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A REVIEW OF PHOSPHORUS REMOVAL TECHNOLOGY

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The quality of the nation's surface water supplies has deteriorated through accelerated eutrophication. Phosphorus has been identified as a limiting nutrient in eutrophication that is contributed by man's wastewaters and amenable to control. Wastewater effluent limits on phosphorus concentrations are embodied in the National Pollutant Discharge Elimination System. The Department of the Army wastewater treatment facilities must apply for and receive discharge permits under this system for all wastewater discharges.

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State-of-the-art of phosphorus removal technology was examined to include biological, chemical-biological, chemical-physical and physical techniques for phosphorus removal. Criteria for process selection for application at Army wastewater treatment facilities include permit limitations, process effectiveness and reliability, applicability to trickling-filter treatment schemes (the Army's predominant secondary process), economics, simplicity of operation and maintenance and maximum use of existing facilities and equipment. Upgrading biological treatment by chemical precipitation of phosphorus was identified as the process of choice. Lime, iron salts or aluminum salts are the chemicals commonly used. Points of chemical addition were identified and actual full-scale experiences were discussed, to include sludge production. Recommendations were made concerning process selection, applicability and research needs.

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INTRODUCTION

Accelerated eutrophication of the nation's lakes, rivers, and streams continues to be of major concern. An American Water Works Association (AWWA) Task Group[1] estimated that over one-half of the surface water supplies in the United States have water quality and water treatment problems attributed to excessive growth of algae and aquatic plants. Such plant and algae growth are characteristic of accelerated eutrophication. Other indicators include depletion of dissolved oxygen, excessive turbidity, odors, tastes, a deterioration of fish life, a buildup of nutrients and increasing restrictions on water use.[2,3]

The process of eutrophication involves the alteration of the aquatic food chain.[2-4] Algae, the base of the aquatic food pyramid, consume nutrients for growth and reproduction. These nutrients include carbon dioxide, inorganic nitrogen, orthophosphate and trace elements.[1,5] Plankton also consume algae and are, in turn, consumed by higher orders of life in the predator-prey pyramid.

The environmental conditions of an aquatic system and the population of all species of life ultimately depend on the amount of nutrients in the food chain. As more nutrients are introduced into the aquatic system, the food chain is altered. The result is a continuous, dynamic natural process occurring very slowly. This process, called eutrophication, is a natural aging process of aquatic systems. Bodies of water, such as lakes, undergo eutrophication over periods of tens of thousands of years. Man can significantly alter the rate of eutrophication to achieve the same effect after only a few decades through the discharge of untreated wastewaters.

The net availability and the accumulation rate of the nutrients required for algae and aquatic plant growth are keys to the rate of eutrophication.[2-4] Controlling those nutrients required by algae can control the rate of this aging process. Carbon, nitrogen and phosphorus are required by algae in large amounts; while trace elements are required in minute quantities.

Examination of the availability of these nutrients required for algal growth can indicate which nutrients are most frequently in growth-limiting concentrations and which could be controlled by man.[2-4] More carbon is required by algae than any other nutrient. Carbon, as carbon dioxide, is readily available through atmospheric cycles and from the natural carbonate in water. Nitrogen can be drawn from the atmosphere by nitrogen-fixing blue-green algae. The amount of nitrogen available in surface runoff virtually eliminates nitrogen as an easily controlled nutrient. Trace elements are required in only minute quantities and are available in sediments and surface runoff. Consequently, they are rarely present in growth limiting concentrations and are not amenable to control by man. Phosphorus is not available through atmospheric cycles. The sedimentation cycle of phosphorus further limits its biological availability. It

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is required in relatively large amounts by algae for growth. The chemistry of phosphorus in aquatic systems indicates a control technology (chemical precipitation). Phosphorus remains as the nutrient contributed by man's wastewaters that most frequently limits aquatic production.[6-9] Ockershausen[7,10,11] stated that of all the nutrients contributed by man that can cause excessive algal growth, phosphorus is the most amenable to removal.

Several investigators assert that the elimination of phosphorus in waste streams is essential to the control of accelerated eutrophication.[6,12-17] Thomas discusses a study of 40 central European lakes, the purpose of which was to determine minimum substances for the general production of plankton.[4] He concluded that only the phosphorus and nitrogen compounds could be considered as growth-limiting nutrients in the lakes studied.

Man's wastewaters contribute large amounts of phosphorus in short periods of time. An American Water Works Association report compared the total phosphorus concentrations in U.S. rivers (0.01 to 1 mg/l as P), lakes (0.005 to 0.113 mg/l as P) and the ocean (0.07 mg/l as P) to total phosphorus concentrations in raw sewage (10-20 mg/l as P) and in secondary effluents (4-9 mg/l as P).[1,5,18-20] Hething and Sykes determined that 72 percent of the soluble phosphorus entering one eutrophic lake came from wastewater discharges.[21] Others have shown that wastewater accounts for 57 to 94 percent of the input phosphorus in culturally-eutrophic lakes.[22,23] Wallis reported that the amount of phosphorus added to aquatic systems from U.S. treatment plant effluents was six times the phosphorus added by overland runoff.[24]

Phosphorus reduction in wastewater discharges has successfully reduced the rate of eutrophication.[11,25-27] Complete diversion of wastewaters from one lake in Denmark reduced eutrophication.[28] Stern and Dryden found that algal blooms and growth rates were significantly inhibited by reducing wastewater phosphate concentrations.[29]

The elimination of phosphorus in detergents has reduced the phosphorus loading exerted on natural water systems, but has not significantly reduced eutrophication.[30,31] One study showed that algal growth was significantly decreased only when wastewater effluent phosphorus levels were reduced to less than 1.2 mg/l total phosphorus (as P).[7] Another study concluded that 90 to 95 percent phosphorus reduction must be attained to significantly reduce accelerated eutrophication.[32]

These findings on the role of phosphorus in accelerated eutrophication have led to stream and effluent standards.[33-37] These standards attempt to limit the amount of phosphorus added to natural systems by man. The Federal Water Pollution Control Act and Amendments of 1972 (PL 92-500) set a goal of zero discharge for all contaminants.[38] Guidelines from the United States Environmental Protection Agency (EPA) and state standards provide additional impetus to remove nutrients from wastewater.[39,40]

Standards can take one of three forms: Antidegradation statements, numerical stream standards, and effluent standards. Anti-degradation statements use naturally-occurring nitrogen and phosphorus levels as standards in declaring that such levels shall not be altered by municipal, industrial, agricultural or other discharges. Numerical stream standards are based on naturally-occurring nutrient levels as well as critical values at which stream quality degradation occurs.[33] These stream standards differ as waters are classed according to use. For example, in reservoirs or lakes to be used for public water supplies, standards for phosphorus levels vary from 0.007 mg/l to 0.30 mg/l total phosphorus (as P).[41] Lake Michigan has phosphorus limits of 0.03 to 0.04 mg/l total phosphorus (as P) while Lake Erie's standard is 0.025 mg/l total phosphorus (as P).[41] Other waters are not as stringent as streams and vary from 0.020 mg/l to 1.0 mg/l total phosphorus (as P) for mean annual concentration values.[41] Most stream standards, however, are based on naturally occuring levels and are in the range of 0.05 mg/l to 0.5 mg/l total phosphorus (as P).[41] Other waters, classified for uses other than water supply, recreation or wildlife, have allowable phosphorus levels up to 1.0 mg/l total phosphorus (as P).[41]

In addition to receiving body standards, effluent limitations are also imposed. The requirement for secondary treatment in Minnesota, for example, has been defined to mean a 1.0 mg/l or less effluent total phosphorus concentration (as P).[42] Existing limits on phosphorus in wastewater discharges vary from 1.0 to 2.0 mg/l total phosphorus (as P), with many set at the 1.0 mg/l value.[35-37] Treatment efficiency requirements for phosphorus removal vary from 80 to 95 percent.[36,37]

Public Law 92-500 embodied these standards into a national program with the creation of the National Pollutant Discharge Elimination System (NPDES).[38] The system tasks the EPA with the issuance of discharge permits. Department of the Army (DA) facilities, like municipalities and private industry, must apply for and receive these permits for all their wastewater discharges. The permit system sets effluent limitations on such parameters as BOD, pH, SS, fecal coliforms, temperature, dissolved oxygen and nutrients (nitrogen and phosphorus). It is anticipated that, as these permits require reissue, more of them will include nutrient effluent limitations as well as greater restrictions on other parameters.

Compliance with the NPDES permits will require treatment beyond secondary treatment to meet effluent limitations. Many treatment plants will require additions and/or modifications. In some instances, the improvement of existing secondary treatment efficiency alone may be satisfactory. Other facilities will need to construct or provide a phosphorus removal process. The degree of addition or modification will depend on wastewater characteristics, the type of treatment system in use, the system's efficiency and the standards which apply.

PURPOSE

The purpose of this report is to examine the literature on phosphorus removal technology and to provide some guidance on processes to be evaluated as applicable to fixed Army installations.

Army wastewater treatment systems consist primarily of trickling filters as a secondary treatment process even though a few activated sludge systems and several extended aeration package plants exist. The most economical alternatives to achieve permit limitations should be selected. Alternatives recommended should successfully meet permit requirements, require the minimum amount of capital expenditure and operation and maintenance costs, be easily operated by current treatment plant operating personnel with a minimum of training and supervision, and should utilize existing facilities and resources, if at all possible.

This review of the literature will define the state-of-the-art for phosphorus removal. Contact with other federal agencies, a review of the NPDES permits already issued to Army treatment facilities, and selected site visits should be accomplished to relate existing technology to DA requirements. Those process criteria selected should then logically be examined in laboratory and pilot scale systems prior to evaluation in a demonstration project. Ultimately some design parameters must be described for use in upgrading Army wastewater treatment plants to meet current and future NPDES permit limitations.

PHOSPHORUS CHEMISTRY

Phosphorus in domestic wastewater exists in basically three forms: organically bound phosphorus; inorganic condensed phosphorus; and orthophosphate (see Appendix A). Organically bound phosphorus, the least abundant of the three forms, is found in ester and anhydride configurations ($R\text{-}OPO_3^{-2}$, $R\text{-}OPO_3PO_3^{-2}$) and as a phosphogen ($R\text{-}NPO_3^{-2}$). These configurations are parts of proteins, phospholipids, nucleic acids and bacterial cell mass. Organic phosphorus is broken down by enzyme action, and does not precipitate with metallic salts. Inorganic condensed phosphates contain two or more phosphorus atoms in a ring or chain structure. An example is sodium polymetaphosphate ($[NaPO_3]_n$), a chain molecule. Detergents contribute most of this form as poly- and pyrophosphates. The rest comes from the metabolic breakdown of proteins in human waste. All the inorganic forms slowly hydrolyze in an aqueous environment to the ortho form. Orthophosphate is the simplest and the most reactive form for chemical and biological removal. Orthophosphate equilibria include H_3PO_4, $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3} in a pH-determined system. The chemistry of these forms when confronted with a removal system will be described later in this report in the discussion on individual removal systems.

The relative concentrations of the three forms of phosphorus in wastewater change as the phosphorus moves through a treatment system. The complex, dynamic chemistry of a treatment system includes the degradation of organic phosphorus by enzymes and hydrolytic action; the hydrolysis of condensed forms to the ortho form; the precipitation and redissolution of the ortho form; the adsorption and release of all three forms; the uptake of all forms by microorganisms; and the incorporation of all forms into inorganic and organic sludges.

Total phosphorus concentrations (all forms, dissolved + suspended) in domestic wastewater vary from one wastestream to another and they vary over time in any single wastestream. Most concentrations are in the 5-20 mg/l (as P) range (0.15-0.6 millimoles [mM]) with 10 mg/l as an average value.[18,19,45] Roughly half this amount will be in the ortho form, 40 percent as inorganic condensed phosphorus, and 10 percent or less as organic phosphorus. Prior to the use of synthetic detergents (70-80 percent by weight phosphate builders), domestic wastewater contained 2-3 mg/l inorganic phosphorus (as P) and 0.5 to 1.0 mg/l organic phosphorus (as P).[46] Detergents have increased the inorganic fraction 2-3 times. Detergents currently contribute 20-70 percent of the phosphorus in domestic wastewater, while human body wastes contribute most of the remainder.[3,30,47] Phosphorus addition to potable water supplies also contribute phosphorus to a waste stream. Hydrolysis and enzyme action convert the condensed and organic phosphorus to the ortho form while the phosphorus travels through collection, transport and treatment facilities. One of the major detergent phosphate forms, sodium tripolyphosphate, may not be completely hydrolyzed (50-80 percent) in conventional secondary treatment.[48,49] The rate of hydrolysis depends on pH, extracellular enzyme concentrations, bacterial cell levels and residence time in the entire system. The result of these dynamic processes is a secondary treatment plant effluent containing 4-9 mg/l phosphorus (0.1-0.3 mM), most of which is in the ortho form -- the easiest to remove by existing technology.[1]

PHOSPHORUS REMOVAL METHODS

General

Phosphorus removal encompasses several technologies. Biological, chemical-physical, chemical-biological and physical techniques have successfully removed phosphorus from wastewaters. Biological techniques employ microorganisms to remove phosphorus through synthesis, metabolic processes and adsorption incorporating the phosphorus into biological solids. Chemical-physical techniques utilize precipitation, coagulation, flocculation, adsorption, sedimentation and filtration to incorporate the phosphorus in a chemical sludge. Common chemicals used include lime, iron salts, alum, sodium aluminate and polyelectrolytes. Rare earth elements have also successfully precipitated phosphorus. Chemical-biological efforts combine unit processes to produce a chemical-biological

sludge. For example, some biological systems provide a good environment for chemical precipitation and adsorption of phosphorus. Other systems utilize a sequence of separate chemical and biological processes to produce a low phosphorus effluent. All of these techniques involve the conversion of phosphorus to a solid form amenable to conventional solid-liquid separation technology. Physical techniques of phosphorus removal include reverse osmosis, electrochemistry, ion exchange and chemical adsorption. Land application of wastewater containing phosphorus can include all of the above techniques. Reviews of phosphorus removal technology discuss the history and applications of these processes.[5,11,18,44,50-53]

Biological Removal

General: Microorganisms remove dissolved orthophosphate from wastewater for synthesis and respiration. The overall amount of phosphorus removed across a biological unit is determined by the maximum amount of phosphorus that may be incorporated into the cell mass, and the cell wasting rate. Chemical precipitation may also occur, but usually is not the primary removal mechanism in a biological system. Average phosphorus content of an activated sludge volatile cell fraction has been reported to contain 2-3 percent phosphorus by weight.[5,54,55] This implies phosphorus removals of 10-30 percent of the average sewage content of 10 mg/l phosphorus (as P). This assumes a net viable cell production, and wastage, of 35 to 100 mg/l. This low removal is related to the high carbon to phosphorus ratio (C:P) required for cell growth (100:1).[56,57] Since available carbon to phosphorus ratios in sewage are usually much lower than 100:1, a nutritionally unbalanced situation exists with phosphorus in excess and carbon the limiting nutrient.[58] Several investigators have observed that increasing the available carbon content of the waste (BOD) results in higher phosphorus removals, but the 100:1 ratio of carbon to phosphorus is still observed.[5] Kreissl reports that, in conventional flow schemes, a trickling filter system can be expected to remove 20-30 percent phosphorus and an activated sludge system can remove 30-50 percent phosphorus.[50] These removals may be insufficient to meet present and future phosphorus removal requirements. Higher removals have been reported in biological treatment schemes, but are attributed to unique wastewater characteristics and/or chemical precipitation phenomena.[50,54]

The two biological treatment processes of interest to the Army are activated sludge and trickling filters, since these two systems constitute nearly all of DA installation wastewater treatment facilities.

Trickling Filters - Enhanced Phosphorus Removal: Phosphorus removal by trickling filter biomass is controlled by the amount of phosphorus that may be incorporated into new cells by synthesis, and by how many of these cells are removed through sludge wasting. Little has been reported on enhanced phosphorus removal (removal in addition to the removal by synthesis) in trickling filter systems. Vacker et al., reported that four trickling filter plants in Texas were removing about 15 percent of the

total phosphorus.[56] Barth et al., reported 13 percent and 4 percent removals across two parallel trickling filters.[59] Jebens and Boyle studied the influence of operational parameters on removal of phosphorus in trickling filter systems.[60] They found no relationship between phosphorus removal and the operational parameters of hydraulic load, depth, recirculation or waste strength. They did observe phosphorus removals greater than that which could be attributed to biological uptake and they postulated a chemical precipitation mechanism to explain this enhanced phosphorus removal. Apparently, the waste stream pH was elevated by CO_2 stripping, and the phosphorus solution equilibria shifted, precipitating the phosphorus in wastewater containing sufficient hardness. The precipitant is then trapped in the biological solids and removed along with excess biological sludges. However, this phenomena is not well understood and is unreliable, erratic and insufficient to meet present regulatory standards. Zanoni asserts that phosphorus removals of 20 percent or less will usually be achieved, even under ideal conditions. He states that biological uptake is very difficult to control, especially in attached growth systems, (the biomass state in trickling filters). He contends that chemical addition would be required to obtain higher phosphorus removals.[61] The conclusion is that a trickling filter system must be modified by additional treatment processes if phosphorus standards are to be met.

