P	P	F	F	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	116	98	83	62	48	31
% TOTAL SS REMOVED	–	16	28	47	59	73
TOTAL P mg/L	42.17	1.67	1.27	1.01	0.88	0.70
TOTAL PO_4, mg/L	6.59	5.07	3.84	3.09	2.42	2.13
ΔPO_4, mg/L	–	1.52	2.75	3.50	4.17	4.46
ΔP, mg/L	–	0.50	0.91	1.16	1.38	1.47
Fe:P RATIO	–	22.4	18.5	19.3	20.4	22.9
% REMOVAL, TOTAL P	–	23	42	53	63	68
	7.4	7.1	6.9	6.8	6.7	6.5

TABLE 21

IRON(II) CHLORIDE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
Fe Cl_2, mg/L	0	40	60	80	100	120
Fe^{+2}, mg/L	0.0	11.24	16.86	22.48	28.10	33.72
FLOCCULATION	VS	S	S	M	M-L	M
SEDIMENTATION	P	P	F	G	G	G
TOTAL, SUSPENDED SOLIDS, mg/L	142	115	99	72	54	38
% TOTAL SS REMOVED	–	19	30	49	62	73
TOTAL P mg/L	5.77	4.27	3.12	2.65	2.25	1.73
TOTAL PO_4, mg/L	17.49	12.94	9.44	6.85	5.99	5.75
ΔPO_4, mg/L	-	4.55	8.05	9.45	10.67	12.24
ΔP, mg/L	-	1.50	2.66	3.12	3.52	4.04
Fe:P RATIO	–	7.5	6.3	7.2	8.0	8.3
% REMOVAL, TOTAL P	-	26	46	54	61	70
pH	7.1	7.0	6.9	6.7	6.6	6.5

TABLE 22

IRON(II) CHLORIDE AND 0.5 mg/L POLYMER

BEAKER #	1	2	3	4	5	6
Fe Cl_2, mg/L	0	40	60	80	100	120
Fe^{+2}, mg/L	0.0	11.24	16.86	22.48	28.10	33.72
NALCO 7766 mg/L	0.0	0.50	0.50	0.50	0.50	0.50
FLOCCULATION	-	M	M	M	M	M
SEDIMENTATION	-	G	G	E	F	F
TOTAL, SUSPENDED SOLIDS, mg/L	289	216	169	114	88	32
% TOTAL SS REMOVED	-	25	42	61	70	89
TOTAL P mg/L	5.88	4.08	32.58	21.67	0.72	0.53
TOTAL PO_4, mg/L	17.81	12.36	7.82	5.11	2.19	1.61
ΔPO_4, mg/L	-	5.45	9.99	12.70	15.62	16.20
ΔP, mg/L	-	1.80	3.30	4.19	5.15	5.35
Fe:P **RATIO**	-	6.2	5.1	5.4	5.4	6.3
% REMOVAL, TOTAL P	-	31	56	71	88	91
pH	7.3	7.2	7.2	7.1	6.9	6.9

TABLE 23

IRON(II) CHLORIDE AND VARIABLE POLYMER

BEAKER #	1	2	3	4	5	6
Fe Cl_2, mg/L	0	90	90	90	90	90
Fe^{+2}, mg/L	0.0	25.29	25.29	25.29	25.29	25.29
NALCO 7766 mg/L	0.0	0.10	0.30	0.50	0.70	1.00
FLOCCULATION	-	M	M	M	M	L
SEDIMENTATION	-	F	F	G	G	G
TOTAL P mg/L	4.61	2.74	2.02	1.40	0.98	0.82
TOTAL PO_4, mg/L	13.96	8.29	6.11	4.24	2.98	0.82
ΔPO_4, mg/L		5.67	7.85	9.72	10.98	11.49
ΔP, mg/L	-	1.87	2.59	3.21	3.62	3.79
Fe:P RATIO	-	13.48	9.73	7.85	6.96	6.65
% REMOVAL, TOTAL P	-	41	56	70	79	82
pH	7.3	7.2	7.2	7.1	6.9	6.8

