

# Tertiary Phosphorus Removal

Last updated November 4, 2008

## Acknowledgements

A formal technical review of the draft document was conducted by professionals with experience in wastewater treatment in accordance with WERF Peer Review Guidelines. While every effort was made to accommodate all of the Peer Review comments, the results and conclusions do not indicate consensus and may not represent the views of all the reviewers. The technical reviewers of this document included the following:

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## Table of Contents

Acknowledgements.....	1
Overview (Last updated November 4, 2008).....	1
Chemical Reactions (Last updated November 4, 2008) .....	8
Solids Separation (Last updated November 4, 2008) .....	14
References.....	16

## Overview (Last updated November 4, 2008)

Chemical and biological phosphorus removal processes have been used to reliably reduce phosphorus to 1 mg/L and often to 0.5 mg/L. Lower permit limits, such as the 0.07 mg/L or 70 ug/L TP limit at two Clean Water Services treatment plants in Oregon, have been achieved using tertiary sedimentation and filtration processes since the early 1990s. A 0.5 to 1.0 mg/L limit appears achievable by many conventional chemical and biological processes, while lower limits are attainable with advanced processes.

Neethling et al. (2005) showed that many biological phosphorus removal processes can reduce total phosphorus concentrations to low limits. Secondary effluent from five, full-scale plants were statistically analyzed to show that total phosphorus concentrations can be reduced to 1 mg/L between 80 and 99 percent of the time in four facilities and can be reduced to 0.5 mg/L between 50 and 95 percent of the time, also in four facilities. The fifth facility was less stable, producing 1 mg/L 64 percent of the time and 0.5 mg/L only 24 percent of the time. Chemical phosphorus removal can achieve similar results.

Additional tertiary processes are required to polish effluent phosphorus to achieve greater reliability and reduce phosphorus to lower limits. In order to reliably produce effluent phosphorus concentrations below 0.5-1 mg/L, additional polishing processes are typically added to conventional biological processes.

Filtration (conventional solids separation processes) can be used to remove suspended solids and, when coupled with additional chemical removal, can often reduce total phosphorus concentrations to 0.2-0.3 mg/L (some facilities can do better, others worse, depending on the process arrangements).

This section on tertiary phosphorus removal focuses on factors that need to be considered to reduce phosphorus below 0.5 mg/L and, in particular, the requirements to reduce phosphorus to very low limits, below 0.05 mg/L (50 ug/L) or lower.

*What is the “Conventional Phosphorus Removal” processes?*

Biological and chemical processes have been used for many years to remove phosphorus.

Enhanced Biological Phosphorus Removal (EBPR) is a modification of the activated sludge process that will remove phosphorus from wastewater. In the 1950s, Greenburg *et al.* (1955) proposed that activated sludge could take up phosphate at a level beyond its normal microbial growth requirements. Levin and Shapiro (1965) were the first to report EBPR in the District of Columbia activated-sludge plant and, by the 1970s, work in the U.S. and South Africa (Barnard, 1974) clearly demonstrated that EBPR can occur. EBPR processes will reduce the effluent total phosphorus to 0.5-1.0 mg/L without filtration.

Chemical phosphorus removal is achieved by adding chemicals to the wastewater at a well-mixed location, followed by flocculation and solids removal. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)) and calcium (Ca(II)). In wastewater treatment, the chemicals can be added before a primary clarifier or other solids separation device. The effluent phosphorus concentration is determined by the dose and other chemical reactions. An effluent of 0.5-1 mg/L can typically be achieved without constructing specific post-secondary treatment facilities.

*What effluent phosphorus concentration can be achieved with “Conventional Phosphorus Removal” processes?*

Conventional Phosphorus Removal ([What is “Conventional Phosphorus Removal” processes?](#)) processes using chemical addition or EBPR can achieve 0.5-1.0 mg/L. Additional polishing with filtration or other tertiary processes is required to reduce phosphorus reliably below these limits.

*What are the essential elements of tertiary phosphorus removal?*

Wastewater treatment processes that achieve low phosphorus concentrations (<50 ug/L) typically follow Conventional Phosphorus Removal ([What is “Conventional Phosphorus Removal” processes?](#)). Many tertiary processes, which are mostly physical and chemical processes, have been used to polish effluents. The chemical process first converts soluble reactive phosphorus to a solid particle followed by removal of particulate phosphorus by a physical process. These include some of the following elements:

- Chemical addition to react with the soluble phosphorus species and produce a solid precipitant. See [Aluminum Reactions](#) and [Iron Reactions](#).
- Chemical flocculants to capture small particulates for removal in solids separation processes. [Does polymer improve phosphorus removal?](#)
- Chemical removal onto a reactive surface of preformed precipitants or other surfaces (such as iron oxide coated sand).
- Solids separation to remove particulate phosphate species. [Solids Separation](#).
- Adsorption through the contact of phosphorous in water phase to solid phase, such as the flocs retained by filters (Jenkins, 2007).