Activated Sludge - Enhanced Phosphorus Removal: Higher than average phosphorus removal in activated sludge plants have been reported by several authors. Two hypotheses attempt to explain this phosphorus removal beyond that required for cell growth. One theory involves cellular uptake and storage (termed "luxury uptake") while the other theory is one of simple chemical precipitation and enmeshment in the biological floc.

Several investigators all observed phosphorus uptake by microorganisms in excess of that required for cell growth as predicted from the cellular ratio (C:N:P) of carbon, nitrogen and phosphorus of 106:16:1.[62-65] Levin and Shapiro took this early research as the basis for their efforts to modify aeration units in sewage treatment plants to produce low phosphorus effluents.[66] Their results confirmed the biological uptake of phosphorus in excess of the cellular carbon to phosphorus (C:P) ratio. They concluded that the rate of application of air determined the amount of phosphorus ultimately removed. Full scale tests at the Washington, DC, sewage treatment plant showed "luxury uptake" of phosphorus with increased aeration. However, long term investigations of the ultimate fate of the phosphorus as well as steady state conditions were not conducted.

Vacker et al., reported higher than expected phosphorus removal in several Texas plants.[56] Nine major plants were studied in efforts to compare phosphorus removal efficiency through various types and degrees of treatment. They hoped to observe what parameters resulted in effective phosphorus removal and how to relate these parameters to such removal. Plants studied showed similar BOD and suspended solids reductions but

significant inter- and intraplant variations in phosphorus removal. The San Antonio Rilling Plant was notably effective in phosphorus removal (87-88 percent) at times while two parallel plants were not so effective during the same periods (33-49 percent, 48-53 percent). The Rilling plant was a 24 mgd conventional activated sludge plant having four two-pass aeration tanks. Ceramic tubes supply diffused air to the system. The East plant was a 25 mgd conventional activated sludge plant with four three-pass aeration tanks, two three-pass reaeration tanks and one single-pass reaeration tank. Thirty percent of the total aeration volume was used for return sludge reaeration. Air was supplied by square ceramic diffusion plates in the floor of one side of the aeration tanks. The West plant was a 33 mgd conventional activated sludge plant with no reaeration. There were nine single-pass aeration tanks, seven of which were equipped with cylindrical saran-wrapped diffusion tubes and two with sprayer-type diffusers in a "tapered" air distribution mode. All three received approximately the same influent.

They reported that parameters of effective phosphorus removal at San Antonio included the Food to Microorganism Ratio (0.5), Sludge Volume Index (150), Dissolved Oxygen (D.O.) (midpoint of tank - 2.0 mg/l), and D.O. (end of tank - 5 mg/l). Connell and Vacker updated their earlier work at San Antonio with studies of Mixed Liquor Suspended Solids (MLSS), air supply and dissolved oxygen as phosphate removal control parameters.[67] They concluded that phosphorus removal to less than 1 mg/l total phosphorus (as PO_4) depended on adequate aeration (D.O. > 2 mg/l), sufficient BOD, and a supply of utilizable cations. The BOD/PO_4 influent ratio was found to be a major limiting factor in metabolic uptake. Precise control to maintain a fairly constant BOD/MLSS ratio and to avoid significant endogenous respiration was required to effect a high uptake of phosphorus through metabolic and enrichment mechanisms. Cationic precipitation and adsorption were identified as probable additional removal mechanisms.

Based on San Antonio's performance, the Federal Water Pollution Control Agency (currently the EPA) studied 13 plants to test the operating conditions described by Connell and Vacker.[5] Of the 13 plants surveyed, only the Back River plant in Baltimore, MD, showed enhanced phosphorus removal. Scalf et al., reported that the critical parameters for the Back River plant were suspended solids, BOD, phosphate and dissolved oxygen concentrations.[68]

Levin and Shapiro demonstrated luxury uptake when they incorporated as much as 7.5 percent phosphorus (as P) into activated cell mass (average cells contain 2-3 percent phosphorus as P).[66] Successful attempts to show luxury uptake were conducted by Spiegel and by Carberry and Tenny in bench scale, batch activated sludge systems.[51,69] Wells described phosphorus incorporation into biological sludges as a combination of metabolic and cationic mechanisms.[70] He showed that phosphorus uptake rates were affected by MLSS concentrations in a very regular manner. Mulbarger et al., were unable to achieve phosphorus removals greater than 50 percent using

published operating criteria.[71] Menar and Jenkins fared similarly in their pilot studies using conditions similar to those reported in the Rilling Plant.[19] Shindala discussed the Federal Water Pollution Control Agency study of the 13 plants and concluded that the phosphorus removal rates were generally low and erratic.[5] He listed six plant scale efforts to produce low phosphorus effluents, all of which showed erratic results.

The second hypothesis for enhanced phosphorus removal in activated sludge systems explains that shifts in phosphorus equilibria caused by pH changes result in precipitation of calcium phosphate and the enmeshment of this precipitate into the biological flocs. Menar and Jenkins proposed this hypothesis as a result of their pilot scale studies in an activated sludge plant.[19] Ferguson and Jenkins supported this theory in their studies and identified seven characteristics reported to describe metabolic luxury uptake as also forming a basis for calcium phosphate precipitation at slightly alkaline pH values.[72] Wells cited the calcium carbonate scale on the diffusers in the Rilling activated sludge plant as evidence of cationic precipitation in the luxury uptake phenomenon.[70] Shindala discussed several tests of the precipitation theory and their failure to produce consistent results.[5]

The exact mechanisms of phosphorus removal in excess of that required for cell reproduction are not well understood. Field and laboratory data are required to define these mechanisms and their relevant environmental factors before design and operation guidance for full-scale systems can be given.

Levin, Topal and Tarnay operated a full scale biological phosphorus removal plant utilizing metabolic uptake and release.[73] The activated sludge system was piloted first, with a synthetic waste, then with municipal sewage in Baltimore, MD, Washington, DC, Piscataway, MD, and Chicago, IL. The full scale study was conducted at Seneca Falls, NY. This patented "Phostrip" process utilized a combination of biological uptake and chemical precipitation to achieve consistent 90 percent or better removals of total phosphorus from domestic wastewater. Aeration is said to induce the activated sludge to take up dissolved phosphorus in excess of that required for all growth (luxury uptake). The relatively phosphorus-free effluent is discharged from the secondary clarifier, while the sludge is subjected to anoxic conditions causing phosphorus release. The phosphorus-rich supernatant is drawn from the anoxic stripper and treated chemically while the microorganisms, now relatively low in phosphorus content, are returned to the aeration tank to pick up another luxury uptake load of phosphorus. The phosphorus is removed from the system in wasted solids and in a concentrated, small sidestream. The pilot studies in the four municipal systems showed 83.7 percent to 92.2 percent removal of total, unfiltered phosphorus to achieve effluent residuals of 0.20 to 0.92 mg/l total phosphorus (as P).

The first full scale operation of the "Phostrip" process resulted in a 30-day average effluent concentration of 0.55 mg/l total phosphorus (as P). The effluent at the Seneca Falls, NY, plant continued to average less than 1.0 mg/l total phosphorus (as P) for 9 months of continuous operation. The chemically dosed supernatant stream required a pH of only 9.2, with lime as the precipitant, to remove the phosphorus. Lime dose, if based on total flow of the plant, amounted to only 24 mg/l CaO. The chemical sludge was sent to the digester. Although sludge volume increased 20 to 30 percent (vs the 100 percent sludge volume increase typical of lime addition systems and 50 percent increases typical of mineral addition systems) no adverse effects were observed in the digestion process. Peirano applied the "Phostrip" process to the Reno-Sparks plant in Nevada.[74] The activated sludge systems (three parallel diffused air systems) were slightly modified to provide one "Phostrip" system and two standard activated sludge systems. Consistent removals of 90 percent or better total phosphorus (as P) were observed with ease of operation. A flow of 6.5 mgd was treated in the "Phostrip" system to yield a stripper supernatant stream of 0.75 mgd containing 50 - 65 mg/l total phosphorus (as PO_4). A lime dose of 320 mg/l in the stripper stream gave a pH of 9.5 in removing the phosphorus. Peirano estimated a $600,000 - $800,000 per annum savings in operation and maintenance costs over a conventional lime or mineral phosphorus removal scheme.[74] Design criteria were provided.

Careful operation of an activated sludge plant in a luxury uptake configuration may enable some treatment facilities to achieve low effluent phosphorus levels. Compliance with NPDES permit limitations may then require only minor capital investment and minimal operation and maintenance costs.

Luxury uptake for phosphorus removal should not be considered for use in Department of the Army wastewater treatment systems. The Department of the Army operates relatively few conventional activated sludge systems. The majority of systems are trickling filters for which no luxury uptake configuration has been defined.

The current state of luxury uptake removal technology is not sufficiently developed for general full scale application. Union Carbide Corporation is conducting pilot studies on Tonawanda, NY, in five operating phases and further studies at the Reno-Sparks plant in Nevada, where six operating phases are planned.[75] Operational reliability has been indicated, but more field data is required. Strict controls over the environmental conditions are necessary in both phases of the process to consistently achieve low phosphorus effluents. The questions of shock loads and system losses from toxic substances are yet to be tested.

Chemical-Physical Removal

General: Phosphorus removal can be successfully accomplished by chemical-physical processes. Over 300 full-scale plants in this country are currently using chemical treatment to remove phosphorus, either in a chemical-biological scheme, or in a chemical-physical scheme.[76] More than 500 chemical treatment plants, either with or without biological treatment, are in operation in Sweden.[77] Physical-chemical processes include precipitation, coagulation, flocculation, sedimentation, filtration and flotation. Several of these are combined in series to effect phosphorus removal to desired levels. The phosphorus must first be insolubilized, then the solid must be separated from the liquid and disposed of in such a way as not to readily re-enter the environment. The physical-chemical process combinations must be able to remove both ortho and condensed phosphate forms from the widely varying waste streams.

Chemical coagulation of sewage was practiced in Paris in 1740 with lime as the chemical of choice.[78] The design and operation of physical-chemical systems are well known and used in water treatment technology. The use of lime, alum, sodium aluminate, ferrous and ferric salts to remove phosphorus is common practice in wastewater treatment. Many reviews of the state-of-the-art have been written and an engineering design manual with proven full scale design criteria was issued in 1971 by the Environmental Protection Agency.[5,18,44,50,52,79] Several investigators have asserted that chemical precipitation to remove phosphorus is developed to a degree where sufficient full scale design criteria exist.[18,80,81] Dogmel reports that most communities attempting phosphorus removal are doing so by treating with chemical precipitants and by limiting the use of high phosphate detergents.[7] Convery states in his survey of phosphorus removal techniques that chemical precipitation is the most practical and most economical method available in the current state-of-the-art. All the design engineer need do essentially is to determine which chemical to use at what point in the existing treatment scheme.[80] Keinath recommends chemical coagulation and flocculation to remove phosphorus.[82] His requirements for a phosphorus removal system were: first, it must be placed on line quickly; second, it must be controllable such that variable efficiencies of treatment can be attained; and finally, the cost must be minimal while achieving imposed standards. He added that coagulation with flocculation has been shown to remove particulate matter as well as solution-phase organics and inorganic pollutants. Menar and Jenkins argue that among the treatment processes suggested for phosphorus removal to a level greater than that of primary and secondary treatment, those using precipitation with metal salts are the only ones to have found wide application and economic feasibility.[19] The U.S. Environmental Protection Agency states in its Process Design Manual for Phosphorus Removal that efforts of the many research and demonstration studies in past years to arrive at practical phosphorus removal procedures have resulted in the process design manual.[18] "The manual is intended to summarize process design information for the best developed

removal methods that have resulted from this governmental and private effort." The manual consists of chemical precipitation methods.

Chemicals: As stated, several chemicals are available in current phosphorus removal practice: lime, aluminum salts (alum and sodium aluminate) and iron salts (ferric chloride, ferrous and ferric sulfate and waste pickle liquor). These are readily available except for waste pickle liquor, the availability of which is restricted to areas with steel finishing operations. Waste pickle liquor consists of an acid solution containing Fe(II) and either sulfuric or hydrochloric acid. Alkali addition may be required to neutralize the excess acid in the pickle liquor when used in wastewater treatment as a source of Fe(II) in phosphorus removal. Should pickle liquor be locally available, it should be considered as a precipitant. Because such availability is limited, it will not be an integral part of the chemical precipitation schemes in this report.

Chemical Precipitation - General: This section will cover physical-chemical systems without a biological step. Such steps will be added in a later discussion.

The best developed of the physical-chemical process combinations treating domestic wastewater are those using a primary chemical precipitation-clarification step followed by activated carbon adsorption. Suspended solids and phosphorus are removed in the first step while soluble organics are adsorbed by the carbon columns.[83] Chemical precipitation processes have been studied intensively and have yielded reliable design data and operation with minimum cost.[52,84] Efficient phosphate reductions by precipitation with lime, iron or aluminum salts have occurred for many years in industrial and municipal water treatment plants. Several reviews discuss the status of technology of phosphorus removal by chemical precipitation.[18,80,85]

Chemical Precipitation - Lime: Lime is commonly used in phosphorus removal practice and is well studied (see Appendix B). The metal cation, Ca(II), reacts with orthophosphate to form a crystalline precipitate. A variable composition material, this hydroxyapatite precipitate can be described by the general formula $Ca_5(OH)(PO_4)_3$.[43,86] Hydrogen ion and magnesium substitution of the calcium in the crystal lattice and on the crystal surface may contribute to the variable composition observed in apatite crystals.[87] Stumm and Leakie proposed a three stage mechanism of calcium phosphate precipitation.[88] An amorphous material forms as a first stage and changes into small apatite crystals. Crystal growth and adsorption complete the proposed mechanism. Menar and Jenkins add that apatite recycle enhances phosphorus removal at lower pH values (8 or less) by providing sites for growth and adsorption without the need for the rate limiting amorphous phase formation and subsequent transformation to the crystal phase.[19]

A computer model of calcium phosphate precipitation indicated that CO_2 exchange could have a large role in calcium phosphate precipitation regardless of the method of treatment or initial wastewater composition.[89] The model combined empirical data with basic chemical equilibria data to simulate a chemical system of calcium oxide, magnesium oxide, carbonic acid, phosphoric acid and water.

Calcium phosphate precipitation can occur without any metal salt addition. The chemistry of this precipitation has been studied in model systems designed to simulate wastewater.[45,89-91] Changes in pH can induce this precipitation. Carbonate and magnesium concentrations are important factors in the system's kinetics. These studies support the chemical precipitation theory proposed to explain enhanced phosphorus removal (luxury uptake) in some biological systems. The carbonate-magnesium-pH environment found successful in the model systems were approximated by those biological systems reporting unusually high phosphorus removals. These conditions were not present in full scale operations and experimental attempts which failed to achieve enhanced phosphorus removal.

Lime reacts with other domestic wastewater constituents such as carbon dioxide, calcium and magnesium bicarbonate, magnesium sulfate, sodium carbonate and bicarbonate, and ammonium bicarbonate. This complex chemical system renders stoichiometric dose calculations extremely difficult. Jar tests are commonly used to determine optimum dose and pH for each waste stream, and pH is used to control the lime dosing in plant operation.

Chemical precipitation of phosphorus with lime as the metal cation source (Ca[II]) depends on alkalinity and pH.[19,52,78,80,87,91] Alkalinity competes with phosphate for the cation to form $CaCO_3$. This floc aids the phosphorus removal process by enmeshing the hydroxyapatite precipitate. The apatite forms negatively charged colloids and does not coagulate well. The carbonate floc can bring down most of the apatite if sufficient alkalinity is present to form the carbonate floc. The amount of floc formed is a function of pH. At pH less than 9.5, phosphorus does not form apatite rapidly, consequently, some phosphorus is adsorbed on nucleating carbonate crystals, inhibiting further crystal growth and floc formation. The result is a colloidal carbonate suspension in addition to the apatite suspension. If the pH is greater than 9.5, the orthophosphate is rapidly insolubilized as apatite and a good carbonate floc can form (see Fig. 1, Appendix D). If the initial alkalinity in the wastewater is greater than 200 mg/l, enough $CaCO_3$ floc is formed to bring down most of the apatite. Removal is improved by addition of a colloidal destabilizer, a coagulant aid such as an Fe(III) salt. Residual phosphorus levels of 1-2 mg/l can be attained in this manner.

Additional removal to achieve phosphorus levels of 0.3 mg/l or less require the formation of another floc - $Mg(OH)_2$. This floc is formed at a pH of 11 or higher from the magnesium hardness available in the wastewater. This floc brings down the remaining apatite. If initial

alkalinity of the wastewater is less than 150 mg/l, not enough $CaCO_3$ is formed when the pH is raised to 9.5-10. The $Mg(OH)_2$ floc must be formed in this case to achieve good phosphorus removals. That means a pH of 11 or greater. This presents no problem in a strictly physical-chemical scheme, and recarbonation can be used to adjust the pH downward. The $Mg(OH)_2$ floc has a high surface area and a positive surface charge. However, the floc is gelatinous and adversely affects sludge dewatering characteristics.