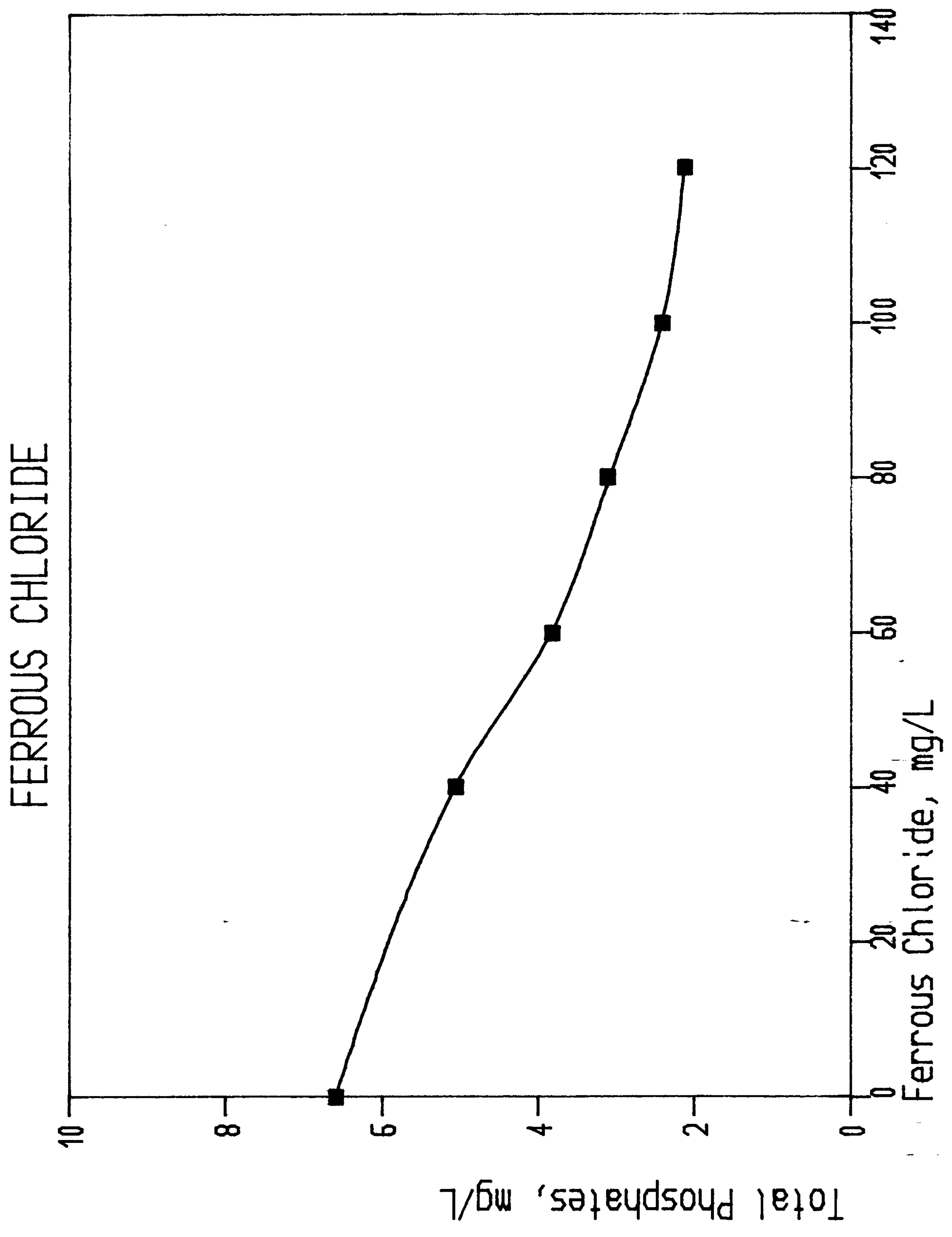

FERROUS CHLORIDE
Total Phosphates, mg/L
10
8
6
4
2
0
Ferrous Chloride, mg/L
0
20
40
60
80
100
120
140

Figure 19

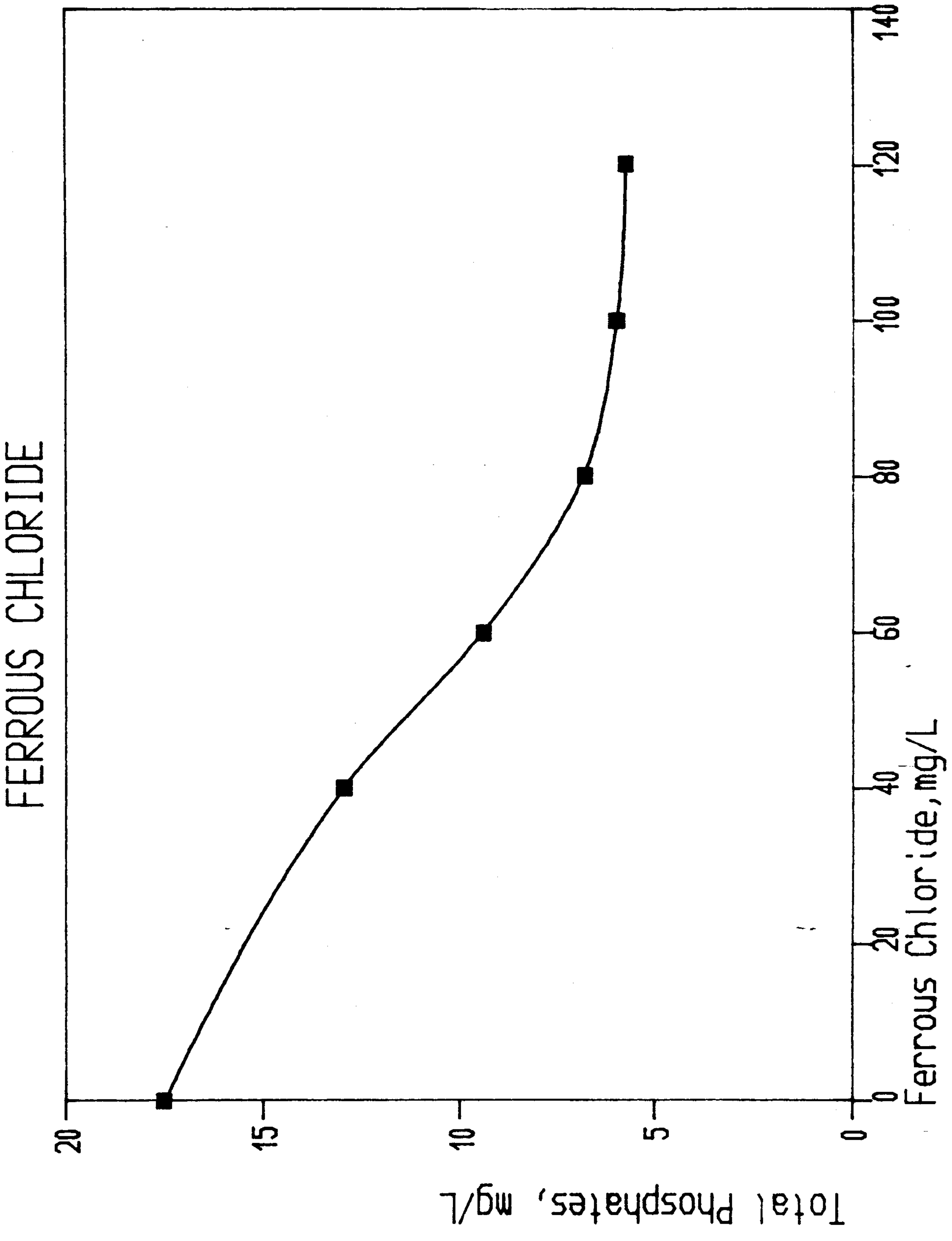

FERROUS CHLORIDE
Total Phosphates, mg/L
0
5
10
15
20
Ferrous Chloride,mg/L
0
20
40
60
80
100
120
140