### *What are the soluble Phosphorus Species in Wastewater?*

Dissolved phosphorus is defined as the phosphorus species passing through a 0.45 um filter by both EPA method 365.2 and Standard Methods 4500-P, including both colloidal and truly soluble species. Other filter sizes can be used, but 0.45 um is most commonly used in the wastewater industry. ‘Soluble’ is often used interchangeably with ‘dissolved’, and ‘particulate’ is often used in place of ‘insoluble’ or ‘suspended.’ Phosphorus compounds are not isolated and identified directly; rather, phosphorus compounds are grouped into fractions and defined by the analytical method used to measure them. While there are other methods of analysis, the Standard Methods and EPA method of colorimetric analyses following some level of digestion is most common. There are three analyses that are typically performed: direct colorimetry, sulfuric acid digestion/colorimetry, and persulfate digestion/colorimetry. The differences between these analyses define the three dissolved phosphorus fractions.

Direct colorimetry measures mostly orthophosphate. While EPA Method 365.3 suggests this fraction is comprised entirely of orthophosphates, Standard Methods 4500-P recognizes that some small quantity of other phosphorus compounds respond to direct colorimetry, and, thus, more accurately identifies this fraction as being simply ‘reactive phosphorus’ rather than ‘orthophosphate phosphorus’. The difference between sulfuric acid digestion/colorimetry and direct colorimetry analyses defines the ‘acid-hydrolyzable phosphorus’ fraction, comprised mostly of condensed phosphates (polyphosphates (chain structure)) and metaphosphates (ring structure). The difference between the persulfate digestion/colorimetry and the sulfuric acid digestion/colorimetry analyses defines the ‘organic phosphorus’ fraction, comprised mostly of the organically bound phosphorus in phospholipids, sugar phosphates, nucleotides, and phosphoamides.

See also discussion in [Low P Concentration Measurement Compendium](#).

### *What are the Solid Phosphorus Species in Wastewater?*

Particulate phosphorus species include the particles excluded by filtration. It is more technically accurate to define these as “non-filterable” phosphorus – representing particles retained by 0.45 um filtration. Particulate phosphorus represents organic and inorganic phosphorus, chemical precipitants, and biomass – all particles larger than the filter exclusion size. Some colloidal particulates will pass through the filter, be detected in the soluble fraction, and be missing from the particulate fraction – even though it is a small particle.

See [Low P Concentration Measurement Compendium](#).

### *How are the different chemical species removed from wastewater?*

Phosphorus species must be converted to a solid form in order to remove it from water. All the phosphorus entering a treatment plant therefore exits the treatment plant as a solid (residual) stream or leaves with the effluent (liquid stream).

The following table summarizes the processes used to convert/remove phosphorus species from wastewater. (Note that the species are not distinct.)

Species	Common conversion or removal process
Organic-P	Organic phosphorus can be converted to orthophosphate and polyphosphate, some organics degrade very slowly
Orthophosphate	Most abundant phosphorus species

	Reactive species in chemical reactions and consumed in biological growth
Polyphosphates	Condensed orthophosphates Possibly reacts with metal salts Can be used for biological growth
Chemical phosphorus	Precipitated phosphates formed by reacting orthophosphate with metal salts, or precipitates as phosphate hydroxides
Biological phosphorus	Phosphorus incorporated into the biomass for growth Excess phosphorus may accumulate under certain conditions

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#### *How is reactive phosphorus removed from wastewater by chemical treatment?*

Reactive phosphorus is defined in Standard Methods as, “Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample.” Standard Methods continues, stating, “While reactive phosphorus is largely a measure of orthophosphate, a small fraction of any condensed phosphate present usually is hydrolyzed unavoidably in the procedure. Reactive phosphorus occurs in both dissolved and suspended forms.” Reactive phosphorus is therefore primarily orthophosphate, and defined based on the standard analytical technique used.