Lime dose determinations are easily made by a jar test procedure. A pH is selected as an operating point from this procedure. The lime dose at this pH achieves the desired phosphorus removal by satisfying the alkalinity, phosphorus and magnesium demands. Control of such a lime precipitation process by pH operating points is easy, inexpensive and dependable.

Chemical Precipitation - Aluminum:[10,11,13,46,50,52,76,79,80,85,86,92-95] The trivalent cation, Al(III), is available in three forms in phosphorus removal practice (see Appendix C). Alum (aluminum sulfate), aluminum chloride, and sodium aluminate have successfully removed phosphorus. One hundred thirty-five cities out of the 300 that practice full scale phosphorus removal with chemical addition use aluminum sulfate (alum). Although used more in biological treatment schemes, aluminum forms can be used in physical-chemical plants. Alum is used in 85 to 90 percent of Sweden's chemical treatment systems.[44]

The chemistry and equilibria considerations of aluminum precipitation of phosphorus parallels that of Fe(III). Both are trivalent cations with equal affinities for orthophosphate and bicarbonate alkalinity. The aluminum hydroxide precipitation enmeshes the fine aluminum phosphate precipitate into a settleable floc. Aluminum precipitation of phosphate occurs over a broad pH range with optimal conditions in the range of 5.7 to 6.3. Minimum solubility of $AlPO_4$ is reported to be 0.01 mg/l at pH 6.3 (see Fig. 1, Appendix D). Aluminum sulfate and aluminum chloride addition tend to depress the pH by releasing hydrogen ions and shifting the bicarbonate equilibria causing CO_2 formation. Sodium aluminate, however, tends to increase the pH through hydroxide formation in its precipitation reaction with orthophosphate. Sodium aluminate is not as well studied as aluminum sulfate.

The chemical dose, as with iron, depends on the phosphorus concentration, desired effluent levels and floc settling and dewatering requirements. The theoretical Al/P weight ratio of 0.87 is often changed to a ratio of 2-3 to meet the actual chemical demand in achieving desired removals. Again, each waste stream must be tested to determine what Al/P ratio and pH will achieve the desired effluent phosphorus concentration. As with Fe(III), as the pH decreases, the competing alkalinity decreases and the $AlPO_4$ formation increases with respect to $Al(OH)_3$ formation.

Successful use of aluminum salts to precipitate orthophosphate depends on successful solid-liquid separation of the colloidal precipitates. This requires careful pH control, knowledge of chelating agents in the waste stream and good design of precipitation and sludge separation units. Residual SO_4^{-2} and Cl^- concentrations in the effluent must also be considered. These anions of the aluminum salts can easily exceed desired effluent levels. Care must be taken in choosing which aluminum salt to use.

Chemical Precipitation - Iron:[5,11,46,52,80,93,96] Iron is available as a trivalent salt, Fe(III), and a bivalent salt, Fe(II), usually with sulfate or chloride (see Appendix D) (waste pickle liquor contains Fe[II]). The iron combines with orthophosphate in the precipitating reaction and with hydroxide in a competing reaction. Both reactions are necessary for successful phosphate removal. Fe(III) forms $FePO_4$ while Fe(II) forms $Fe_3(PO_4)_2 \cdot 8H_2O$ (Vivianite). The iron hydroxide floc destabilizes the negatively charged iron phosphate colloids, enmeshes the colloids in the floc and provides an adsorption capability for condensed phosphates. Iron is often used in lime coagulation, because of the iron hydroxide's activity in destabilizing and removing negatively charged calcium phosphate colloids.

High phosphorus removals can occur with either Fe(II) or Fe(III) if optimum conditions are provided. The optimum precipitation environment depends heavily on pH. Fe(II) obtains maximum phosphate removal (and minimum effluent iron concentrations) near the pH of 8.0, while Fe(III) operates more effectively in the pH range of 4.0-5.0. Both precipitate the ortho form more readily than the condensed inorganic forms, although both provide adsorption sites for the condensed forms. Since iron salts are strongly acidic, pH drops will occur on their addition to domestic wastewater systems. Therefore, artificial pH control is required to operate near optimum removal conditions, especially for Fe(II).

Reaction equilibria conditions are very different for Fe(II) and Fe(III) systems. Besides the phosphate-hydroxide formation reactions, Fe(II) is oxidized to Fe(III). The rate of the Fe(II) phosphate-hydroxide formation reactions is on the order of minutes, while the Fe(III) reactions occur in less than 1 second. The oxidation of Fe(II) to Fe(III) depends on the reducing conditions available. High dissolved oxygen concentrations and low pH promote the Fe(II)-to-Fe(III) oxidation while low dissolved oxygen and high pH retard the oxidation. The solubilities and extent of reactions for Fe(II) and Fe(III) are different and vary according to pH. Fe(II) does not hydrolyze as easily as Fe(III) or Al(III) and $Fe(OH)_2$ is much more soluble than $Fe(OH)_3$ at any given pH with $Fe(OH)_3$ being least soluble around a neutral pH. At a lower pH, less hydroxide is available and more Fe(III) phosphate is formed than Fe(II) phosphate. Minimum solubility of $FePO_4$ is reported to be 0.06 mg/l at pH = 5.3 (see Fig. 1, Appendix D). As pH increases, more hydroxide

becomes available to the Fe(III), and Fe(II) phosphate formation increases with respect to Fe(III) phosphate formation. At pH 7.4-7.9, Fe(II) is more effective than Fe(III) or Al(III) in phosphate precipitation. The trivalent cations were largely removed by hydroxide formation. Fe(III) addition at a neutral pH removes little phosphorus and forms much hydroxide floc because of the speed of the Fe(III) reactions. At a neutral or alkaline pH, Fe(II) does not hydrolyze easily. Small quantities are oxidizing to Fe(III) and the remainder reacts with orthophosphate. Consequently, at neutral or alkaline pH, Fe(II) effectively precipitates phosphate, the oxidized Fe(II), i.e. Fe(III), rapidly forms the flocculating hydroxide sludge, little Fe(II) hydrolyzes, and the slow rate of oxidation to Fe(III) permits good mixing of Fe(II). Such conditions exist in primary clarifiers. In an aeration tank, Fe(II) would rapidly oxidize to Fe(III) and must depend on the pH at the addition point to achieve good phosphorus removal.

Iron doses are determined by influent phosphorus concentrations and floc settleability requirements. A higher than stoichiometric Fe/P ratio must be determined and carefully controlled to avoid solids carryover, iron in the effluent and low phosphate removals. Since the precipitation reactions are not usually operated at optimum pH, the Fe/P requirements are determined by floc settleability requirements (can be done in bench jar tests). Theory requires weight ratios of 2.7 for Fe(II), 1.8 for Fe(III) and 0.87 for Al(III). These ratios seem to favor the trivalent cations, however, the trivalent cations hydrolyze to a much greater extent than the bivalent iron. Consequently, larger weight ratios are observed in practice for Fe(III) and Al(III), while ratios closer to stoichiometry requirements are observed for Fe(II). One study determined the weight ratios actually required to obtain 96 percent phosphorus removal in a phosphate system. Weight ratios (Fe/P) of 2.16 for Fe(III), 2.7 for Fe(II) and 1.3 for Al(III) were recorded. Based on an optimum pH and weight equivalence ratios, Fe(II) appears to have more capacity than Fe(III) and Al(III), but based on actual concentrations, Fe(III) and Al(III) can be more effective. Removal efficiencies for condensed phosphates are similar for all three cations.

Effluent iron can pose problems, so an anionic polymer (0.3-0.5 mg/l dose), with filtration (if required), is often added to clear the supernatant of insoluble colloidal forms. The polymers help form a better settling sludge than one that would be formed by additional iron doses to form more hydroxide floc. High effluent iron levels are also avoided.

Application of iron follows several considerations. In a strictly physical-chemical system, pH is not critical, except in the effluent. Therefore, Fe(III) or Fe(II) could easily be used. Operation with Fe(III) at pH 5.3 has revealed some heavy metal removal, while the effluent iron problems of an Fe(II) system are not seen. The Fe(III) sludge is more dense and more easily dewatered than the Fe(II) sludge. However, the use of Fe(II) and a pH of 8 is desired if biological treatment follows. In an Fe(II) system no pH adjustment is required, the

biomass is not acid-shocked, enough alkalinity remains for buffer capacity and the amount of phosphate residual can be controlled to maintain the proper carbon to phosphorus nutrient ratio for the subsequent biological step. An iron-base-polymer scheme can successfully remove phosphorus in physical-chemical systems. The choice between Fe(II) and Fe(III) will be predominantly based on chemical cost and availability.

Current Processes: Physical-chemical treatment of domestic wastewater is usually combined with a biological system. However, some purely physical-chemical plants are successfully treating wastewater. The precipitation and solid-liquid separation processes are followed by filtration and activated carbon in one arrangement. Eimco utilizes such a scheme in their solids contact process in which lime or alum is the chemical of choice followed by a multimedia filter and activated carbon.[51] Nassau County, Long Island, uses alum and a sludge recirculation upflow clarifier with multimedia filtration, carbon adsorption and disinfection before ground injection of the effluent as a barrier against salt water intrusion into the fresh water table.[51] Johns-Manville markets a moving bed countercurrent filter system including a head tank for chemical mixing, precipitation and some coagulation prior to the filtration.[51] The sand is driven countercurrently to the waste flow. The system reportedly removed 80 percent or more of the total phosphorus. Laundry wastes were treated with ferric chloride prior to diatomaceous earth filtration to achieve 94 percent removal of the high phosphate content (100-200 mg/l).[97] Further treatment would be required to meet effluent standards. Balmér and Frederiksen used alum, Fe(III) and lime in three parallel precipitation processes following primary treatment to remove 90 percent total phosphorus corresponding to an effluent level of 0.5 mg/l total phosphorus (as P) or less.[14] They reported that pH was the determining factor with favorable pH ranges of 5.0-6.0 for alum, 5.0-5.9 and greater than 8.0 for Fe(III), and above 11.2 for lime.

Rebhun and Streit investigated direct chemical flocculation-clarification of strong, fresh municipal wastewater followed by adsorption on activated carbon.[98] Using ferric chloride and lime in separate tests, they discovered that doses providing maximum turbidity and color removal also gave the best COD and phosphate removals. Total phosphate levels were reduced from 40 mg/l to 0.5 mg/l total phosphate (as PO_4) in the raw wastewater treatment scheme. Secondary effuent was also studied with the chemical treatment achieving total phosphate (as PO_4) levels of 0.2 or less. In the Journal of the Water Pollution Control Federation, the 1974 and 1975 literature reviews of physical and chemical methods of wastewater treatment discuss many schemes for phosphorus removal and their results using chemical precipitation.[99,100] Two Swedish reports were cited as concluding that chemical coagulation was effective in treating raw and secondary wastewater at 38 percent of Sweden's plants.[100]

Unit processes using chemical treatment can be used in either physical-chemical schemes or chemical-biological schemes. The Dorr-Oliver phosphate extraction process treats raw waste with lime in a flocculator-clarifier.[51,101] The effluent is treated biologically in an aeration tank to remove the remaining phosphorus. A portion of the primary sludge is recycled to the solids reactor as a precipitant aid. Dow converts the soluble phosphorus to an insoluble form by the addition of a metallic salt (usually iron chloride).[51,102] An organic polyelectrolyte flocculates the suspended solids to achieve 80-90 percent total phosphorus removal. The Graver Company has successfully operated several full scale plants since the 1950's, using a combination coagulator-clarifier (the "Graver Reactor").[51] This unit uses rapid mixing and recirculation for flash mixing of wastewater, lime and one of the trivalent metals along with the occasional use of a polyelectrolyte. Slow mixing and floc formation occur in the circulation zone of the unit. Infilco uses their solids contact unit, the "Densator Unit," as a tertiary step with lime and iron or aluminum salts.[51] This high density, solids contact lime process removes 80 percent phosphorus at a pH of 10.

A rare earth element, Lanthanum, has been shown to be superior to aluminum for phosphate precipitation, especially in precipitating condensed, or polyphosphates.[103] Lanthanum produced good removals of tripolyphosphate over a broad concentration range at a solution pH of 6, while no tripolyphosphate removals were recorded with aluminum at several pH levels. Lanthanum also appears to have a much broader pH working range than aluminum.

Mennell et al., used a continuous flow, bench scale, pilot plant system to treat primary wastewater with lime precipitation and dissolved air flotation.[104] Consistent removals between 97 percent and 99 percent total phosphate depended on the method of lime addition, mixing level, a countercurrent mode of flotation cycle operation and lime dose. Low suspended solids, 30 percent to 60 percent organic nitrogen removal, high particulate COD removal, 99.9 percent coliform reduction and 94 percent to 99.9 percent trace metal removals were reported.

Zaltek applied chemical precipitation without accompanying sludge production by nucleating orthophosphate crystals on phosphate rocks packed in columns.[105] The second order kinetics for steady state nucleation increased with temperature, solution pH and fluoride concentration, while decreasing with increasing concentrations of magnesium sulfate, ammonium chloride and bicarbonate. The phosphate rock is commercially available, but must have an increased surface area of at least 100 square meters per gallon before being successful as a tertiary treatment step.

Lime can be used in a single stage, low pH mode, or in a two stage, high pH mode.[86] In the single stage mode the pH of the wastewater is raised to a value of 10 by lime addition. For wastewater with moderate to high alkalinity (greater than 200 mg/l), sufficient calcium carbonate

is formed to bring down the apatite. After sedimentation, the pH is adjusted down to 8 or less by CO_2 addition. If the alkalinity is less than 150 mg/l, insufficient $CaCO_3$ is formed and the two stage, high pH mode is used. The pH is first raised to 11 or greater to bring out the $Mg(OH)_2$ floc. The excess calcium is precipitated out in the second stage where CO_2 addition drops the pH to 9.5-10. This sludge can be recalcined since it is almost entirely $CaCO_3$. A final CO_2 addition then brings the pH down to 8 or less to prevent post precipitation of $CaCO_3$ in other units. The two stage process works very well in large plants that can recalcine the lime. The process, if used on high alkalinity waters, can give a high calcium and magnesium recovery.

The treatment systems of Piscataway, MD, and South Lake Tahoe, NV, use the two-stage lime process to treat secondary effluent.[86,106] A full scale physical-chemical treatment plant in Stevenage, UK, uses the two-stage lime to reduce the 14.3 mg/l incoming phosphorus (as P) to 0.27 mg/l.[81] Neely used a two stage mode with lime doses of 300-400 mg/l at a pH of 11.8 to achieve effluent phosphorus levels of 1.0 mg/l total phosphorus (as P).[107] He compared this to a single stage lime treatment of raw wastewater using 175 mg/l lime at a pH of 11.5 to achieve 50 percent reduction of total phosphorus.

Shindala concluded that chemical precipitation appears to be a very reliable, easy, economic method of phosphorus removal as well as providing high suspended solids removal (greater than 90 percent) and moderate BOD reduction (greater than 60 percent) with a variety of chemical available.[5]

Chemical-Biological Removal

General: The majority of wastewater treatment facilities at Army installations contain the conventional physical-biological flow schemes of activated sludge and trickling filters. One successful method of overcoming the poor phosphorus removals of these existing processes lies in their modification to include some chemical treatment scheme. New designs can incorporate chemical-physical treatment as an integral part of the treatment plant package. The modification of, or addition to, existing biological schemes can achieve optimal suspended solids, BOD and COD reductions as well as phosphorus removal at minimum capital expenditures and investment in most cases. The chemical-physical step can be inserted into the conventional flow scheme at several points. The chemicals can be added to raw, degritted sewage; to the primary effluent; to the aeration tank or trickling filter; to the secondary clarifier influent or effluent.

In 1971, there were 65 simultaneous chemical-biological full scale plants operating in Finland and Switzerland.[11] In Sweden there were about 110 post-precipitation plants.[11] The United States had only 10 full scale plants representing all the different precipitation methods. As of

January 1975, the number of full scale plants in the U.S. treating for phosphorus removal in municipal wastewaters had jumped to over 300.[10] One hundred thirty-five were using alum (45 percent), 88 were using $FeCl_3$ (29 percent), 21 were using waste pickle liquor (7 percent), 20 were using lime (7 percent) and 36 were using other chemicals (12 percent). In the next 2 to 3 years several hundred more plants are expected to begin chemical treatment for phosphorus removal. These plants demonstrate the capability of chemical and biological treatment processes, as well as the economic and operational benefits of such treatment.