Figure 20

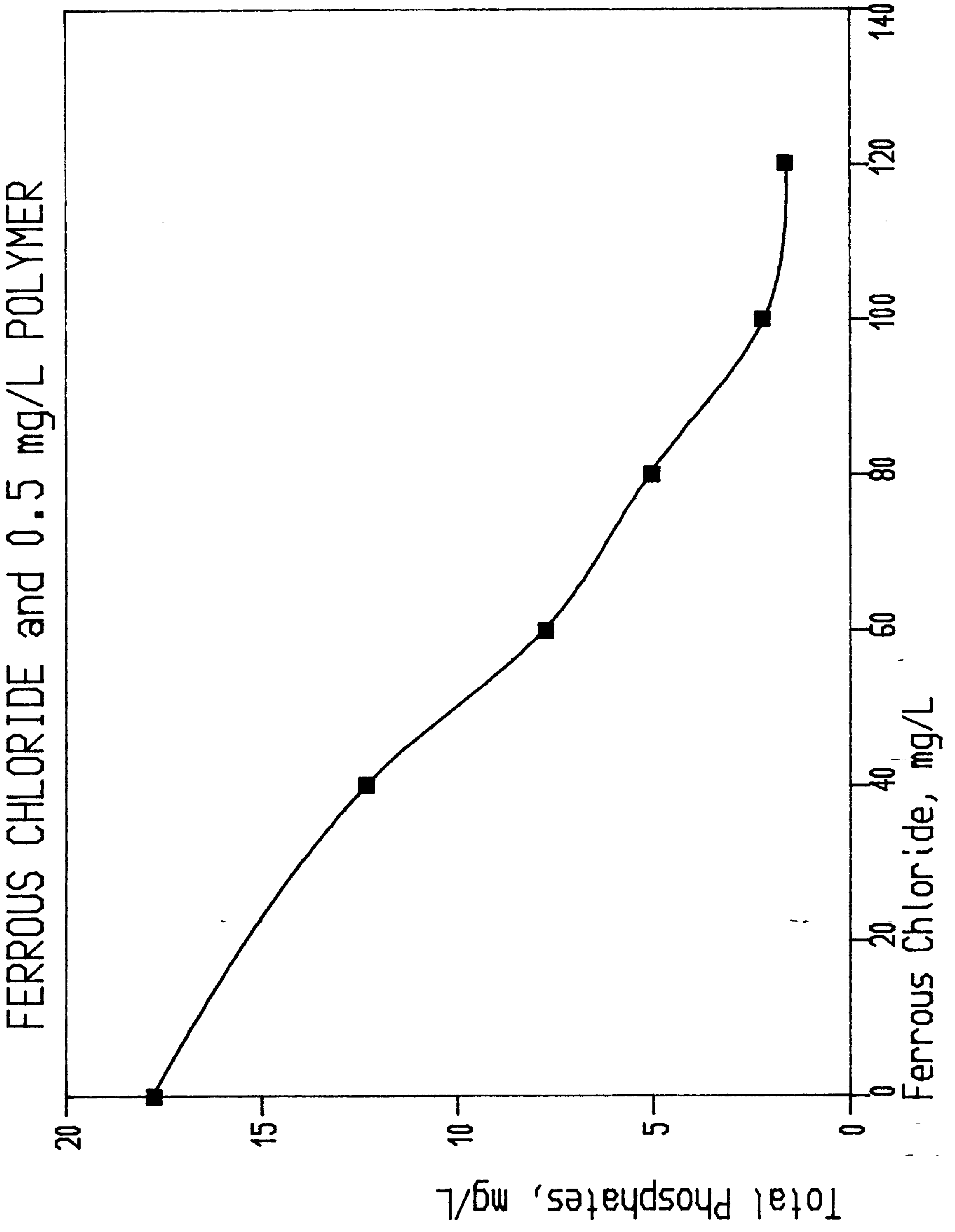

FERROUS CHLORIDE and 0.5 mg/L POLYMER
Total Phosphates, mg/L
0
5
10
15
20
Ferrous Chloride, mg/L
0
20
40
60
80
100
120
140

Figure 21

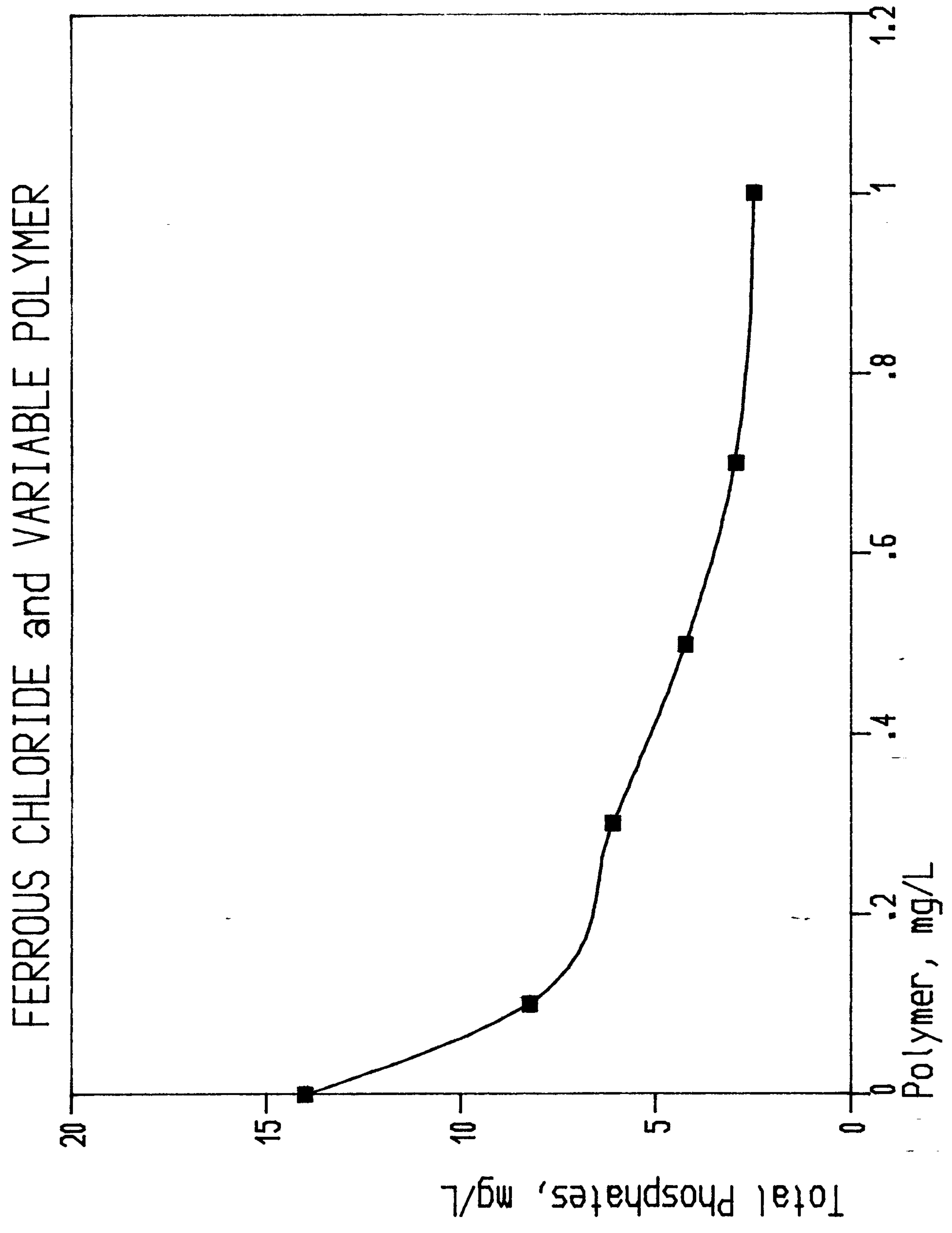

FERROUS CHLORIDE and VARIABLE POLYMER
Total Phosphates, mg/L
0
5
10
15
20
Polymer, mg/L
0
.2
.4
.6
.8
1
1.2

Figure 22

Zirconium Sulfate System

Zirconium sulfate is an acidic salt which upon the addition to sewage will reduce the pH. This system produces flocs that are less resistant to high shear forces but exhibit faster settling rates than the previous systems. Zirconium sulfate's function in wastewater is similar to that shown for the precipitation of aluminum phosphate and will not be shown.