Chemical phosphorus removal utilizes reactions between phosphate in water and other chemical species or compounds, usually multivalent metal ions, to form precipitates of sparingly soluble metal phosphate salts that can subsequently be removed from the liquid using a solids separation process. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)) and calcium (Ca(II)).

The chemical reaction of phosphorus with aluminum and ferric salts in a liquid environment is complex. The classic model of a metal reacting with a phosphate to produce a metal-phosphate precipitant ( $\text{AlPO}_{4(s)}$  or  $\text{FePO}_{4(s)}$ ) does not occur under the conditions in a wastewater treatment plant (Smith et al., 2007). The precipitant is a complex structure where metal hydroxides are formed and phosphate bonds with the metal hydroxide complex.

- The metal reacts with water to produce metal hydroxides. These metal hydroxides (typically shown as the basic chemical form of  $\text{Al(OH)}_{3(s)}$  or  $\text{Fe(OH)}_{3(s)}$ ) actually form hydrated forms and precipitate as an amorphous complex that will change structure and form with time.
- Phosphate forms bonds with the metal hydroxyl complex. These bonds are very strong and bind the phosphate to the structure. The amount of phosphate that binds to the metal hydroxide is still a topic of discussion. Current research suggest that the stoichiometric ratio of metal:phosphorus (Me:P) in the precipitant depends on many factors, including the phosphate concentration in the liquid, chemical dose, age of the hydroxyl complex, mixing, and many other factors (Szabo et al., 2008, de Haas et al., 2000, Yang et al., 2006).

The removal of the efficiency of phosphates depends on the chemical dose, pH, and temperature. To complicate matters, the metal hydroxyl precipitant and reactions also depend on mixing intensity, age of the precipitant, and other factors. The required dose must therefore often be determined from practical experience for a given application.

#### *Research Needs*

Research is ongoing to understand the interactions between reactive phosphorus and metal salts. Reactions with iron (III) and orthophosphate in liquid is being studied (Szabo et al., 2008, de Haas et al.,

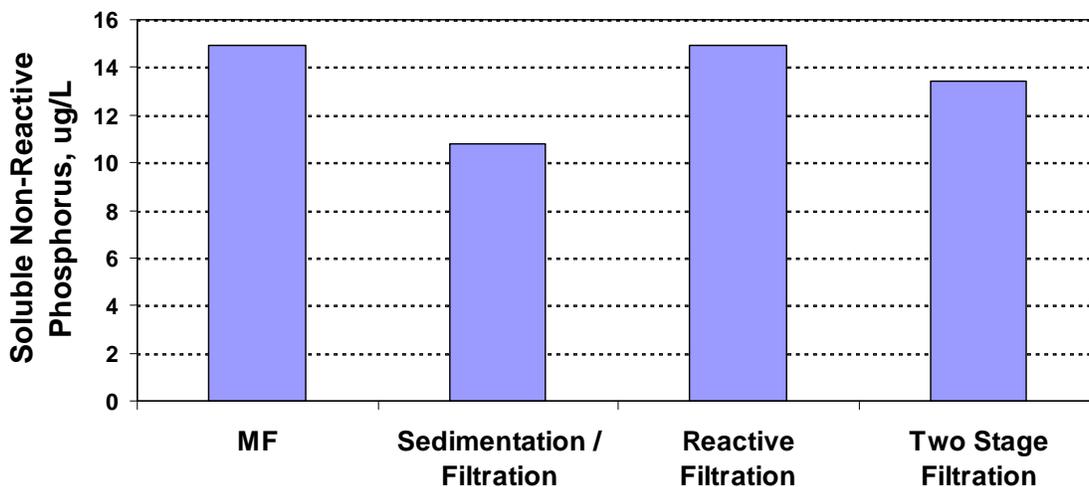
2000, Yang et al., 2006) but many questions remain regarding the reactivity over time, and preformed versus simultaneous precipitation. In addition, many questions regarding the reactions with ferrous iron, aluminum, polyaluminum, and others remain unanswered.

#### *How is Soluble Non-Reactive Phosphorus (sNRP) Removed from Wastewater by Chemical Treatment?*

Soluble non-reactive phosphorus is defined as the difference between the total soluble phosphorus and soluble reactive phosphorus. The chemical species making up the non-reactive phosphorus is unknown, but could include polyphosphates, condensed phosphates, soluble organic phosphorus species, and other phosphorus containing species.

Chemical removal mechanisms are complex and not well understood, but depending on the chemical structure of the compound, can include adsorption, filtration, and coagulation. Depending on the structure, some portion of the dissolved acid-hydrolyzable and/or dissolved organic phosphorus fractions simply can not be removed by tertiary processes, and are considered recalcitrant or non-reactive.