Points of Addition - Raw, Degritted Sewage: Chemical addition to raw wastewater produces an effluent amenable to both trickling filters and activated sludge, as well as physical-chemical schemes. Normal primary treatment removes about 5 to 15 percent phosphorus, 40 percent BOD and 50 percent suspended solids. Chemical addition can improve the removals to 70 percent total phosphorus, 60 percent BOD and 80 percent suspended solids. Levels of 0.2-1.0 mg/l total phosphorus (as P) have been reported in primary systems using aluminum salts, and 0.7-1.5 mg/l total phosphorus (as P) were observed in the effluents of primary systems using lime and iron salts. This significant improvement in solids and organic removals greatly reduces the load on the subsequent biological system.[11,50,96,108]

Any of the aluminum or iron salts can be used in treating raw sewage without large pH variations - a critical parameter to a biological system. These salts have commonly been used as coagulants in water treatment. $FeCl_3$ used at a pH of 8 optimizes the $FeCl_3$ precipitation system while producing an ideal effluent pH for biological treatment. Alum is more successful at a pH of 5.7-6.3, but is still very compatible with a following biological step. The chemistry of these salts was discussed earlier. Buffer capacity is not severely depleted by these chemicals and the amount of residual phosphates can be controlled.[96] A residual phosphate concentration is required for biological treatment. Chemical dosing to reduce total phosphorus (as P) to 2-4 mg/l will provide an adequate nutrient balance for substrate removal in the biological step. The final phosphorus levels will be less than 1 mg/l total phosphorus (as P).

Lime produces similar improvements in suspended solids, BOD, COD and phosphorus removals.[87] The two lime schemes - single and two stage - both require pH adjustment to 9.0 or less before the waste reaches the biological system. A single stage, low lime dose to achieve a pH of 9.5-10 can reduce phosphorus to levels just sufficient to meet the biological system's nutrient demands, without an excessively high pH. A high pH could adversely affect microbial metabolism. The CO_2 production of the microorganisms, while reducing the pH, would also precipitate $CaCO_3$ adding an inorganic solid to the biomass solids. Lime also consumes much

more alkalinity than either aluminum or iron. Lime requires careful mixing provisions not demanded by the less complicated mixing systems of aluminum or iron salt.[44] Residual phosphorus levels are not easily controllable in a lime process since the lime dose usually depends on pH and is independent of phosphorus concentration, whereas aluminum and iron doses are directly related to the phosphorus concentration. In any case, careful control is required to produce a steady phosphorus effluent level.

Sludge recirculation may enhance phosphorus removal and decrease the required chemical dose by providing sites for precipitation and adsorption. Recycle of digester supernatant, however, should be avoided unless treated to remove phosphorus. Up to 25 percent of the total incoming phosphorus can be returned to the primary system by recycle of untreated digested supernatant.[108]

Equipment requirements include chemical storage, feeding and control equipment. These are standard items in water treatment practice. A mixing chamber and additional sludge handling capability are required. The existing primary clarifier can serve as a flocculator-clarifier with little modification. If a secondary precipitation system is desired prior to the biological step, a second clarifier may be required. Although an uncommon practice, secondary precipitation may be desirable if combined chemical-primary sludges are too difficult (expensive) to dewater or cause digestion problems. Such a system is used with lime in plants large enough to economically recalcine the secondary chemical sludge.

Some examples follow.[50] Grayling, MI, compared primary treatment with and without $FeCl_2$, NaOH and a polymer. Overall BOD and suspended solids removals improved by 20 percent while phosphorus removal jumped from zero to 72 percent. Lake Odessa, MI, had similar experiences on the primary of their trickling filter plant. Benton Harbor, MI, used $FeCl_3$ and an anionic polymer in the primary of an activated sludge plant to achieve greater than 80 percent total phosphorus reduction. The Blue Plains, DC, pilot plant used a two stage lime system because of low alkalinity (100-200 mg/l as $CaCO_3$) to achieve excellent removals of phosphorus, organic carbon and suspended solids. Narkis et al., used lime and ferric chloride to treat raw wastewater in a comparative study.[96] $FeCl_3$ achieved good clarification, high phosphate and suspended solids removal, 70 percent COD reduction, 67 percent BOD reduction, 80 percent removal of proteins. Incoming phosphorus was reduced from 56 mg/l to 0.96 mg/l total phosphorus (as P) with $FeCl_3$ and to 0.5 mg/l with lime. They contend that chemical treatment of raw wastewater may give an effluent free of heavy metals and other toxicants, with low BOD. They report a more uniform effluent with respect to strength and composition and a much lower organic load than usual. They argue that this can result in a considerable reduction in capital and operating costs of the biological units.

Schmid and McKinney used relatively low doses of lime (150 mg/l) in a primary system operating at a pH of 9.5 to achieve 80 percent total phosphorus removals, 60 percent BOD removals and 90 percent reduction of suspended solids.[87] They report that both the orthophosphates and condensed phosphates can be readily precipitated with lime in such a system. They utilize the secondary system's activated sludge unit to reduce the pH by microbial production of CO_2. Their combined system removed 90-95 percent of the total phosphorus in a domestic wastewater containing 40-50 mg/l total phosphorus (as PO_4) with lime doses generally less than 150 mg/l as calcium hydroxide.

Ulmgren reported on Swedish experiences in chemical treatment of wastewater.[77] He reported that nearly all new plants are designed for chemical treatment with or without a biological step. Swedish standards call for 90 percent reduction of phosphorus in effluents flowing into inland lakes and smaller rivers. He stated that chemical treatment successfully reduced heavy metals, worm eggs and nitrogen as well as BOD and phosphorus. He cited, as advantages, the ease of operation and quick recovery after disturbances. Performance in cold weather was an important factor in choosing chemical treatment to combine with biological treatment. He asserted that correct pH was the most important parameter in reaching and maintaining low phosphorus levels in effluents. He listed two examples of primary chemical treatment using alum to achieve 92 percent total phosphorus removal, and two more using lime to get 67 percent removal.

Minton and Carlson reported the results of various researchers for primary removal of phosphorus.[20] They reported 60-90 percent removals for lime, 75-92 percent for Fe(III) and 74-93 percent for alum. Dorr-Oliver's phosphorus extraction process, discussed earlier, uses lime to treat raw waste prior to aeration where biomass CO_2 generation reduced the pH.[101] Water and Waste Engineering reported that an El Lago, TX, trickling filter plant added an iron salt or alum with polymer occasionally prior to primary clarification.[109] Nickerson et al., discussed the improvement of a trickling filter plant through the addition of $FeCl_3$ and polymers to the raw waste.[110] Chemical choice and dosage requirements were determined by jar tests and lab scale tests for each individual system. Black and Lewandowski demonstrated high levels of phosphorus removal from raw sewage using moderate levels of lime and the primary clarifier in an existing activated sludge plant.[111] Additional advantages cited were increased organic capacity of the overall plant, increased hydraulic capacity of the primary clarifiers and aeration process; increased overall efficiencies in BOD and suspended solids removal, as well as better oil, grease and scum removal in the primary clarifier.

Points of Addition - the Biological System: The second point of addition is the biological system. This can occur in the primary clarifier effluent line, at any point in the biological reactor, to a flash mix tank in the reactor effluent line, or to the recycled sludge. Chemical precipitation occurs simultaneously with biological phosphorus removal and the phosphorus is removed in one solids stream - the waste activated sludge. Shindala states that 1-2 mg/l phosphate levels can be attained through this point of addition.[5]

Equipment requirements and capital expense are the lowest of any point of addition. A rapid mix chamber and chemical storage, feed and control equipment may be all that is required. An aeration tank can provide mixing and some flocculation, while the secondary clarifier provides the solid-liquid separation.

Improved mixed liquor solid-liquid separation has been reported.[50] Katz et al., state that the metal salts do not interfere with the biological treatment process, yet the combined sludge has better settling and compaction properties than do separate chemical or biological sludges.[5,108] Barth and Ettinger dosed an aeration tank with sodium aluminate and reported a Sludge Volume Index (SVI) drop from 200 to 77.[112] Eberhardt and Nesbitt reported changes in SVI from 220 to 22-25 in their bench scale studies with alum addition to a high-rate activated sludge system.[113]

Reduced chemical requirements are attributed to the large surface area available both from the biomass and from recycled inorganic solids for adsorption.[5] The chemical-biological solids interaction also contributes to lower doses. Kugelman comments on the lower chemical dose requirements compared to dose requirements in the primary system.[79] Kreissl cited a Pomona, CA, study where coagulant savings were demonstrated.[50] He reported the more efficient use of the metal cations due to the natural flocculating ability of activated sludge biomass.

All the chemicals used in physical-chemical treatment can be used in the biological system. Brenner favored aluminum salts over iron salts because effluent iron concentrations may be a problem and because iron salts are acidic while aluminum salts are both basic and acidic and can better match aklalinity conditions.[114] Alum and sodium aluminate are both used in the biological system. The aluminate provides a buffer capacity by the conversion of excess hydroxyl ions to bicarbonate. Alum reacts with alkalinity and can reduce pH. Brenner reported that aluminate is better suited to lower alkalinities (100-200 mg/l $CaCO_3$) while alum and iron are more successful with alkalinities greater than 300 mg/l $CaCO_3$.[114] He also reported that aluminate added six times less dissolved solids than alum and three to six times less dissolved solids than iron.

Examples of aluminum addition follow. Nesbitt and Long compared alum to sodium aluminate in an activated sludge study.[115] They discovered alum to be a better precipitant than sodium aluminate in moderately alkaline wastewater. Their best effluent quality was obtained when the chemical was dosed at the effluent end of the aeration tank because excessive mixing can cause floc deterioration. They also demonstrated enhanced BOD removal in this system. Minton and Carlson discussed the direct dosing of iron and aluminum salts to a biological system at a neutral pH.[20] They reported soluble phosphorus (as P) residuals in the range of 0.1 to 0.5 mg/l but insoluble levels (as P) were typically greater than 1.5 mg/l. Further discussion of alum dosing included variable and unsatisfactory results obtained by several researchers.[20] They concluded that direct dosing is required when using sodium aluminate because a large dispersion hydraulic regime is needed for good phosphorus removal, but that direct dosing was optional for other chemicals. They warn of culture disruption or destruction in direct alum or iron dosing if the total alkalinity is seriously depleted or eliminated. Lin and Carlson dosed Al(III) to the end of the aeration tank in an activated sludge system.[13] They reported effluent total phosphorus (as P) levels of 0.6 mg/l. They, too, mention floc deterioration in the aeration tank. Addition at the end section also gives the aerators time to convert the condensed phosphates to the ortho form. They found alum to be more effective than aluminate. Guter et al., dosed alum to the first stage (activated sludge) of a three stage chemical-biological treatment system to achieve an average of 75 percent phosphorus removal with effluent total phosphorus (as P) values averaging 1.1 mg/l.[116] Shindala discusses several other examples of aluminum salts in combined treatment.[5]

The EPA Design Manual discusses aluminum and iron salts in detail and lists several examples.[18] The main disadvantage of direct dosing is that the addition of dissolved solids may pose effluent problems. The Manassas, VA, plant produced a yellow color in the product water with high iron doses. Iron causes alkalinity losses and may require alkalinity replenishment by chemical addition.[117] The manual reported effluent soluble aluminum levels less than 0.5 mg/l, but 6 mg/l for iron. For phosphorus levels of less than 0.5 mg/l total phosphorus (as P) a multimedia filtration system may be required. Thomas dosed an activated sludge system with low levels of ferric chloride to achieve 85 percent phosphorus removal.[118] He recirculated a portion of the iron-biological sludge dosed with small amounts of Fe(III).

Lime addition is usually avoided because the pH range for good phosphorus precipitation is too high for good biological treatment. Low lime doses have been attempted in activated sludge systems with lower pH ranges.[72] One low lime dose process uses the pH range of 7.5-8.5 to precipitate phosphorus in an aeration tank.[72] Alkalinity below 350 mg/l $CaCO_3$ and magnesium below 24 mg/l Mg is required in this

system to remove 63-87 percent of the initial 10 mg/l total phosphorus (as P). Lime addition at the end of the aerator, or multipoint additions have been used.

There are several problems with a combined chemical-biological flow. Dewatering difficulties can occur; lime, if used, cannot be recovered; high mixed liquor suspended solids must be maintained since the active, biological fraction will decrease. This imposes additional inert loads on sludge handling and mixing systems. Mass transport of substrate and oxygen are hindered by the additional suspended solids. Conflicts in optimum pH levels also occur. Chemical precipitation of phosphorus usually occurs at pH values other than those optimum for biological treatment. Polymers have been used to help minimize the effects of non-optimum pH precipitation.

Direct dosing to trickling filters is rare. Barth et al., used aluminate and dosed their full-scale, low rate filters through the dosing siphon.[59] They succeeded in a 64 percent phosphorus reduction as compared to the 17 percent removal observed in the control filter. They cited five other studies also reporting that mineral addition to trickling filters was not as efficient as dosing activated sludge for phosphorus removal. Cecil cited Fairborn, OH, with unsatisfactory phosphorus removal when mineral addition occurred at the filter inlet.[44] The EPA Design Manual recommends against adding chemicals directly to the trickling filter.[18] The EPA Design Manual cites several examples of poor removal when only filters are dosed. Mineral addition in both the primary and secondary clarifiers is recommended for a trickling filter plant. Lime is not recommended by the EPA Manual.

Points of Addition - Tertiary Treatment: Tertiary phosphorus removal utilizes lime, aluminum or iron salts in a chemical-physical process to treat secondary effluent. The lowest phosphorus levels are encountered in a secondary effluent, but almost all of the phosphorus has been hydrolyzed to the ortho form (the most amenable to chemical precipitation). Chemical doses are low, but capital costs are high, since a complete precipitation, coagulation, flocculation and solid-liquid separation must be provided. Tertiary treatment can achieve a consistent, high quality effluent. Kugelman lists a Nassau County, NY, alum tertiary system producing a 0.08 mg/l total phosphorus (as P) effluent.[79] Lebanon, OH, treats to a 0.1-0.5 mg/l total phosphorus (as P) effluent with lime.[119] Lake Tahoe, CA, also uses lime to achieve a 0.14 mg/l total phosphorus (as P) effluent.[86]

Lime treatment can consist of a single or a two stage process.[18] As a tertiary step, lime treatment adds flexibility to the system, while achieving the desired phosphorus removal in a dependable operation. Lime recovery can be practiced since the sludge is primarily $CaCO_3$. Lime does not pose the metal leakage problems of aluminum or iron salts used in a tertiary step. The choice between the single or two stage

system depends on the amount of phosphorus removal required and the alkalinity. As discussed earlier, low alkalinity streams (less than 150 mg/l $CaCO_3$) will produce a poor floc because of insufficient $CaCO_3$ if the single stage process is used. A high alkalinity stream will produce very low phosphorus levels with pH levels of 9.5-10. Recarbonation will always be required to achieve a permissable effluent pH.

The treatment plant at South Lake Tahoe, CA, uses the two stage system followed by multi-media pressure filters to produce effluent levels less than 0.1 mg/l total phosphorus (as P).[86] Significant BOD and COD removals were also reported. Ockershausen reported that many trickling filter and activated sludge plants obtain suspended solids and BOD effluent values of 20 mg/l or less.[76] Blue Plains, DC, used single and two-stage systems to treat moderately alkaline wastewaters (100-150 mg/l $CaCO_3$), with the two stage system achieving better removals.[50] The second stage included a 6-12 mg/l Fe(III) dose to aid clarification. Dual media filtration followed the clarification step to produce a 0.09 mg/l average effluent total phosphorus (as P). The average BOD was 1.5 mg/l and suspended solids were 3.8 mg/l. Lebanon, OH, has a single stage lime process (pH 9.5) followed by dual media filters which produces a 0.5 mg/l average effluent total phosphorus (as P) in a high alkalinity wastewater (better for single stage).[120] Barnard asserted that lime treatment after the biological step was necessary to produce an effluent of 0.2 mg/l total phosphorus (as P) or less.[121]

Aluminum and iron salts have been evaluated as tertiary coagulants. Since aluminum and iron doses are related to the phosphorus concentration, they are lowest in tertiary treatment. The EPA Design Manual compares a 200 mg/l alum dose for raw wastewater while the effluent required only a 50-100 mg/l dose.[18] Effluent metal levels are of concern in tertiary treatment with mineral salts. For this reason, iron is not commonly used. Optimum pH control can be used in tertiary treatment to reduce the required chemical dose. Polymers may be required to aid in clarification and filtration.

A pilot study at South Lake Tahoe, CA, used alum followed by multimedia filters to produce a 0.03-0.3 mg/l total phosphorus (as P) effluent.[18] Nassau County, NY, produced total phosphorus (as P) effluent levels of 0.08 mg/l with alum and dual media filtration.[18] Chicago's Hanover Park, IL, plant used alum with rapid sand filtration or microstraining to remove up to 82 percent of the secondary effluent phosphorus.[122] Punta Gorda, FL, filtered an alum treated secondary effluent to produce phosphorus concentrations of 0.15 mg/l total phosphorus (as P), 3 mg/l suspended solids and 1 mg/l BOD.[76] Bell et al., removed 90 percent total phosphate from the settled and unsettled effluents of a trickling filter plant using alum and a countercurrent moving bed filter.[123]

Kugelman described five plants using a rapid mix, flocculator-upflow clarifier and dual media filters to achieve excellent phosphorus, BOD and suspended solids removals.[79]

King et al., compared the effectiveness of lime, alum, sodium aluminate and ferric sulfate as tertiary precipitants treating the effluent from a high rate trickling filter.[46] A target effluent total phosphorus (as P) concentration of 0.3 mg/l was set. Substantially higher doses of lime were required to achieve this rigid effluent standard. The aluminum to phosphorus molar ratio was higher than the iron to phosphorus molar ratio. They stated that this reflects the light floc of the aluminum as compared with the heavier ferric system floc. However, the iron system required a lower pH for optimal use than the aluminum systems.