Stoichiometry of The Zirconium Sulfate System

Zirconium ions can combine with phosphate to form zirconium phosphate as follows:

$$3Zr^{+4} + 4PO_4^{-3} \dashrightarrow Zr_3(PO4)_4. \qquad (9)$$

The mole ratio of this reaction is 3:4 or Zr/P=1.3 when both Zr and P are expressed in terms of pound-moles. Using a weight basis, this means that 273 pounds of zirconium ion can react with 380 pounds of phosphate to form 653 pounds of zirconium phosphate. Since each 380 pounds of phosphate contain 124 pounds of P, the weight relationship between Zr and P is 273 pounds of Zr to 124 pounds of P or a ratio of 2.2 for this reaction (Table 24).

TABLE 24

STOICHIOMETRY FOR Zr AND P PRECIPITATION

Mole ratio 3Zr:4P = 0.75

Weight ratio 3Zr:4P = 273:124 = 202:1

Zirconium sulfate, $Zr(SO_4)_2 \cdot 4H_2O$, contains 25.7 % Zr

Zirconium sulfate required per lb. of P = 2.2/.26 = 8.56 lb.

Phosphate Removal With Variable Zirconium Concentration

The zirconium sulfate level ranged from 0 to 40 mg/L. Using Table 25 and 25, zirconium sulfate doses as low as 10 mg/L were enough to meet discharge limits. At high total phosphate influent concentrations (Table 27), 40 mg/L of zirconium sulfate couldn't meet discharge criteria. The average removal percentage rate that meets discharge levels was 69 % and the average Zr:P weight ratio to meet discharge limits was 3.1:1. Figures 23, 24, and 25 indicate that overdosing occurs at zirconium sulfate concentrations above 25 mg/L.

Zirconium Sulfate and 0.5 mg/L Polymer

Table 28 and Figure 26 indicate that a combination of polymer and zirconium sulfate reduced the total phosphate levels below discharge criteria with 30 mg/L zirconium sulfate. This corresponds to a 92 % removal rate with a 1.0:1 weight ratio.

Zirconium Sulfate and Variable Polymer Concentration

For this investigation, the zirconium sulfate concentration was held at 25 mg/L and the polymer level ranged from 0 to 1.0 mg/L. Table 29 and Figure 27 show the results. The discharge limit was met with a 0.5 mg/L concentration of polymer. This was equivalent to a 85 % removal rate and a 1.6:1 weight ratio. Restabilization of the system occurred with polymer levels greater than 0.6 mg/L.

Data Summary

This system was able to meet discharge limits with the minimum amount of precipitant and the use of a polymer may be optional depending on the influent total phosphorus levels.

combinations of Metallic Cations

Various combinations of metallic cations used previously were evaluated for total phosphate removal efficiency. The various combinations were: 17.5 mg/L aluminum sulfate and 17.5 mg/L iron(III) chloride, 5.0 mg/L zirconium sulfate and 17.5 mg/L aluminum sulfate, 10.0 mg/L zirconium sulfate and 35.0 mg/L aluminum sulfate, 5.0 mg/L zirconium sulfate and 17.5 mg/L iron(III) chloride, 10.0 mg/L zirconium sulfate and 35.0 mg/L iron(III) chloride.

TABLE 25

ZIRCONIUM SULFATE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
$Zr(SO_4)_2$, mg/L	0	5	10	20	30	40
Zr^{+4}, mg/L	0.0	1.25	2.57	5.14	7.71	10.28
FLOCCULATION	VS	M	M	L	L	L
SEDIMENTATION	F	G	G	G	E	G
TOTAL SUSPENDED SOLIDS, mg/L	121	73	47	28	17	13
% TOTAL SS REMOVED	–	40	61	77	86	89
TOTAL P mg/L	1.42	1.25	0.83	0.29	0.20	0.13
TOTAL PO_4, mg/L	4.33	3.79	2.53	0.89	0.61	0.39
ΔPO_4, mg/L	–	0.54	1.80	3.44	3.72	3.94
ΔP, mg/L	–	0.18	0.59	1.14	1.23	1.30
Zr:P RATIO	–	7.2	4.4	4.5	6.3	7.9
% REMOVAL, TOTAL P	–	12	42	79	86	91
pH	7.2	7.0	6.8	6.7	6.6	6.5

TABLE 26

ZIRCONIUM SULFATE, VARIABLE CONCENTKATION

BEAKER #	1	2	3	4	5	6
$Zr(SO_4)_2$, mg/L	0	5	10	20	30	40
Zr^{+4}, mg/L	0.0	1.25	2.57	5.14	7.71	10.28
FLOCCULATION	VS	S	M	L	L	L
SEDIMENTATION	F	F	G	G	G	F
TOTAL SUSPENDED SOLIDS, mg/L	151	94	67	39	21	18
% TOTAL SS REMOVED	-	38	56	74	86	88
TOTAL P mg/L	1.97	1.59	1.18	0.38	0.28	0.20
TOTAL PO_4, mg/L	5.98	4.83	3.59	1.14	0.85	0.61
ΔPO_4, mg/L	-	1.15	2.39	4.48	5.13	5.37
ΔP, mg/L	-	0.38	0.79	1.60	1.69	1.77
Zr:P RATIO	-	3.3	3.3	3.2	4.6	5.8
% REMOVAL, TOTAL P	-	19	40	81	86	90
pH	7.4	7.1	7.0	6.8	6.7	6.6

TABLE 27

ZIRCONIUM SULFATE, VARIABLE CONCENTRATION

BEAKER #	1	2	3	4	5	6
$Zr(SO_4)_2$, mg/L	0	5	10	20	30	40
Zr^{+4}, mg/L	0.0	1.25	2.57	5.14	7.71	10.28
FLOCCULATION	S	M	M	L	L	M
SEDIMENTATION	F	F	G	E	G	G
TOTAL SUSPENDED SOLIDS, mg/L	169	107	83	39	24	20
% TOTAL SS REMOVED	–	37	51	77	86	88
TOTAL P mg/L	6.71	5.63	4.46	1.60	1.28	1.08
TOTAL PO_4, mg/L	20.33	17.07	13.52	4.84	3.88	3.28
ΔPO_4, mg/L	–	3.25	6.81	15.49	16.45	17.05
ΔP, mg/L	–	1.07	2.24	5.11	5.43	5.63
Zr:P RATIO	–	1.2	1.5	1.1	1.4	1.8
% REMOVAL, TOTAL P	–	16	33	76	81	84
pH	7.5	7.3	7.1	7.0	6.8	6.7