A recent pilot study of four tertiary processes in Coeur D'Alene, Idaho, for mostly domestic wastewater revealed dissolved recalcitrant phosphorus passing through the pilot units ranging in concentration between 11- 15 ug P/L (Benisch et al., 2007). The soluble non-reactive phosphorus fraction is not easy to remove from wastewater. The graph below shows the data from that study.



*Phosphorus species remaining following four different chemical treatment options using alum and ferric. Results show the persistence of soluble non-reactive phosphorus in all processes (data taken from Benisch et al., 2007).*

A similar but shorter pilot study of three tertiary pilot units in Marlborough, Massachusetts, for a domestic wastewater with nearly 50 percent commercial and industrial components revealed intermittent recalcitrant phosphorus concentrations up to 500 ug/L (Lancaster and Madden, 2008). It is suspected that recalcitrant phosphorus is mostly, if not entirely, comprised of dissolved organic phosphorus (Neethling, et al., 2007).

#### *Research Needs*

There remain questions about the composition, reactivity, fate, and nature of the non-reactive phosphorus fraction. The fraction is measured as the soluble phosphorus species that are not orthophosphate, and could be a number of phosphorus containing compounds, ranging from small colloidal particles (that pass

through the filtration step), condensed phosphates, organic phosphates, and other compounds. Research is required to address the nature and treatability of these compounds.

The environmental impacts of non-reactive phosphorus have not been established. There could be similarities between the soluble non-reactive phosphorus and refractory organic nitrogen (rDON) in terms of the type of compounds, significance, and environmental fate and impact. The biodegradation (technology based) and bioavailability (environmental impact) of the sNRP remains in question.

*How is acid hydrolysable phosphorus removed from wastewater by chemical treatment?*

Acid hydrolysable phosphorus refers to phosphorus compounds that are converted to orthophosphate (reactive phosphorus) under mild acid/boiling conditions. The sample pH is adjusted to the phenolphthalein endpoint (<8.2) before boiling for 90 minutes. Standard Methods states that these compounds “include condensed phosphates such as pyro-, tripoly-, and higher-molecular-weight species such as hexametaphosphate. In addition, some natural waters contain organic phosphate compounds that are hydrolyzed to orthophosphate under the test conditions. Polyphosphates generally do not respond to reactive phosphorus tests but can be hydrolyzed to orthophosphate by boiling with acid.”

There are no specific reports on the removal of acid hydrolysable phosphorus. It is possible that the phosphate species in this group may react with metals salts (aluminum and iron) similar to orthophosphate and may be removed by a similar mechanism.

*Research needs*

The acid hydrolysable phosphorus fraction is typically small in wastewater effluent, likely <10 ug/L. However, as the effluent requirements are moved lower, this fraction becomes more significant. It forms a portion of the [soluble non-reactive phosphorus](#). Additional research is required to determine the importance and removal methods for this group of compounds.

*How is soluble organic phosphorus removed from wastewater by chemical treatment?*

Organic phosphorus includes soluble and particulate forms of phosphorus contained in organic compounds. There is no simple analytical procedure to measure organic phosphorus making it difficult to track its removal. The Soluble Organic Phosphorus is the portion that is in solution (not particulate) and is measured as the fraction that passes a 0.45 um filter. Technically, it should be referred to as the “filterable” fraction.

Organic phosphorus compounds are calculated from total phosphorus measurements, which include a digestion step to oxidize all organic compounds. Standard Methods recognize three digestive methods using perchloric acid, nitric acid-sulfuric acid, or persulfate oxidation. Standard Methods states that these organic phosphorus compounds represent “phosphate fractions that are converted to orthophosphate only by oxidation destruction of the organic matter present are considered ‘organic’ or ‘organically bound’ phosphorus. The severity of the oxidation required for this conversion depends on the form—and to some extent on the amount—of the organic phosphorus present.”

The above analytical definition of organic phosphorus is tied to the “severity of oxidation.” The analytical challenge is to measure the inorganic phosphorus fraction independently which requires the ability to differentiate between the polyphosphates, condensed phosphates and organic phosphorus. The current methods rely on differing acid hydrolysis methods cannot distinguish between these fractions.

There are no specific reports on the removal of soluble organic phosphorus. It is possible that the phosphate species in this group may react with metals salts (aluminum and iron) similarly to orthophosphate and may be removed by a similar mechanism.