Physical Removal

General: Physical techniques for phosphorus removal include ion exchange, chemical adsorption, reverse osmosis and electrochemical processes. These techniques are characterized by the extent that physical forces play in the removal of materials. Since these processes have only recently been applied to phosphorus removal from wastewater, the available data only describe laboratory or small pilot systems. Full scale operational and cost data are not available. The feed water for all these processes (except electrochemical) must be a well treated secondary effluent with virtually no suspended solids. The usual pretreatment is multi-media filtration of a secondary effluent.

Sorption:[124] Sorption describes an interphase accumulation or concentration of substances at a surface or interface. Three types of sorption are exchange sorption, chemical sorption and physical sorption. (The term "adsorption" will be used instead of "sorption" in subsequent discussion, although sorption includes both adsorption and absorption). Exchange adsorption is the process occurring in ion exchange phenomena. Chemical adsorption can be observed in activated carbon surface phenomena or in the sorption of phosphates occurring on the surfaces of clays and activated alumina, or silicates. Physical adsorption is a relatively low energy adsorption process of van der Waals attraction.

Exchange adsorption, as observed in liquid ion exchange, is driven by electrostatic attraction between ions in the liquid phase and charged sites on the solid phase. Selected ions in solution are concentrated on the surface of the solid phase by these electrostatic forces, while the ions originally associated with the charges sites are driven into the liquid phase. When applied to phosphate removal, the solid phase is usually an organic resin or an organometallic compound and the liquid phase is filtered secondary effluent. The phosphate ion in solution exchanges with hydroxyl or chloride ions associated with the charged sites.

Chemical adsorption, observed in phosphate removal by clays, silicates and activated alumina, is driven predominantly by chemical forces. Chemically adsorbed ions are held by strong chemical bonds and are not free to move on the surface or within the interface. Some partial movement can be observed in the weaker, electrostatic bonds of exchange adsorption. In chemical adsorption no "exchange" ion is added to the liquid phase.

Physical adsorption is driven by the low energy forces of van der Waals attraction. These weak attractive forces between molecules are somewhat weaker than hydrogen bonds and far weaker than chemical bonds. Molecules held by these forces are not fixed to a specific site, but can move freely within the interface.

These three types of forces all contribute to surface phenomena. Since all are present in each type of sorption, it is difficult to segregate the sorption processes. The distinction is based on the predominant type of forces involved in each situation. Some organic molecules not only form several chemical bonds, but are strongly held at other parts of the molecule by electrostatic forces. Such large molecules exhibit the total spectrum of sorption energies. Sorption processes examined for phosphorus removal include ion exchange and chemical adsorption on activated alumina, silicates and clays.

Ion Exchange: Ion exchange for phosphorus removal uses synthetic resins to treat filtered secondary effluent.[5,51,52] The resin contains many surface functional groups which are charged and hold ions by electrostatic forces. Phosphates are exchanged with the ions on the functional groups. The selectivity and degree of affinity for the phosphate anion determines the effectiveness of the ion exchange. Selectivity depends on ion charge characteristics.[124] An anion exchange resin will prefer a trivalent (phosphate) anion to a monovalent (chloride) anion, for example. The degree of affinity describes the selectively of anions whose charge characteristics are similar. Size plays an important role in affinity and selectivity. For example, OH is preferred to NO_2 and NO_3.[86] Commercial anion exchange resins do not have the selectively and affinity for phosphorus.[86] Modified resins, such as organometallics, have shown improved selectivity for the phosphate anion.[51,86,125-127]

The applied process involves passing a filtered secondary effluent through a series of columns containing the exchange resin. After a certain number of bed volumes of wastewater have passed through the first column, the resin's exchange capacity is exhausted. The column must be removed from service for regeneration. A relatively small amount (several bed volumes) of a regenerant solution is passed through the column. This solution strips the phosphorus from the functional groups in a reverse of the ion exchange process, restoring the hydroxyl or chloride anion to the functional groups. After regeneration and

rinsing, the exchange column is ready to be placed back into operation. The waste regenerant solution is then chemically treated, usually with lime, to precipitate the phosphorus and the restored regenerant is ready for another column. Sodium hydroxide or ferric chloride solutions are typical regenerant solutions in phosphorus removal ion exchange.[52]

Nesbitt discusses two studies of orthophosphate reduction by ion exchange.[53] Both studies used highly porous, strongly basic anion exchange resins. One resin reduced orthophosphate from 2.8 to 0.16 mg/l total phosphorus (as P) and another reduced the ortho form in a sewage treatment plant effluent from 7.55 to 0.11 mg/l total phosphorus (as P). One operational problem was fouling of the resin by suspended solids and dissolved organic matter. Another problem was disposal of waste regenerant.

Another laboratory study tested two organic resins for phosphate removal.[125] A polyol resin and a resin/metal sorbent were compared. Only the resin/metal sorbent demonstrated a satisfactory capacity for phosphorus removal. Dilute ferric chloride solutions were used in regeneration. Filtered secondary effluent was passed through the columns on a schedule requiring daily regeneration. Backwashing, rinsing and product water storage were required. The waste regenerant was treated with lime and returned to the secondary clarifier to settle the precipitated phosphorus. Treatment costs were estimated at 20 cents per 1000 gallons.

One study screened a variety of organic compounds for liquid ion exchange to remove phosphorus.[126] Only certain resin/metal sorbents showed significant affinity and capacity for phosphorus. This affinity seemed to be concentrated in minor constituents present in the solvents. No resin of those screened was totally selective for phosphate exclusively. Other anions are also exchanged. Because of the low selectivity, operating costs were estimated to be several times that of conventional lime treatment. The best removal obtained for the resins studied was 52 percent.

Inorganic aluminum vermiculites (a hydrated silicate containing magnesium and aluminum) were tested for phosphate removal.[128] Highest removals were obtained at low pH levels (pH 3) and dilute aluminum concentrations (0.1 to 0.05 Molar). Higher pH values and aluminum concentrations resulted in deteriorating performance.

Boari and Liberti describe their work with anion exchange resins.[127] Adverse influences of chlorides and sulfates, poor selectivity, excessive regenerant levels and resin consumption rates resulted in very high cost estimates.

Shindala discusses two studies which used anion exchange resins.[5] One study applied filtered activated sludge effluent to a commercially available anion exchanger and achieved 97 percent phosphorus reduction. The other study involved a pressurized anion exchange system operating on a bicarbonate cycle and regenerated with ammonium hydroxide and carbon dioxide. Shindala concludes that ion exchange for phosphorus removal would be best suited where chemical precipitation is not feasible and where sludge disposal creates major problems.

Some trends are clear in the use of ion exchange for phosphorus reduction. Only filtered, well-treated secondary effluents should be used to avoid fouling of the exchange beds by suspended solids and dissolved organic materials. Waste regenerant disposal problems must be solved, or a chemical precipitation system used to restore the regenerant. A precipitation system would require a solids-liquid separation process and a sludge disposal system. Careful monitoring and operation will be required on a continuous basis by well trained operators. Daily regeneration cycles can be expected. System costs will be high, compared to other alternatives. Product water quality will be far superior to the quality required by the NPDES system.

Design data are needed from full scale operation of ion exchange systems. Scale factors, operation and maintenance problems and cost data are not yet completely available. Based on existing data, ion exchange for phosphorus reduction is not yet ready for general application to domestic waste treatment systems.

Chemical Adsorption: Chemical adsorption for phosphate removal has been tested using activated alumina.[51,129-133] This material is a highly porous (high surface area) aluminum oxide that has been heated or treated with nitric acid to remove moisture and adsorbed gases from pore sites. Successful adsorption of phosphate requires the presence of Ca (II) and Mg (II).[131] This indicates the chemical binding nature of the adsorption mechanism. The formation of a calcium or magnesium phosphorus complex is probably part of overall surface or interface phenomena. The activated alumina can be regenerated with NaOH. The regenerant solution is then treated with lime to precipitate apatite and $CaCO_3$.

Activated alumina shows more selectivity for the phosphate anion than resins.[52] The material seems to adsorb both ortho and condensed inorganic forms of phosphorus. Effluent levels less than 0.1 mg/l total phosphorus (as P) can be obtained. No ions are added to the liquid by the adsorption process. The process appears to be relatively unaffected by influent composition, except for suspended solids fouling the bed. No pH changes occur during the process. Normal feed water would be a filtered secondary effluent.

Yee pioneered phosphate adsorption on activated alumina, regenerating the alumina with NaOH and nitric acid.[130] Ames reported on further work which obtained 95 to 99+ percent removal.[129] Effluent concentrations were less than 0.03 mg/l total phosphorus (as P) with flows of 10 column volumes per hour and with 500 column volumes before regeneration was required. The need for more operating data, a requirement for highly trained operators and cost figures of 3 to 6 cents per 1000 gallons were discussed.

Fly ash, the waste product of coal combustion for thermal power generation, has shown excellent potential to remove phosphorus. Gangoli and Thodus compared the reaction kinetics of two aluminas and fly ash.[132,133] In an earlier study, they determined that fly ash possessed a significant adsorptive capacity for phosphate and was more promising than AHB alumina and Fl alumina. McNeice determined that coal itself could adsorb phosphate to achieve up to 75 percent reduction.[134] The degree of adsorption depended on the ferric ion concentration in the coal, indicating a chemical adsorption phenomenon. Randall et al., tested both coal and fly ash in batch and column reactors for phosphate removal.[135] They also observed the relationship between phosphate removal and the iron content of the coal tested. They also reported that a high alumina fly ash would exhibit much greater surface adsorption of phosphate than a low alumina fly ash. The need for pilot and full scale data was identified.

Edzwald et al., evaluated the phosphate adsorptive capacity of three clays at low and high ionic strengths and at neutral pH conditions.[136] The pH dependence of adsorptive capacity of montmorillonite and illite was examined. The basic chemical adsorptive phenomenon was attributed to a reaction between orthophosphate ions and aluminate surface groups. Speigel and Forest discussed the use of an activated bentonite compound, which contains a polymer and calcium and aluminum salts, to chemically adsorb phosphate.[51] Removals similar to those observed with chemical precipitation were reported, but at doses much smaller than reported lime or alum doses.

Chemical adsorption technology for phosphate removal is in an early state of development. There is a lack of full scale operating and cost data. Feedwater requirements include a filtered, well-treated secondary effluent. Highly trained operators are required to operate the process and its regeneration cycles. Waste regenerant solution and chemical sludge disposal remain as problems. The complexity of operation and equipment requirements can result in significant costs. However, the effluent levels attainable with chemical adsorption are far below NPDES limitations.

Reverse Osmosis: Osmosis describes the fluid movement across a membrane which separates two solutions of different solvent activities.[137] Fluid transport across the membrane attempts to reduce the chemical potential until a thermodynamic equilibrium across the membrane is achieved. The application of external pressure (usually several orders of magnitude higher than the osmotic pressure) to overcome the chemical activity potential can reverse the fluid movement. This reversal of the osmotic process is used to concentrate undesirable components into a small volume while producing a clean effluent. The membranes used are asymetric polymeric films, like cellulose acetate, and aromatic polyamides. These materials selectively pass and reject solution components.

Process efficiency is usually determined by the nature of the membrane-solution interactions.[137] The use of cellulose acetate, for example, is restricted to a pH range of 3.5 to 8. Outside this range, rapid hydrolysis of the membrane occurs, greatly reducing membrane life.

The most extensive use of reverse osmosis has been in the desalination of sea water.[137] The application of membrane technology is also directed toward renovation of wastewater. Johnston and Lim described the limited efforts to apply reverse osmosis to wastewaters in a literature review.[138] The application has so far been limited to bench and pilot scale systems to remove nutrients and residual chemicals used in municipal treatment facilities, such as alum, lime, ferric chloride and polymers. Feedwater has been a well-treated secondary effluent virtually free of suspended solids. Cellulose acetate membranes with 70, 75 and 90 percent salt rejection were used. Johnston and Lim conclude that the application of reverse osmosis, as a tertiary treatment step in municipal systems, is conceivable.[138]

In their own research, Lim and Johnston obtained phosphate removals approaching 100 percent using cellulose acetate membranes in bench and pilot tests.[137] The membranes also removed 97 percent of the Fe (II), Fe (III) and $SO_4^{(-2)}$ ions in the solution. Reductions of 92 percent were reported for the Ca (II) cation and 83 percent for the chloride anion. Variability in operating conditions had little effect on membrane selectivity, but greatly affected permeate flux, or the rate of fluid transport across the membrane. Physical and chemical cleaning techniques were required to ensure consistent and successful operation. Surface fouling was the greatest problem.

Culp and Culp discuss operational considerations of the application of reverse osmosis to wastewater treatment.[86] The extensive removal of bicarbonate from the wastewater poses two problems. The natural buffering capacity (alkalinity) of the wastewater is greatly reduced. The concentration of bicarbonate in the waste brine leads to severe scaling and

membrane fouling. Feedwaters containing high sulfate concentrations will result in $CaSO_4$ precipitation in the brine and on the membrane. Iron and manganese will also precipitate unless the pH is kept below a value of 6. Adjustment of pH will be required to minimize the calcium carbonate precipitation as well. Brine disposal poses another problem. Successful operation of a reverse osmosis system can require activated carbon adsorption as a pretreatment step. Commercial units are of limited capacity and operational costs are high. More research in membrane technology is required to develop membranes that have longer life and higher flux rates which could operate with a minimum of pretreatment.

Electrochemical: Two applications of electrochemistry to phosphorus removal have been studied. Shindala describes one process designed to precipitate phosphorus and ammonia.[5] Wastewater is mixed with seawater (20 percent by volume) and passed through a cell containing carbon electrodes. The seawater provides the magnesium ions required for successful precipitation of the phosphorus and ammonia. The relative densities of the two fluids cause the seawater to accumulate at the bottom of the cell, where the anode is placed. The wastewater moves to the top of the cell where the cathode is placed. Electric current is passed through the cell raising the pH. The phosphorus precipitates as $Ca_3(PO_4)_2$ and $MgNH_4PO_4$ and is brought down by the formation of $Mg(OH)_2$. Hydrogen bubbles lift the solids to the surface to be skimmed off. The effluent is then discharged to the ocean.

Sadek used sacrificial electrodes (Al or Fe) to chemically precipitate and adsorb phosphorus.[139] The electrodes donate the metal ions to the solution by the flow of current. The metal ions react with the phosphate anions to form a floc. This method is in an early developmental stage and needs further research and testing before pilot and full scale application can be attempted.

Nesbitt discusses electrochemical methods and their limitations.[53] A source of magnesium ions is required (or sacrificial electrodes). The seawater source has obvious limitations. The process would be difficult to apply generally to remove phosphorus but could produce effluents nearly phosphorus free.

SOLIDS PRODUCTION

Experience indicates that requirements for sludge handling and disposal may contribute 30 percent of the initial capital cost and 50 percent of annual operating expense in a secondary treatment plant.[140] Consequently, the addition of a unit process that would increase overall solids production must take into consideration the amount and nature of additional solids produced. The use of chemical precipitation to remove phosphorus will not only increase overall sludge production (in tons/million gallons), but will also alter the handling, dewatering and disposal properties of a combined secondary treatment plant sludge. The following is a brief discussion of the types of sludges observed in chemical-biological treatment schemes.[5,11,14,18,44,50,76,79,80,86,87,93,95,98,108,140-145]

In general, chemical precipitation for phosphorus removal will result in increased sludge mass from the combined effects of increased suspended solids removal and metal precipitation. Increases may be estimated by stoichiometric calculations in some cases and by jar tests in others. Combined chemical-biological sludges do not, as a rule, significantly affect the anaerobic digestion process and yield minimal phosphorus release during the digestion process. Sludge conditioning may now be improved with anionic polymers, as opposed to the cationic or $FeCl_3$-$Ca(OH)_2$ systems usually successful with biological sludges. However, these generalizations must be tempered with the observation that sludge volume and characteristics vary considerably and must be determined for each site application for effective engineering design.

Experiences illustrate the changes in mass and nature of sludges. Chemical addition to the primary clarifier can produce various sludges. Alum was used in a primary clarifier to remove phosphorus in Lebanon, Ohio.[18] The chemical-biological sludge concentrated to 2-3 percent by weight in the clarifier, but exhibited very poor settling and dewatering characteristics. Aluminum salts generally produce gelatinous hydroxide flocs that are very difficult to dewater.

Iron was used in Mentor, OH, and although sludge production increased, sludge volume was never more than twice the usual biological sludge volume.[18] Iron forms a well-flocculating hydroxide precipitate that often possesses good dewatering characteristics. The use of iron in primary precipitation may increase primary sludge production by 100 percent, but the improved suspended solids and BOD removals may result in decreased secondary sludge production (by as much as 30 percent). Thus, total net sludge production may show only a 25 percent increase of which 15 percent may be due to formation of iron-phosphate-hydroxide sludge.