TABLE 28

ZIRCONIUM SULFATE AND 0.5 mg/L POLYMER

BEAKER #	1	2	3	4	5	6
$Zr(SO_4)_2$, mg/L	0	5	10	20	30	40
Zr^{+4}, mg/L	0.0	1.29	2.57	5.14	7.71	10.28
NALCO 7766, mg/L	0.0	0.50	0.50	0.50	0.50	0.50
FLOCCULATION	–	M	M	L	L	L
SEDIMENTATION	–	G	G	G	G	E
TOTAL SUSPENDED SOLIDS, mg/L	188	101	71	33	20	12
% TOTAL SS REMOVED	–	46	62	82	89	94
TOTAL P mg/L	6.04	4.31	2.48	1.04	0.49	0.37
TOTAL PO_4, mg/L	18.29	13.07	7.53	3.16	1.49	1.13
ΔPO_4, mg/L	–	5.22	10.76	15.13	16.80	17.16
ΔP, mg/L	–	1.72	3.55	4.99	5.54	5.66
Zr:P RATIO	–	0.75	0.72	1.03	1.39	1.82
% REMOVAL, TOTAL P	–	29	59	83	92	94
pH	7.1	7.1	7.1	7.0	7.0	7.0

TABLE 29

ZIRCONIUM SULFATE AND VARIABLE POLYMER

BEAKER #	1	2	3	4	5	6
$Zr(SO_4)_2$, mg/L	0	25	25	25	25	25
Zr^{+4}, mg/L	0.0	6.43	6.43	6.43	6.43	6.43
NALCO 7766, mg/L	0.0	0.10	0.30	0.50	0.70	1.00
FLOCCULATION	–	S	M	L	L	M
SEDIMENTATION	–	P	G	G	F	F
TOTAL P mg/L	4.78	3.94	2.64	0.70	0.59	0.44
TOTAL PO_4, mg/L	14.49	11.94	7.99	2.13	1.79	1.34
ΔPO_4, mg/L	–	2.55	6.50	12.36	12.70	13.15
ΔP, mg/L	–	0.84	2.15	4.08	4.19	4.34
Zr:P RATIO	–	7.65	2.99	1.58	1.53	1.48
% REMOVAL, TOTAL P	–	18	45	85	88	9.2
pH	7.2	7.2	7.2	7.1	7.1	7.0

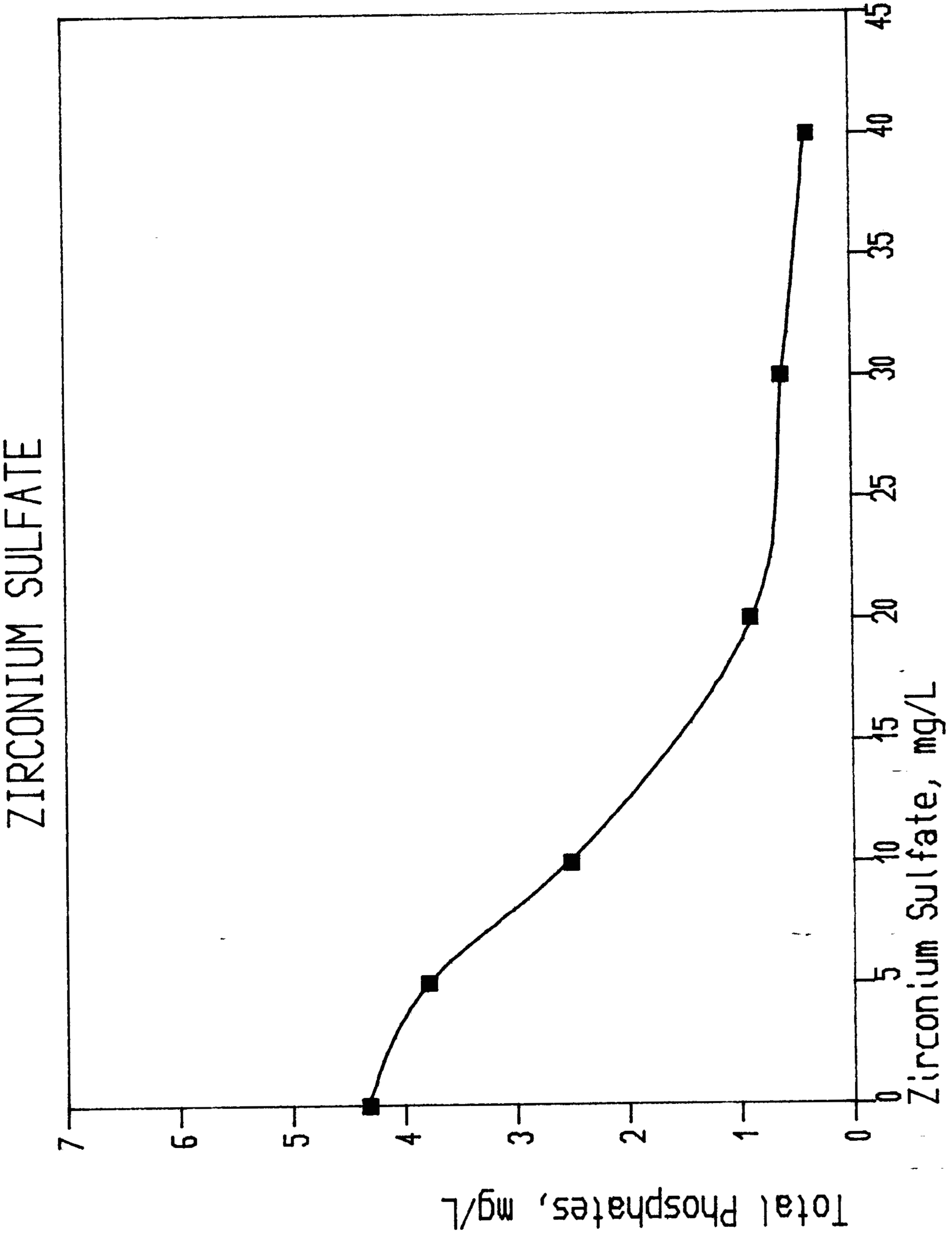

ZIRCONIUM SULFATE
Total Phosphates, mg/L
0
1
2
3
4
5
6
7
Zirconium Sulfate, mg/L
0
5
10
15
20
25
30
35
40
45