Lime often forms a fragile floc that may require a coagulant aid for effective sedimentation. Lime sludges are very difficult to dewater, although odor problems are rare. Gravity thickening can increase the solids in a 6-8 percent lime-phosphate-primary sludge to as much as 10-12 percent. Rochester, NY, observed 65 tons/day sludge production without lime and estimated that 175 tons/day could be expected if lime were used in the primary clarifier.[18] Considering a decrease in activated sludge production (from 75 tons/day down to 30 tons/day), the net sludge increase of 70 tons/day represents a 110 percent sludge mass increase for Rochester. Newmarket, Ontario, used lime in their activated sludge plant in the primary system and reported that the combined lime primary-secondary solids were easily handled and had excellent dewatering characteristics.[146] (Ten percent solids in clarifier underflow to centrifuges and a 97 percent capture to reach a 31 percent solid cake.) The weight increase in solids, however, was threefold. Investigators at Windsor, Ontario, studied lime in the primary clarifier in comparison with alum in the aeration tanks in the Little River Plant.[146] They observed that lime produced 50 percent more sludge, but required lower chemical conditioning costs than the normal solids flow.

Aluminum and iron addition to the aeration tanks also alters the amount and nature of the secondary sludge, usually generating a dense, stable secondary sludge. In Manassas, VA, improvements in sludge density were observed in a 1-year study of alum addition to aeration tanks, although 4 pounds of additional solids were produced per pound of Al (III) added. Aluminum - biological sludges are amenable to digestion with minimal system upset and phosphorus release. Few data are available on iron-organic sludges. Investigators at North Toronto, Ontario, used $FeCl_3$ at the end of the aeration basins.[146] The system operated at a reasonable processing rate and acceptable cake solids concentration with chemical conditioning. Researchers at Windsor Little River, Ontario, compared lime in their primary system to alum addition in the aeration tanks.[146] They reported a 50 percent increase in sludge mass, but lower chemical conditioning costs with the lime-primary sludge. The alum-biological sludge also produced 50 percent more sludge mass, but with lower filter yields and higher dewatering costs. The alum-biological sludge density was one-half the density of the lime-primary sludge (5.7 percent vs. 11.6 percent). Aluminum or iron addition to aeration tanks can achieve total phosphorus (as P) levels of less than 1 mg/l when anionic polymers and mixed media filtration are used.

Lime addition as a tertiary step yields a recoverable sludge. Recalcined lime is recycled following a thickener - centrifuge or vacuum filter-calciner sequence. Sludge volumes are in the range of 1.5 percent or more of feed volumes and are generally 1-5 percent solids by weight. Aluminum or iron addition as a tertiary system requires anionic polymers and mixed-media filtration to achieve low phosphorus levels. The sludge disposal problem is greater since there is no chemical regeneration. Sludge dewatering may be difficult, but can be accomplished with conservative design of conventional dewatering equipment.

SUMMARY

Accelerated eutrophication is causing serious deterioration of the nation's waterways. Surface water supplies have deteriorated, creating water supply and treatment problems. Fish life and recreation continue to be adversely affected. Such increasing restrictions on water uses are attributed to the addition of sufficient critical nutrients which stimulate excessive algal and aquatic plant growth. Phosphorus has long been identified as one of these limiting nutrients. Since man's wastewaters are primary sources of phosphorus and other nutrients, control over accelerated eutrophication can be exerted. Research has indicated that phosphorus is the most frequently limiting nutrient and is the most amenable to removal in wastewater treatment systems.

The identification of phosphorus as a limiting nutrient and its concentrations in man's wastestreams have resulted in limitations on these concentrations. These limits are embodied in the National Pollutant Discharge Elimination System (NPDES) and applies to all categories of treatment plants. The Department of the Army must apply for and receive discharge permits for all their wastewater discharges. Existing permits already impose phosphorus limitations, in many cases, on Army wastewater treatment plant effluents.

Army wastewater treatment systems consist primarily of trickling filters as secondary treatment processes, while there are only a few activated sludge systems and extended aeration package plants. Army plants are often flow underloaded and are stressed by drastic seasonal and daily changes in loadings. The small size of Army plants (0.1-5.0 million gallons per day) require simplicity in operation and maintenance.

NPDES permit limitations for phosphorus exist for many Army treatment plants. The range for phosphorus levels is 0.2 to 2.0 mg/l total phosphorus (as P) with a modal value of 1.0 mg/l. These limits are for permits after 1 July 1977, and prior to 1980. The permits also include standards for ammonia nitrogen, BOD and suspended solids levels.

Domestic sewage contains roughly 5 to 20 mg/l phosphorus (as P). About 50 percent of this will be in the ortho form, 40 percent in an inorganic condensed form and 10 percent organically bound. Detergents contribute 20 to 70 percent of the phosphorus in domestic wastewater. The inorganic condensed and organic forms are partially converted to the ortho form as the phosphorus moves through a treatment plant.

Phosphorus removal encompasses several technologies. Biological, chemical-physical, chemical-biological and physical techniques have successfully removed phosphorus from wastewater.

Biological removal occurs in trickling filters and activated sludge plants through microbial action. Microorganisms adsorb the phosphorus

(usually in the ortho form) and incorporate it into new cell mass. The cell mass is removed and treated by solid waste disposal techniques. Overall phosphorus removal depends on the phosphorus capacity of the cells, the rate of uptake, the rate of all growth and cell wastage. Expected removals across a trickling filter are 20 to 30 percent while an activated sludge plant can expect to remove 30 to 50 percent.

Phosphorus can be removed from a wastestream and incorporated into a sludge by chemical precipitation. The use of lime, alum, sodium aluminate and iron salts to precipitate phosphorus is common practice in wastewater treatment. The chemicals are used in full scale plants in several different flow schemes. Expected effluent concentrations from a chemical-physical process are from 0.5 to 2.0 mg/l total phosphorus (as P). Chemical-physical techniques are most successful with the ortho-form. Phosphorus removal using lime is a function of pH and alkalinity. Alum, aluminate and iron salt dosages depend on phosphorus concentrations and alkalinity. Successful lime treatment is accomplished at pH levels greater than 9.0. Alum is most successful at pH levels of 5.7 to 6.3. Ferrous salts are successful near the pH of 8.0 while ferric salts are more effective in the pH range of 4.0 to 5.0. Although physical-chemical treatment to remove phosphorus can be operated as a separate system, the usual method is to combine chemical treatment with a biological system.

Chemical-biological removal is accomplished with the same chemicals used in purely chemical-physical removal. The chemicals can be added to raw, degritted sewage; to the primary effluent; to the aeration tank or trickling filter; to the secondary clarifier influent or effluent. The choice of chemical and point of addition depend on effluent standards, alkalinity, pH, sludge dewatering, sludge disposal, chemical costs and chemical availability. Effluent levels will rarely be less than 1.0 mg/l total phosphorus (as P).

Physical techniques to remove phosphorus include ion exchange, chemical adsorption, reverse osmosis and electrochemistry. These techniques can produce nearly phosphorus free water. Full scale application, design data and cost estimates are not available.

Sludge dewatering and disposal is an expensive part of wastewater treatment. All the existing phosphorus removal techniques ultimately concentrate the phosphorus into a sludge, whether a chemical, biological or a combination. Chemical addition for phosphorus removal will result in higher sludge volumes of varying degrees of dewaterability.

CONCLUSIONS

The over-fertilization and accelerated eutrophication of the nation's surface waters have resulted from the input of large amounts of the limiting nutrients required for plant and algal growth. Since man's wastewaters are primary sources of phosphorus and other nutrients, control over accelerated eutrophication can, and must, be exerted. To this purpose, the National Pollutant Discharge Elimination System has been established. Effluent limitations are set on phosphorus, nitrogen, BOD, suspended solids, pH, dissolved oxygen and fecal coliforms. Research has indicated that phosphorus is the most frequently limiting nutrient and is the most amenable to removal in a wastewater treatment system.

Department of the Army installations must apply for and receive NPDES permits prior to discharging wastewaters. Current permit limitations reveal that treatment beyond existing secondary treatment must be carried out to meet effluent limitations on phosphorus. The application of phosphorus removal technology to comply with the permits will take various forms. Many plants will require additions, or modifications. In some cases, the improvement of existing treatment efficiency alone may be satisfactory. Other facilities will need to provide or construct a phosphorus removal process. The degree of addition or modification will depend on the standards which apply, the type of existing facilities, wastewater characteristics and operation and maintenance of existing facilities.

Department of the Army treatment plants are primarily trickling filter plants providing secondary treatment. Their small size (0.1 to 5.0 million gallons per day) is reflected in the simplicity of operation. These plants are subject to drastic seasonal and daily load variations not typical of municipal systems. The policy of cost-effectiveness dictates a careful approach in applying standard advanced wastewater treatment techniques to these facilities.

Process selection criteria must be based on permit limitations, treatment plant facilities and costs. A phosphorus removal process must be able to meet permit limitations under the flow and load variations typical of Army wastewater flows. It must be simple to operate and maintain, both in terms of the skill level of the operator and man-hours required. It must require minimal laboratory support. The technique should be a well-tested process with a substantial full scale design, operation, maintenance and cost record. The process should require little or no pretreatment. Processes that make maximum use of existing facilities and equipment and that require little initial capital investment should be preferred. Processes that require all new facilities and equipment, such as tertiary step, will need a large initial capital investment and should be avoided. A process that, in addition to reducing phosphorus, effects a reduction of BOD, suspended solids, nitrogen

and fecal coliforms should be preferred to a process which only reduces phosphorus. Guided by these criteria, some conclusions about existing phosphorus removal techniques can be drawn.

The application of biological process control alone to a trickling filter system will not meet permit limitations. Biological uptake of phosphorus by a trickling filter is erratic and not subject to control to any extent. Only 20 to 30 percent reduction of phosphorus can be expected, even under the best operating conditions. Biological control of an activated sludge process for substantial phosphorus reduction is in the developmental stage. Therefore, phosphorus reduction at Army treatment plants must be accomplished by the modification of, or addition to, the biological system to include a chemical or physical removal process.

Chemical-biological treatment can successfully overcome the trickling filter's usual poor biological phosphorus removal and meet permit limitations. Chemical processes can consistently meet permit limitations under flow and load variations typical of Army wastewater treatment systems. The chemical dose can be made to match these variations and to achieve consistent removals without wasting chemicals, or adversely affecting other unit processes in the treatment plant. The addition of a chemical step to a biological plant can substantially improve suspended solids, BOD and COD removals. Chemical treatment processes to remove phosphorus have a long history of full-scale operation. Such processes are easier to operate and maintain than biological or physical systems: no pretreatment is required, laboratory support is minimal and the chemical process can be inserted into the biological flow scheme at several points. This flexibility allows for maximum use of existing facilities and equipment while achieving the desired phosphorus reduction.

Chemical addition can occur prior to the primary clarifier. The clarifier is used for solid-liquid separation. Chemical addition to the biological step can occur in the activated sludge process, but generally is not done in trickling filter systems. The chemicals can be added prior to the secondary clarifier, using this clarifier for solid-liquid separation. These addition points make maximum use of existing facilities and equipment and require minimal capital investment. Tertiary chemical treatment can be considered, but requires large capital investment to construct all the facilities needed to effect the desired phosphorus reduction. Tertiary treatment does not reduce the suspended solids and organic loading on the biological step because of its position in the flow scheme.

Several chemicals are available to reduce phosphorus. Lime, alum and iron salts are commonly used in phosphorus reduction. Lime dosage depends on alkalinity and the desired pH while alum and iron salts depend on alkalinity and the phosphorus concentration. Control of a lime feed system requires only pH monitoring, while alum and iron doses should

be made in a proportion to the influent phosphorus concentration. Consequently, a lime precipitation scheme is the simplest of the three chemical schemes commonly used. Alum and iron salts could be dosed at one set level, or based on daily jar tests. However, fluctuating phosphorus levels result in significant chemical wastage in such a control scheme.

A chemical-biological process can produce effluent phosphorus levels of 1.0 mg/l total phosphorus (as P) consistently. Should effluent levels of 1.0 mg/l or less be required, a filtration step following the secondary clarifier, or tertiary clarifier, can be added. The actual choice of the chemical and the addition point must be made on a plant-by-plant basis. Variations in permits and in wastewater characteristics are significant factors in this selection. A process should be selected on its capability of meeting effluent limitations, not on its ability to produce a nearly phosphorus-free product water. Attempts to reduce phosphorus concentrations to levels far below those required by permits will result in excessive costs not justified by any benefit or standard. In general, the modification of a biological treatment system to include a chemical precipitation step will be characterized by favorable economics, simplicity and reliability.

The addition of a chemical precipitation process will increase overall sludge production. Sludge handling, dewatering and disposal properties will also change. These properties depend on the chemical used and the point of chemical application. Sludge dewatering and disposal can contribute 30 percent of initial capital costs and up to 50 percent of annual operating costs in a secondary plant. Consequently, process selection efforts must consider the amount and nature of additional solids produced for each scheme considered.

Current phosphorus removal technology also includes techniques such as ion exchange, adsorption, reverse osmosis and electrochemistry. These physical techniques are still in the development phase. Extensive pretreatment requirements, complexity of operation and excessive costs characterize these techniques at their current state-of-the-art. These processes should not be considered for application of Army treatment facilities.

RECOMMENDATIONS

It is recommended that process selection for phosphorus removal to be applied at Army wastewater treatment plants place emphasis on achieving NPDES limitations and not on obtaining the lowest effluent phosphorus concentrations possible.

It is recommended that process selection for compliance with permit limitations on phosphorus be directed toward upgrading existing plants rather than toward completely replacing existing facilities. Process selection should include a high priority on making maximum use of existing facilities and equipment to minimize costs.

It is recommended that high priority be placed on simplicity of operation and maintenance, both from skill levels required and manhours consumed. Little or no pretreatment should be required. Laboratory support requirements should be minimal.

It is recommended that processes considered for application in Army wastewater treatment plants for phosphorus reduction be limited to chemical precipitation techniques that possess a strong history of full scale operation and maintenance.

It is recommended that chemical choice and location of application be accomplished on a plant-by-plant basis. Site specific facilities, standards, operator skill level and availability, chemical availability and the nature and amount of sludge produced should be primary variables of concern.

It is recommended that studies be conducted on the modification of a biological treatment system, specifically a trickling filter system, by the addition of chemical treatment processes. The overall purpose of the studies is to provide data on the application of current advanced waste treatment technology to Army treatment facilities to meet permit limitations. These studies should examine chemical addition at several points in the biological process, treating a typical Army wastestream. Lime, alum and iron salts should be examined alone and with the addition of adjunct materials such as clays and polymers. The objectives of these studies should be:

To demonstrate successful application of chemical precipitation techniques to Army wastewater treatment facilities, making maximum use of existing facilities and equipment;

To demonstrate the flexibility of chemical precipitation processes in being applicable to any Army wastewater treatment facility with any type of flow and load variations;

To demonstrate successful process performance in meeting permit limitations for phosphorus consistently in Army facilities;

To demonstrate process control to achieve various effluent phosphorus concentrations;

To demonstrate improvement in removal of permit limited parameters other than phosphorus, such as suspended solids, BOD and COD;

To demonstrate simplicity of operation and control, process consistency, process reliability and economic desirability.

LITERATURE CITED

1. "Chemistry of Nitrogen and Phosphorus in Water," Committee Report, Water Quality Division Committee on Nutrients in Water, J. Am. Water Works Assoc., p. 127-140 (Feb 1970).

2. Hammer, M.S., "Water and Wastewater Technology," Wiley & Sons, NY (1975).

3. Doyle, K.F., "Phosphates - An Unresolved Water Quality Problem," Environment Reporter, Vol. 2, No. 16, Monograph No. 9 (1971).

4. Thomas, E.A., "Phosphorus and Eutrophication," Environmental Phosphorus Handbook, Wiley & Sons, NY (1973).

5. Shindala, A., "Evaluation of Current Techniques for Nutrients Removal from Wastewaters," Water Resources Research Institute (June 1971).

6. Stumm, W., "Man's Acceleration of Hygrogeochemical Cycling of Phosphorus: Eutrophication of Inland and Coastal Waters," Water Pollut. Control, 74(2):124-133 (1975).

7. Dogmel, W.N. and A.E. Brooks, "Detergent P and Algal Growth," Water Res., 9:713-719 (1975).

8. Doyle, K.F., "Phosphates - An Unresolved Water Quality Problem," Environment Reporter, Vol. 2, No. 16 (Aug 1971).

9. David, M.H., F.J. Schroeder, J.J. Peirce, E.F. Joeres, and D.A. Braash, "Statistical Study of Phosphorus Removal in Wisconsin," J. Env. Eng. Div., ASCE, EE2 (April 1976).

10. Ockershausen, R.W., "Alum vs. Phosphates: It's No Contest," Water & Waste Eng., 11(11) (Nov 1974).

11. "Report of the Expert Group on Treatment Processes," Water Management Sector Group, Organization for Economic Cooperation and Development (1972).

12. Bradshaw, J.S., R.B. SunDrud, D.A. White, J.R. Barton, D.K. Fuhriman, E.L. Loveridge and D.R. Pratt, "Chemical Response of Utah Lake to Nutrient Flow," J. Water Pollut. Control Fed., 45(5):880-888 (May 1973).

13. Lin, S.S. and D.A. Carlson, "Phosphorus Removal by the Addition of Aluminum (III) to the Activated Sludge Process," J. Water Pollut. Control Fed., 47:1978 (1975).

14. Balmér, P. and O.F. Frederiksen, "A Pilot Plant Scale Evaluation of Potential Precipitants in the Secondary Precipitation Process," Water Res., 9:721-727 (1975).

15. Huang, V.H., J. Mase and E.G. Fruh, "Nutrient Studies in Texas Impoundments," J. Water Pollut. Control Fed., 45(1) (Jan 1973).

16. Federal Register, 38(206):29646 (Oct 26, 1973).

17. Toerien, D.F., "South African Eutrophication Problems: A Perspective," Water Pollution Control, 74(2):134-142 (1975).

18. "Process Design Manual for Phosphorus Removal," Environmental Protection Agency, Program #17010 GNP Contract #14-12-936 (Oct 1971).

19. Menar, A.B. and D. Jenkins, "Calcium Phosphate Precipitation in Wastewater Treatment," Environmental Protection Agency, Grant #17080 DAR, EPA-R2-72-064 (Dec 1972).

20. Minton, G.R. and D.A. Carlson, "Primary Sludges Produced by the Addition of Lime to Raw Wastewater," Water Res., 7:1821-1847 (1973).

21. Hething, L.J. and R.M. Sykes, "Sources of Nutrients in Conandarago Lake," J. Water Pollut. Control Fed., 45(1) (Jan 1973).

22. Mackenthum, K.M., L.E. Leup and R.K. Stewart, "Nutrients and Algae in Lake Sebasticook, Maine," J. Water Pollut. Control Fed., 40(R72) (1968).

23. "Report to the International Joint Commission on the Pollution of Lake Erie, Lake Ontario, and the International Section of the St. Lawrence River," Vol. 1, Queen's Printer, Ottawa, Ontario, Canada (1969).

24. Wallis, I.G., "The Balance Between Waste Treatment and Waste Discharge in the U.S., 1957-2000," J. Water Pollut. Control Fed., 46(3) (March 1974).

25. Pollio, F.K. and R. Kunn, "Tertiary Treatment of Municipal Sewage Effluents," Environ. Sci. Technol., 2:54 (1968).

26. Thomas, E.A., "The Process of Eutrophication in Central European Lakes," In: Eutrophication: Causes, Consequences and Correctives, National Academy of Sciences, Washington, DC (1969).

27. Stumm, W. and J.J. Morgan, "Stream Pollution by Algal Nutrients," Trans. 12th Annual Conference of Sanitary Engineering, University of Kansas (1962).

28. Emery, R.M., C.E. Moon and E.B. Welch, "Delayed Recovery of a Mesotrophic Lake after Nutrient Diversion," J. Water Pollut. Control Fed., 45(5) (May 1973).

29. Stern, G. and F.D. Dryden, "Renovated Wastewater Creates Recreational Lake," Environ. Sci. Technol., 2:268 (1968).

30. Francisco, D.E., M. Strauss and B.A. Dempsey, "Phosphorus Removal with Alum from Secondary Effluent," J. Water Pollut. Control Fed. 48(8) (Aug 1976).

31. Francisco, D.E. and C.M. Weiss, "Algal Response to Detergent Phosphate Levels," J. Water Pollut. Control Fed., 45(3) (March 1973).

32. Rohlich, G.A. and P.D. Uttormark, "Wastewater Treatment and Eutrophication," In: The Limiting Nutrient Controversy, G. Likens (ed), pp. 231-242, American Society of Limnology and Oceanography.

33. Environment Reporter, State Water Laws, 716:0603 (1974).

34. Environment Reporter, State Water Laws, 621:0701 (1972).

35. Environment Reporter, State Water Laws, 811:1043 (1974).

36. Environment Reporter State Water Laws, 771:0503 (1974).

37. Environment Reporter, State Water Laws, 771:0504 (1974).

38. Environment Reporter, "Federal Water Pollution Control Act," 71:5101 (1975).

39. US Environmental Protection Agency, "Guidelines for Developing or Revising Water Quality Standards" (1973).

40. "Water Quality Criteria - Notice of Publication," Federal Register, 38(206):29644 (Oct 1973).

41. Environment Reporter, "State Standards for Phosphates," 621·0701 (1972).

42. Environment Reporter, State Water Laws, 816:0603, p. 131.

43. VanWazer, J.R., "The Compounds of Phosphorus," In: Environmental Phosphorus Handbook, Wiley-Interscience.

44. Cecil, L.K., "Evaluation of Processes Available for Removal of Phosphorus from Wastewater," EPA, Project #17010DRF, Contract #14-12-581, Oct 1971, PB 211-191.

45. Ferguson, J.F., D. Jenkins and W. Stumm, "Calcium Phosphate Precipitation in Wastewater Treatment," Chem. Eng. Progress Symposium - Water, 107(67) (1970).

46. King, P.H., J.D. Jenkins, R.C. Hoehn and C.W. Randall, "Comparative Effectiveness of Selected Precipitants for Phosphorus Removal in Tertiary Treatment," Presented at 4th Annual Environmental Engineering and Science Conference, Louisville, KY (Mar 1974).

47. "Phosphates in Sewage and Sewage Effluents," Notes on Water Pollution, Water Pollution Research Laboratory, Stevenage, England, No. 49 (June 1970).

48. Finstein, M.S. and J.V. Hunter, "Hydrolysis of Condensed Phosphates During Aerobic Biological Sewage Treatment," Water Res., 1:247 (1967).

49. Heinke, G.W. and J.D. Norman, "Hydrolysis of Condensed Phosphates in Wastewater," Proc. 24th Ind. Waste Conf., Purdue University, W. Lafayette, IN, Ext. Ser. 135, p. 644 (1969).

50. Kreissl, J.F., "Phosphorus Removal Practice," Presented at the Sanitary Engineering Institute, University of Wisconsin (Mar 1971).

51. Spiegel, M. and T.H. Forrest, "Phosphate Removal: Summary of Papers," J. Am. Soc. Civil Eng., Sanit. Eng. Div., 5A5, p. 803 (Oct 1969).

52. Cohen, J.M., "Nutrient Removal from Wastewater by Physical Chemical Processes," Proc. of Symposium on "Nutrients in Natural Waters," 161th National ACS Meeting (Mar 1971).

53. Nesbitt, J.B., "Phosphorus Removal - The State of the Art," J. Water Pollut. Control Fed., 41(5):701 (1969).

54. University of Texas-Medical Branch, "Phosphorus Removal and Disposal from Municipal Wastewater," EPA #17010DYB 02h1 (Feb 1971).

55. Morgan, W.E. and E.G. Fruh, "Phosphate Incorporation in Activated Sludge," J. Water Pollut. Control Fed., 46(11) (Nov 74).

56. Vacker, D., C.H. Connell and W.N. Wells, "Phosphate Removal Through Municipal Wastewater Treatment at San Antonio, Texas," J. Water Pollut. Control Fed., 39(5) (1967).

57. Odum, E.P., "Fundamentals of Ecology," W.B. Saunders Co., Philadelphia, PA (1959).

58. Stumm, W. and J.J. Morgan, "Stream Pollution by Algal Nutrients," Kansas University Bulletin of Engineering and Architecture, 50:16 (1962).

59. Barth, E.F., B.N. Jackson, R.F. Lewis and R.C. Brenner, "Phosphorus Removal from Wastewater by Direct Dosing of Aluminate to a Trickling Filter," J. Water Pollut. Control Fed., 41:1932-1942 (1969).

60. Jebens, H.J. and W.C. Boyle, "Enhanced Phosphorus Removal in Trickle Filters," J. Am. Soc. Civil Eng., Sanitary Engineering Division, pp. 547-560 (Jun 1972).

61. Zanoni, A.E., "Phosphorus Removal by Trickle Filter Slimes," EPA-R2-73-279 (Jul 1973).

62. Harris, E., "Radiophosphorus Metabolism in Zoo Plankton and Microorganisms," Can. J. Zool., 35:769 (1957).

63. Alarcon, G.O., "Removal of Phosphorus from Sewage," Master's Essay, The Johns Hopkins University, Baltimore, MD (1961).

64. Srinath, E.G. et al., "Rapid Removal of Phosphorus from Sewage by Activated Sludge," Experientia, 15:339 (1959).

65. Feng, T.H., "Phosphorus and the Activated Sludge Process," Water & Sewage Works, 109:431 (Nov 1962).

66. Levin, G.V. and Shapiro, J., "Metabolic Uptake of Phosphorus by Wastewater Organisms," J. Water Pollut. Control Fed., 37(6):800-821 (Jun 1965).

67. Connell, C.H. and D. Vacker, "Parameters of Phosphate Removal by Activated Sludge," Purdue 7th Industrial Water and Waste Conference (Jun 1967).

68. Scalf, M.R., F.M. Pfeffer and D. Lively, "Phosphate Removal at Baltimore, Maryland," Proc. Am. Society Civil Engineers, 5A5:817 (Oct 1969).

69. Carberry, J.B. and M.W. Tenney, "Luxury Uptake of Phosphate by Activated Sludge," J. Water Pollut. Control Fed., 45:2444 (1973).

70. Wells, W.N., "Rate of Phosphorus Uptake by Activated Sludge," Water & Sewage Works, pp. 36-39 (Jan 1975).

71. Mulbarger, M.C., D.G. Shifflett, M.C. Murphy and D.D. Huffman, "Phosphorus Removal by Luxury Uptake," J. Water Pollut. Control Fed., 43(8):1617 (1971).

72. Ferguson, J.F., D. Jenkins and J. Eastman, "Calcium Phosphate Precipitation at Slightly Alkaline pH Values," J. Water Pollut Control Fed., 45:620 (1973).

73. Levin, G.V., G.J. Topol and A.G. Tarnay, "Operation of a Full Scale Biological Removal Plant," J. Water Pollut. Control Fed., 47(3) (1975).

74. Peirano, L.E., "Low Cost Phosphorus Removal at Reno-Sparks, NEV," Water Pollution Control Federation Conference (Oct 1975).

75. Brochure, Union Carbide Corp., Env. Systems Dept., Linde Div, NY.

76. Ockershausen, R.W., "Alum vs. Phosphate-Wastewater Treatment," Water & Sewage Works, p. 80 (Jul 1975).

77. Ulmgren, L., "Swedish Experiences in Chemical Treatment of Wastewater," J. Water Pollut. Control Fed., 47(4) (Apr 1975).

78. Parsons, W.A., "Chemical Treatment of Sewage and Industrial Wastes," National Lime Assoc. (1965).

79. Kugelman, I.J., "Status of Advanced Waste Treatment," National Technical Information Service, PB 213-819 (1971).

80. Convery, J.J., "Treatment Techniques for Removing Phosphorus from Municipal Wastewaters," Water Pollution Control Federation Report 17010 -- 01/70 (Jan 1970).

81. Horstkotte, G.A., D.G. Niles, D.S. Parker and D.H. Caldwell, "Full Scale Testing of A Water Reclamation System," J. Water Pollut Control Fed., 46:181 (1974).

82. Keinath, T.M., "Removal of Impurities from Trickling Filter Effluents," Water Resources Research Institute, Clemson University, Report No. 31, NTIS, PB 212-006 (Jul 1972).

83. Bishop, D.F., T.P. O'Farrell and J.B. Stamberg, "Physical-Chemical Treatment of Municipal Wastewater," J. Water Pollut. Control Fed. 44(3):361 (1972).

84. Melkersson, K.A., "Phosphorus in Chemical and Physical Treatment Processes," Water Research, 7:145 (1973).

85. Jenkins, D., J.F. Ferguson and A.B. Menar, "Chemical Processes for Phosphate Removal," Water Research, 5:369 (July 1971).

86. Culp, R.L. and G.L. Culp, "Advanced Wastewater Treatment," Van Nostrand Reinhold Co. (1971).

87. Schmid, L.A. and R.E. McKinney, "Phosphate Removal by a Lime-Biological Treatment Scheme," J. Water Pollut. Control Fed. p. 1259 (1969).

88. Stumm, W. and J.O. Leckie, "Phosphate Exchange with Sediments; Its Role in the Productivity of Surface Waters," Presented at 5th International Water Pollution Research Conference, San Francisco, CA (1970).

89. Deboice, J.N. and J.F. Thomas, "Chemical Treatment for Phosphate Control," J. Water Pollut. Control Fed., 47:2246 (1975).

90. Menar, A.B. and D. Jenkins, "The Fate of Phosphorus in Sewage Treatment Processes. II. Mechanism of Enhanced Phosphate Removal by Activated Sludge," SERL Report No. 68-6, University of California, Berkeley, CA (1968).

91. Ferguson, J.F. and P.L. McCarty, "Effects of Carbonate and Magnesium on Calcium Phosphate Precipitation," Environ. Sci. Technol., 5(6):534 (Jun 1971).

92. Recht, H.L. and M. Ghassemi, "Kinetics and Mechanisms of Precipitation and Nature of the Precipitate Obtained in Phosphate Removal from Wastewater Using Aluminum (III) and Iron (III) Salts," Federal Water Quality Administration, Report No. 17010 EKl 04/70 (Apr 1970).

93. Cooper, B, "Physical and Chemical Methods of Sewage Treatment-Review of Present State of Technology," Water Pollut. Control, p. 303 (1975).

94. Mulbarger, M.C. and D.G. Shifflett, "Combined Biological and Chemical Treatment for Phosphorus Removal," Chemical Engineering Progress Symposium Series - Water, 107(67):107-116 (1970).

95. Minton, G.R. and D.A. Carlson, "Combined Biological-Chemical Phosphorus Removal," J. Water Pollut. Control Fed., 44(9):1736 (1972).

96. Narkis, N., M. Rebhun and R. Offer, "Ferric Chloride or Lime for Chemical Treatment," Water & Sewage Works (Jan 1975).

97. Galonian, G.E. and D.B. Aulenbaca, "Phosphate Removal from Laundry Wastewater," J. Water Pollut. Control Fed., 45(8) (Aug 1973).

98. Rebhun, M. and S. Streit, "Physico-Chemical Treatment of Strong Municipal Wastewater," Water Res., 8:195-201 (1974).

99. Digiano, F.A. and A.B. Scaramelli, "Wastewater Treatment - Physical and Chemical Methods," J. Water Pollut. Control Fed., 46(6) (Jun 1974).

100. Scaramelli, A.B. and F.A. Digiano, "Wastewater Treatment - Physical and Chemical Methods," J. Water Pollut. Control Fed., 47(6) (Jun 1975).

101. Albertson, O.E. and R.J. Sherwood, "Phosphate Extraction Process," J. Water Pollut. Control Fed., 41(8):1972 (1971).

102. "Phosphorus Removal from Wastewater by Chemical Precipitation and Flocculation," Dow Chemical Co. Brochure (1972).

103. Recht, H.L. and M. Ghassemi, "Phosphate Removal from Wastewaters Using Lanthanum Precipitation," Federal Water Quality Administration Report 17010-EFX (Apr 1970).

104. Mennell, M., D.T. Merrill and R.M. Jorden, "Treatment of Primary Effluent by Lime Precipitation and Dissolved Air Flotation," J. Water Pollut. Control Fed., 49(11) (Nov 1974).

105. Zaltek, J., "Phosphorus Removal by Orthophosphate Nucleation," J. Water Pollut. Control Fed., 46(11) (Nov 1974).

106. Euler, L.M. "We're Aiming for High Level Removal," Am. City (Sep 1972).

107. Neely, A.B., "Chemical-Biological Treatment with Biological Filters," Water Pollut. Control, 74(2):160-165 (1975).

108. Katz, W.J., A. Geinopolos and D.G. Mason, "The Interrelationship of Phosphate Removal and Solids Handling in the Activated Sludge Process," Chem. Eng. Symp. Series - Water, No. 10700167 (1970).

109. "AWT - How Far Have We Come? Where Are We Going?," Water and Wastes Eng., 9(11) (1972).

110. Nickerson, G.L. Robson, C.M. and R. Morrison, "Chemicals Boost Trickling Filter Plant Efficiency," Water and Wastes Eng., 9(12) (1972).

111. Black, S.A. and W. Lewandoski, "Phosphorus Removal by Lime Addition to a Conventional Activated Sludge Plant," Div. of Research Pub. No. 36, Ontario Water Resources Commission, Toronto (1969).

112. Barth, E.F. and M.B. Ettinger, "Mineral Controlled Phosphorus Removal in the Activated Sludge Process," J. Water Pollut. Control Fed., 39:1362-1368 (Aug 1967).

113. Eberhardt, W.A. and J.B. Nesbitt, "Chemical Precipitation of Phosphate Within a High Rate Biooxidation System," Proceedings of 22nd Industrial Waste Conference, Purdue University (May 1967).

114. Brenner, R.C., "Combined Biological-Chemical Treatment for Control of Phosphorus," Symposium on Advanced Waste Treatment, Dallas, TX (Jan 1971).