Figure 23

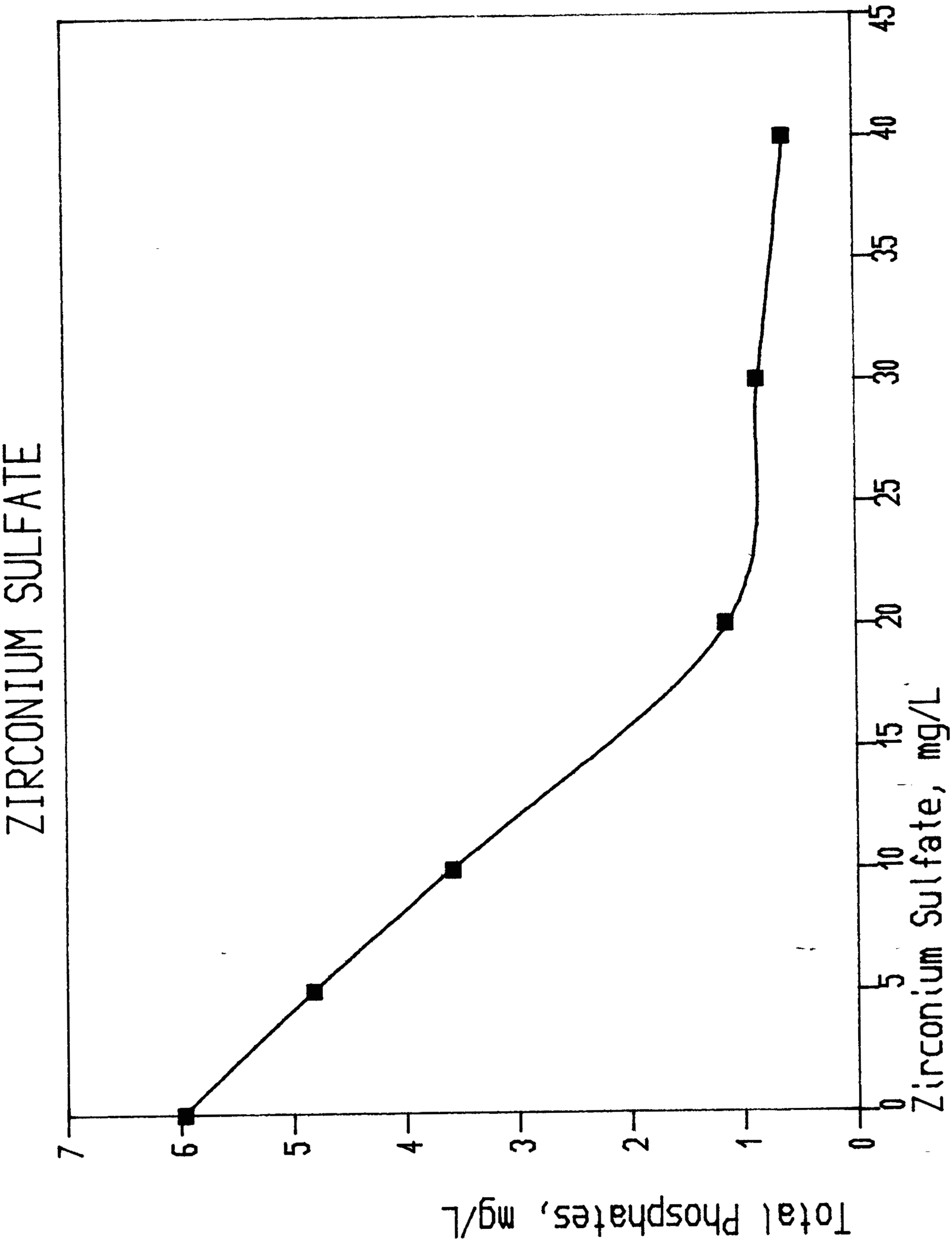

ZIRCONIUM SULFATE
Total Phosphates, mg/L
0
1
2
3
4
5
6
7
Zirconium Sulfate, mg/L
0
5
10
15
20
25
30
35
40
45

Figure 24

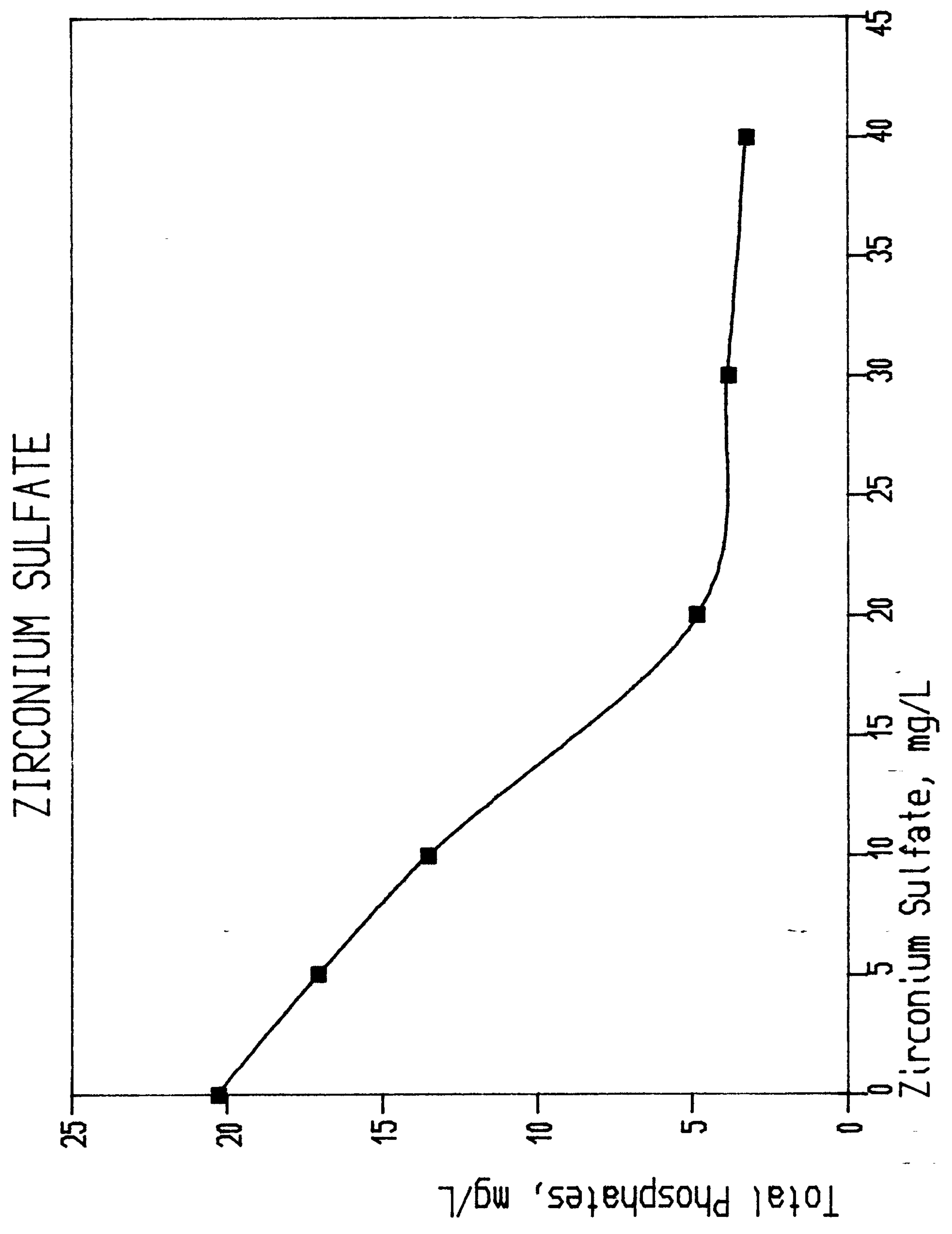

ZIRCONIUM SULFATE
Total Phosphates, mg/L
0
5
10
15
20
25
Zirconium Sulfate, mg/L
0
5
10
15
20
25
30
35
40
45

Figure *25*

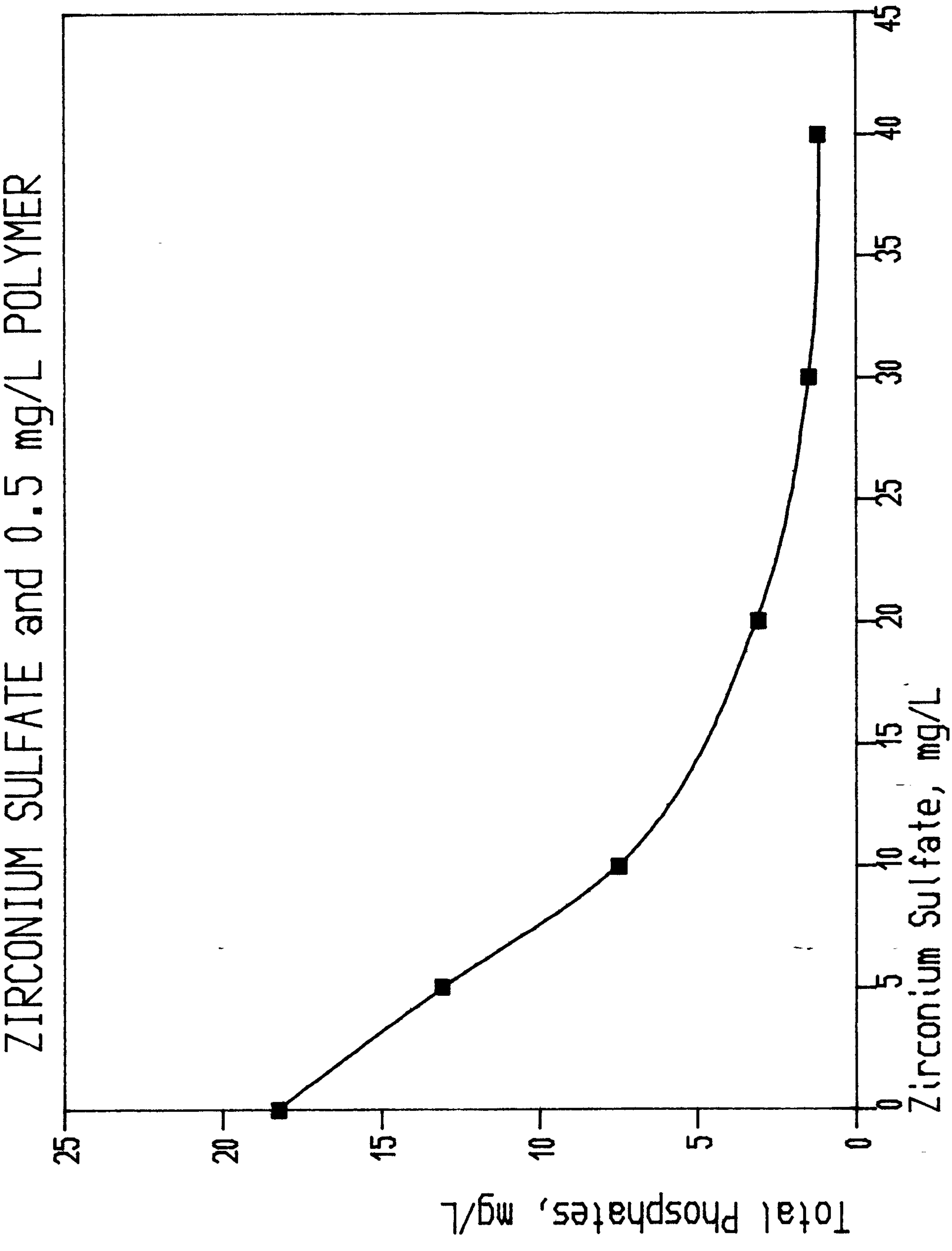
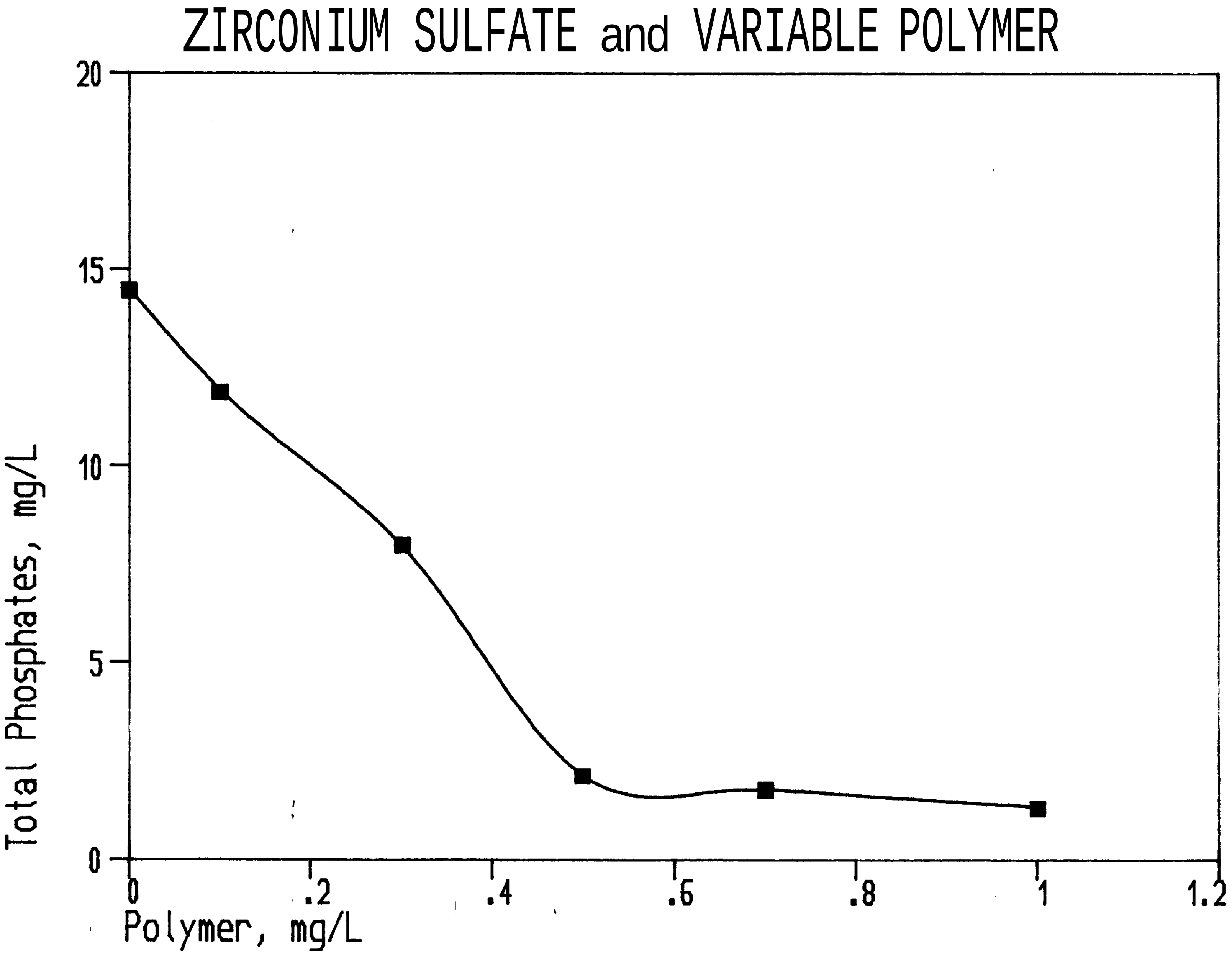