115. Long, D.A. and J.B. Nesbitt, "Removal of Soluble Phosphorus in an Activated Sludge Plant," J. Water Pollut. Control Fed., 47(1) (Jan 1975).

116. Guter, K.J., W.F. Echelberger and M.W. Tenney, "Removal of Organic & Inorganic Pollutants from Wastewater by Combined Chemical & Biological Treatment," Proceedings of 3rd Annual Environmental Engineering & Science Conference, Louisville, KY (Mar 1973).

117. Mulbarger, M.C., "The Three Sludge System for Nitrogen and Phosphorus Removal," 44th Annual Conference of Water Pollution Control Federation, San Francisco, CA (Oct 1971).

118. Thomas, E.A., "Phosphate Removal by Recirculating Iron Sludge," J. Water Pollut. Control Fed., 44:176 (1972).

119. Berg, E.L., C.A. Brunner and R.T. Williams, "Single Stage Lime Clarification of Secondary Effluent," Water and Wastes Eng. 7(3):42 (1970).

120. Stamberg, J.B., D.F. Bishop, H.R. Warner and S.H. Griggs, "Lime Precipitation in Municipal Wastewaters," Chem. Eng. Symposium Series - Water, 107(67):310-320 (1970).

121. Barnard, J.L., "Nutrient Removal in Biological Systems," Water Pollut. Control, 74(2):124-133 (1975).

122. Lynam, B., G. Ettelt and T. McAloon, "Tertiary Treatment at Metro Chicago by Means of Rapid Sand Filtration and Microstrainers," J. Water Pollut. Control Fed., 41(2, Part 1):247 (1969).

123. Bell, G.R., D.R. Libby and D.T. Lordi, "Phosphorus Removal Using Chemical Coagulation, and a Continuous Counter Current Filtration," Federal Water Quality Administration Report #17010 EDO 06/70, Cincinnati, Ohi

124. Weber, W.J., "Physiochemical Processes for Water Quality Control," Wiley-Interscience, NY (1972).

125. Envirogenics Co., "Investigation of a New Phosphate Removal Process," EPA Report No. 17010DJA11/70 (Nov 1970).

126. General Mills Chemicals, "Feasibility of Liquid Ion Exchange for Extracting Phosphate from Wastewater," EPA Report No. 17010EAP10/70 (Oct 1970).

127. Boari, G. and L. Liberti, "Selective Renovation of Eutrophic Wastes-Phosphate Removal," Water Research, 10:421-428 (1976).

128. Block, J., "Chemically Exfoliated Vermiculite for Removal of Phosphate from Wastewaters," EPA Report No. 1701DHK08/69 (Aug 1969).

129. Ames, L.L., "Mobile Pilot Plant for Removal of Phosphate from Wastewaters by Adsorption on Alumina," National Technical Information Service, PB 212374 (1970).

130. Yee, W.C., "Selective Removal of Mixed Phosphates by Activated Alumina," J. Am. Water Works Assoc., 58(2):239-247 (1966).

131. Ames, L.L., "Evaluation of Operating Parameters of Alumina Columns for the Selective Removal of Phosphates from Wastewater and the Ultimate Disposal of Phosphorus as Calcium Phosphate," Robert A. Taft Water Research Center, Report No. TWRC-8 (March 1969).

132. Gangoli, N. and G. Thodos, "Kinetics of Phosphate Adsorption on Alumina and Fly Ash," J. Water Pollut. Control Fed., 46:2026 (1974).

133. Gangoli, N. and G. Thodos, "Phosphate Removal Studies," J. Water Pollut. Control Fed., 45:842 (1973).

134. McNeice, F.R., "The Role of Iron in Phosphate Adsorption on Coal," Master's Thesis, Virginia Polytechnic Institute and State College (1968).

135. Randall, C.W., E.H. Rowell and P.H. King, "The Adsorption and Removal of Phosphate by Fly Ash and Coal Contact Systems," Presented at the 20th Southern Water Resources and Pollution Control Conference, University of N. Carolina, Chapel Hill (1970).

136. Edzwald, J.K. D.C. Toensing and M.C. Leung, "Phosphate Adsorption Reactions with Clay Minerals, " Environ. Science Technol., 10(5) (May 1976).

137. Lim, H.S. and H.K. Johnston, "Reverse Osmosis as an Advanced Treatment Process," J. Water Pollut. Control Fed., 48(7) (1976).

138. Johnston, H.K. and H.S. Lim, "Bibliography on the Application of Reverse Osmosis to Industrial and Municipal Wastewaters," Report No. 18, Canada-Ontario Agreement on Great Lakes Water Quality (1974).

139. Sadek, S.E., "An Electrochemical Method for Removal of Phosphates from Wastewaters," Water Pollution Control Research Series, Report No. 17010-02/70 (1970).

140. Vesilind, P.A., "Treatment and Disposal of Wastewater Sludges," Ann. Arbor Science (1974).

141. McKendrick, J., G.R. Bates and E.R. Swart, "The Physico-Chemical Treatment of Crude Sewage," Water Pollut. Control, 74(2):155-159 (1975).

142. DoBolyi, E., "Plant Scale Phosphorus Removal Experiments at the Balaton Füred Sewage Treatment Plant," Water Research, 7:1767-1780 (1973).

143. Schmid, L., "Pilot Plant Demonstration of a Lime Biological Treatment Phosphorus Removal Method," EPA-R2-73-159 (June 1973).

144. Boyko, B.I. and J.W.G. Rupke, "Technical Implementation of Ontario's Phosphorus Removal Programme," Ontario Ministry of the Environment, Toronto.

145. Parker, D.S., F.J. Zadick and K.E. Train, "Sludge Processing for Combined Physical-Chemical-Biological Sludges," EPA-R2-73-250 (July 1973).

146. "Process Design Manual for Sludge Treatment and Disposal," EPA, Publication No. 625/1-74-006 (Oct 1974).

APPENDIX A

PHOSPHORUS CHEMISTRY

Form		Concentration mg/l	Concentration mM
Total		10	0.32
Ortho		5	0.16
Tripoly	Inorganic Condensed	3	0.032
Pyro		1	0.016
Organic		≤1	0.016

Organic: Proteins, Nucleic Acids, Enzymes, phospholipids, cell mass

Orthophosphate

Trisodium Na_3PO_4

Disodium Na_2HPO_4

Monosodium NaH_2PO_4

Diammonium $(NH_4)_2\ HPO_4$

Inorganic (Condensed)

Sodium Trimetaphosphate $Na_2(PO_3)_3$ - a ring

Sodium Polymetaphosphate $(NaPO_3)_n$ - long chain

Sodium Tripolyphosphate $Na_5P_3O_{10}$

Tetrasodium Pyrophosphate $Na_4P_2O_7$

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All polyphosphates gradually hydrolyze in aqueous solution and revert to ortho form from which they were derived. The rate of hydrolysis is proportional to temperature, pH, and active bacterial enzyme availability.

H_3PO_4 -- ($P_2O_5 \cdot 3H_2O$) Orthophosphoric

HPO_3 -- ($P_2O_5 \cdot 2H_2O$) Metaphosphoric

"Ortho" designates most highly hydrated acid, or its salt

"Meta" designates less highly hydrated acid, or its salt

Ref: Sneed, M.C. and J.L. Maynard, General Inorganic Chemistry, pp. 560-600.

APPENDIX B

LIME CHEMISTRY

Forms: CaO (quick lime); $Ca(OH)_2$ (slaked lime)

Reactions:

-- Precipitates phosphorus (as PO_4) as a highly insoluble hydroxyapatite: $Ca_5(OH)(PO_4)_3$ - a general formula

-- Most successful in precipitating the ortho form.

-- Some inorganic condensed and organic forms may be precipitated.

Some reactions in a lime process:

$$3\ NaH_2PO_4 + 5\ Ca(OH)_2 \longrightarrow Ca_5(OH)(PO_4)_3 + 3\ NaOH + 6\ H_2O$$

$$H_2O + x\ Ca(OH)_2 \longrightarrow \text{desired pH}$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underline{CaCO_3} + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ \underline{CaCO_3} + 2\ H_2O$$

$$Mg(HCO_3)_2 + 2\ Ca(OH)_2 \longrightarrow \underline{Mg(OH)_2} + 2\ \underline{CaCO_3} + 2\ H_2O$$

$$Mg(SO_4) + Ca(OH)_2 \longrightarrow \underline{Mg(OH)_2} + CaSO_4$$

$$2\ NaHCO_3 + Ca(OH)_2 \longrightarrow \underline{CaCO_3} + Na_2CO_3 + 2\ H_2O$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow \underline{CaCO_3} + 2\ NaOH$$

$$NH_4HCO_3 + Ca(OH)_2 \longrightarrow \underline{CaCO_3} + NH_3 + 2H_2O$$

APPENDIX C

ALUM CHEMISTRY

Forms: Al(III) Alum: $Al_2(SO_4)_3 \cdot 14H_2O$; Aluminate: $Na_2Al_2O_4$; $AlCl_3 \cdot 6H_2O$

Reactions:

$$Al(III) + PO_4^{-3} \rightleftharpoons \underline{AlPO_4}$$

$$Al_2(SO_4)_3 \cdot 14H_2O + 2\ NaH_2PO_4 \rightleftharpoons 2\ \underline{AlPO_4} + SO_4^{-} + 2\ H_2SO_4 + 14\ H_2O$$

$$Al_2(SO_4)_3 \cdot 14\ H_2O + 6\ HCO_3^{-} \rightleftharpoons 2\ \underline{Al(OH)_3} + 6\ CO_2 + 3SO_4^{-} + 14\ H_2O$$

$$H_2SO_4 + Ca(HCO_3)_2 \rightleftharpoons CaSO_4 + 2\ CO_2 + 2\ H_2O$$

$$AlCl_3 + NaH_2PO_4 \rightleftharpoons \underline{AlPO_4} + NaCl + 2\ HCl$$

$$2\ HCl + Ca(HCO_3)_2 \rightleftharpoons CaCl_2 + 2\ CO_2 + 2\ H_2O$$

$$Na_2O \cdot Al_2O_3 + 2\ PO_4^{-3} + 4\ H_2O \rightleftharpoons 2\ AlPO_4 + 2\ NaOH + 6\ OH^{-}$$

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

Conditions: Optimum pH - 5.7-6.3

$Al_2(SO_4)_3$ and $AlCl_3$ produce acid, lowering pH

$Na_2O \cdot Al_2O_3$ produce caustic, raising pH

Minimum solubility of $AlPO_4$ is 0.01 mg/l at pH of 6.3

Doses: Stoichiometric: Mole Ratio: 1; Wt. Ratio: 0.87 Al/P

Practice:

Mole Ratio: 1.5-3 or 4 for 0.1-0.5 mg/l residual P

Wt. Ratio: 1.3-2.6 or 3.5

	75% Reduction	85% P	95% P
Mole Ratio	1.38	1.72	2.3
Wt. Ratio	1.2	1.5	2.0

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APPENDIX D

IRON CHEMISTRY

Forms: Fe(II), Fe(III) usually with sulfate or chloride

Reactions:

Fe(II): $3Fe(II) + 2\ PO_4^{-3} \rightarrow \underline{Fe_3(PO_4)_2}$ (Reaction Time - minutes)

$3FeSO_4 + 2\ NaH_2PO_4 \rightarrow \underline{Fe_3(PO_4)_2} + Na_2SO_4 + 2\ H_2SO_4$

$3FeCl_2 + 2\ NaH_2PO_4 \rightarrow \underline{Fe_3(PO_4)_2} + 2\ NaCl + 4\ HCl$

Fe(III): $Fe(III) + PO_4^{-3} \rightarrow FePO_4$ (Reaction Time <1 sec)

$Fe_2(SO_4)_3 + 2\ NaH_2PO_4 \rightarrow 2\ \underline{FePO_4} + Na_2SO_4 + 2\ H_2SO_4$

$FeCl_3 + NaH_2PO_4 \rightarrow \underline{FePO_4} + NaCl + 2\ HCl$

OH^{-1}: $Fe(II) + 2\ OH^{-1} \rightarrow Fe(OH)_2$; $Ksp = 5 \times 10^{-15}$

$Fe(III) + 3\ OH^{-1} \rightarrow Fe(OH)_3$; $Ksp = 10^{-36}$

$Al(III) + 3\ OH^{-1} \rightarrow Al(OH)_3$; $Ksp = 10^{-32}$

(Fe(II) has less tendency to hydrolyze, therefore, more available for PO_4^{-3} reactions.)

Conditions:

Fe(II): Optimum pH for PO_4^{-3} removal - 7.0-8.0

Oxidizes rapidly in presence of dissolved oxygen to Fe(III).

At pH 7.9: 94% PO_4 and 97% Fe removals were observed.

Removals fell off on either side of the optimum pH.

Fe(III): Optimum pH - 3.5-5.0

pH <7; $FePO_4$ $Ksp = 10^{-23}$

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Doses:

Stoichiometric:	Fe(II)/P	Fe(III)/P
Mole Ratio	3/2	1/1
Wt. Ratio	2.7-3.2/1	1.8/1
Practice: (At Optimum pH)		
Mole Ratio	1.3-20/1	1.2-2.0/1
Wt. Ratio	2.8/1	2.2-3.6

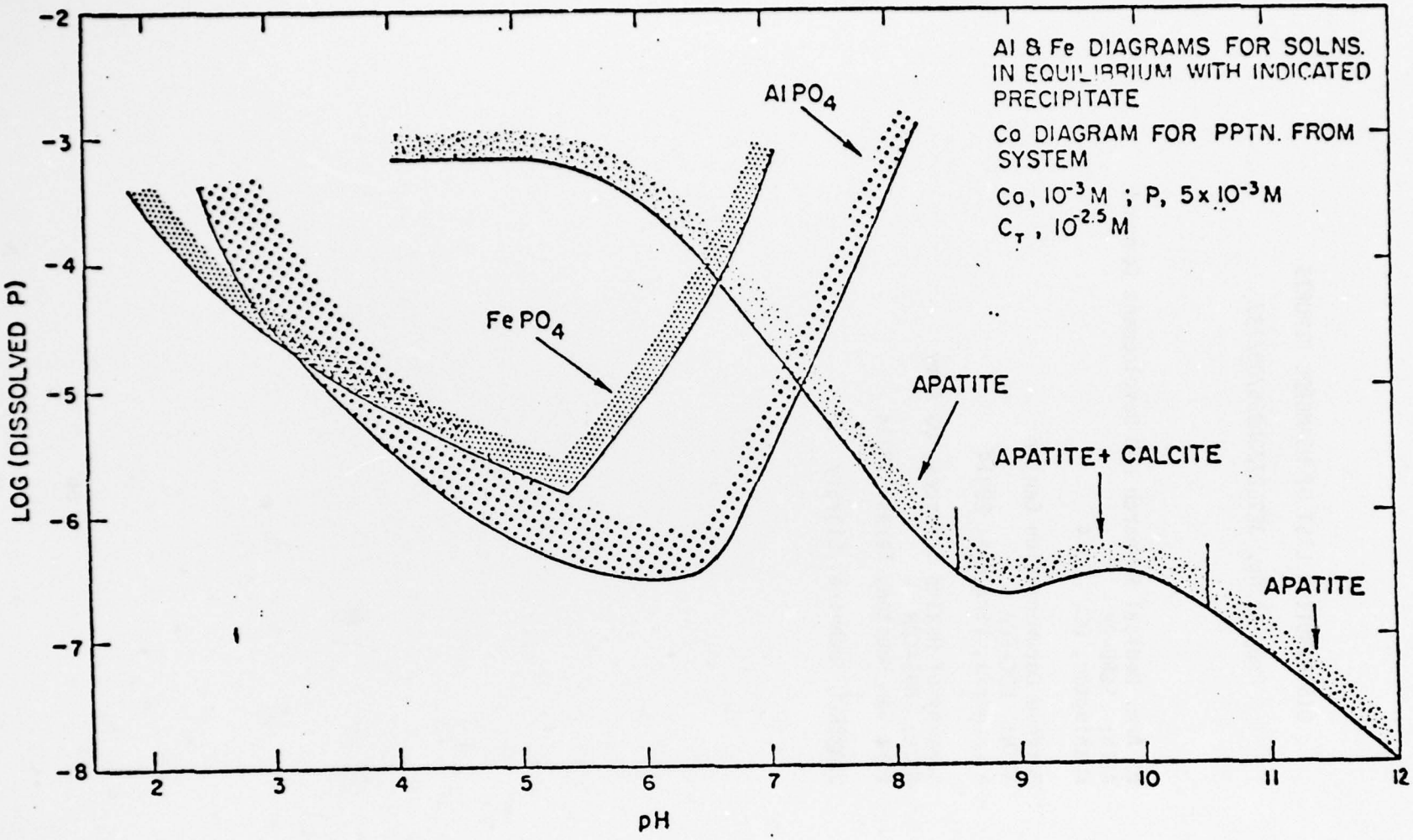


Figure 1. Equilibrium Solubility Diagram for Fe, Al, and Phosphates.
Reference: Stumm, W. and J.J. Morgan, "Aquatic Chemistry," Wiley Interscience.

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