ZIRCONIUM SULFATE and 0.5 mg/L POLYMER
Total Phosphates, mg/L
0
5
10
15
20
25
Zirconium Sulfate, mg/L
0
5
10
15
20
25
30
35
40
45

Figure *26*



ZIRCONIUM SULFATE and VARIABLE POLYMER

Figure 27

Each concentration was chosen because it was either 1/2 or 1/4 of the overdose concentration for each particular cation as shown previously. The overdose concentration is the maximum dose of cation in which adding more cation would result in little or no further phosphorus removal. No polymer was used in this investigation.

The 17.5 mg/L aluminum sulfate and 17.5 mg/L iron(III) system removed 32 % of the total phosphates. Comparatively, 35.0 mg/L of aluminum sulfate removed an average of 43 % of the total phosphates and 35.0 mg/L iron(III) chloride removed 42 % of the total phosphates. The 5.0 mg/L zirconium sulfate and 17.5 mg/L aluminum sulfate combination removed 19 % of the total phosphates in comparison to 5.0 mg/L zirconium sulfate which removed an average of 16 % of the total phosphates. The 10.0 mg/L zirconium sulfate and the 35.0 mg/L aluminum sulfate combination removed 35 % of the total phosphates. An average removal of 38 % total phosphates was accomplished by 10.0 mg/L zirconium sulfate in comparison. The 5.0 mg/L zirconium sulfate and 12.5 mg/L iron(III) system removed 26 % of the total phosphates as compared to 5.0 mg/L zirconium sulfate which removed 16 % of the total phosphatas and iron(III) chloride which removed 18 % of the total phosphates on average. The iron(III) system removed 18 % of the total phosphates at a 17.5 mg/L concentration. The 10.0 mg/L zirconium sulfate and 35.0 , iron(III) chloride combination removed 46 % of the total phosphates in comparison to 10.0 mg/L zirconium sulfate removed an average of 38 % of the total phosphates and 35.0 mg/L iron(III) chloride removed 42 % of the total phosphates.

Data Summary

The Zr and A1 ion combination and the A1 and iron(III) combination didn't improve removal efficiency over using each ion singularly. The Zr and iron(III) combination also didn't demonstrate increased removal efficiency over each ion alone in this wastewater system.

Conclusions

In this study, the efficiency in reducing total phosphorus to 1.OO mg/L (3.00 mg/L total phosphate) of iron(II), zirconium, iron(III), and alum was tested. Once the metal-phosphorus colloids are formed they must be agitated, to form larger particles that can be removed by sedimentation. The use of a polymer as an aid to phosphorus removal was a second variable that was considered.

Insolubilization of soluble phosphorus is a function only of the concentration of the multivalent cations and is independent of the polymer concentration. The four chemical systems (alum, iron(III) chloride, iron(II) chloride, and zirconium sulfate) performed to varying degrees of efficiency. Iron(II) chloride removed phosphorus the poorest. Alum and iron(III) performed equally well, removing 79 % and 77 % of the total phosphorus respectively.

This was at the same dosage of 70.0 mg/L for each. Zirconium sulfate performed the best-removing over 90 % of the total phosphorus with a concentration of 40.0 mg/L. The use of different combination of metallic cations proved not to increase total phosphorus removal.

Each system was aided by the addition of the polymer. Again iron(II) chloride performed the poorest. The doses of both alum and iron(III) chloride was able to be reduced by 20.0 mg/L by adding 0.5 mg/L of Nalco 7766 to obtain a total phosphorus removal of 85 . Required zirconium sulfate levels were reduced by 1/2 by the addition of 0.5 mg/L of polymer for a removal rate of 84 % of the total phosphorus. The polymer was able to reduce the metallic ion concentration by destabilization and adsorbing the insoluble metal-phosphorus colloids, slowing the particle motion, permitting faster settling of the floc, and increasing the removal efficiency. The last consideration in choosing a system to remove phosphorus is a cost comparison. Each system was compared on cost to treat 1 million gallons of wastewater in Table 30.

TABLE 30

COST COMPARISON OF CHEMICAL SYSTEMS

Precipitant, mg/L	Price/lb.	Lbs./million gals.	Cost/M.G.
Alum (50 mg/L)	$44.00	417	$18,348
Iron(III) (50 mg/L)	$20.00	417	$ 8,340
Iron(II) (90 mg/L)	$35.00	751	$26,271
Zirconium (25 mg/L)	$54.00	209	$11,286

Lbs. needed = 8.34 lbs./gals. X Feed rate, mg/L

As can be seen there is a wide gap in treatment costs. The most cost effective for this wastewater system are iron(III) chloride and zirconium sulfate. The polymer cost to be added to each system would be in the range of $104.00 to $146.00 per million gallons of sewage treated. This is based on $25/lb. of polymer and a concentration range of 0.5 to 0.7 mg/L.

Future Treatment Needs in Phosphorus Removal

Every two years the U.S. EPA must report to Congress regarding present and future capacity for the treatment of wastewater. The last report was dated 1982 and projected capacity needs to the year 2000.[20]

In 1982 there were 15,431 treatment plants in the United States and territories. Of that number, 586 were capable of phosphorus control, treating 3,690 mgd or 14 % of the total U.S. flow for phosphorus removal.

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In the year 2000, there are projected 1233 wastewater treatment plants with the capacity of phosphorus control, treating 8456 mgd or 20 % of the total U.S. flow for phosphorus removal.

Future research is needed to reduce phosphorus removal treatment costs. This may include polymers with more active sites that would reduce the amount of metallic ion that is required, treatment plant engineering design changes that better utilize the chemical processes involved, and reducing the phosphorus loading on treatment plants by limiting the phosphate binders found in laundry detergents.

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