#### *Research needs*

The soluble organic phosphorus fraction is typically small in wastewater effluent, likely <10 ug/L. However, as the effluent requirements are moved lower, this fraction becomes more significant. Additional research is required to determine the importance and removal methods for this group of compounds.

#### *How is particulate phosphorus removed from wastewater by chemical treatment?*

Chemicals can be added to enhance particulate removal in unit processes. In this application, the chemical is added to flocculate and capture small phosphorus particles. Various polymers have been used to enhance the solids capture of fine particles to improve their removal in biological processes and with solids separation processes.

Once the phosphorus is converted to a solid form, it still needs to be captured and removed from the liquid. Note that chemically precipitated phosphorus particles will dissolve during the analysis and measure as reactive phosphorus. This will create the appearance of higher orthophosphate in the sample.

#### *Research Needs*

The structure and flocculation of small phosphorus particles have not been established. While the processes are expected to follow the normal solids separation fundamentals, the pH dependency of the phosphorus precipitant and surface chemistry of metal hydroxide/phosphorus complexes are not established. For example, is the optimum pH for phosphorus precipitation the same as for flocculation?

#### *How is particulate chemical phosphorus particles removed from wastewater?*

Particulate phosphorus removal can be achieved with conventional and emerging solids removal equipment. Solids removal equipment must be designed to handle the increased solids loading associated with chemical addition for phosphorus removal.

The following processes are typical of solids separation processes and presented in more detail elsewhere:

- Conventional sedimentation/filtration facilities
- High rate sedimentation/filtration using ballasted sedimentation, solids blanket clarifiers, tube settlers, contact clarification, or other processes
- Direct filtration (without sedimentation facilities) using a variety of filter styles
- Two stage filtration using two filter units in series
- Microfiltration or nanofiltration
- Magnetic based separation using a ballasted separation and magnetic polishing step

See [Solids Separation](#) discussion below.

## Chemical Reactions (Last updated November 4, 2008)

### Overview of Phosphorus Removal Chemistry

Chemical phosphorus removal is achieved by adding chemicals to the wastewater at a well-mixed location, followed by flocculation and solids removal. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)), ferrous (Fe(II)), and calcium (Ca(II)). In wastewater treatment, the chemicals can be added before a primary clarifier or other solids separation device. The effluent phosphorus concentration is determined by the dose and other chemical reactions. An effluent of 0.5-1 mg/L can typically be achieved without constructing specific post secondary treatment facilities.

The understanding of the metal salt-phosphorus chemistry has increased rapidly since early 2000, as the [surface complexation model](#) has emerged and the phosphorus/metal/hydroxyl complex becomes better understood. Prior precipitation-equilibrium relationships are challenged with new data showing that lower concentrations are possible. Other chemical processes, such as adsorption, co-precipitation, crystal changes, and aging, are being studied, improving our understanding of the complex chemistry involved.

This section presents the chemistry of using metal salts to remove phosphorus from wastewater, the reactions, and the factors affecting the process efficiency.

#### *What chemicals are used to precipitate phosphorus?*

Aluminum and iron based salts are typically used for chemical phosphorus removal. Aluminum is dosed in the form of alum, polyaluminum chloride,. Iron is added as ferric or ferrous iron salt (chloride), but in some cases “pickle liquor” (from industrial iron works) that contains primarily ferric chloride, can be used.

#### *Which Aluminum Based Chemicals are Typically Used?*

Alum is the most commonly used trade chemical for Aluminum (Al(III)). Alum is aluminum sulfate and contains 14 waters of crystallization. Other formulations with 18 or even 24 waters of crystallization can be produced, but alum with 14 waters of crystallization is commercially used because it increases the aluminum content of the chemical and is a stable when stored. “Dry Alum” is therefore aluminum sulfate as  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  (preamble to ANSI/AWWA STANDARD B403-03). Note that alum specifications typically state the  $\text{Al}_2\text{O}_3$  or Al content.

When added to precipitate phosphorus, the following equivalents exist for alum:

1 mol alum = 594 g alum = 54 g Al (2 mol aluminum ion)

100 g/L alum = 168 mM alum = 337 mM Al

100 mg/L alum = 9.1 mg/L Al = equivalent of 17.2 mg/L  $\text{Al}_2\text{O}_3$

100% alum = 9.1% Al = 17.2%  $\text{Al}_2\text{O}_3$

Polyaluminum chloride (PACl) is another aluminum based chemicals commonly used. Various different formulations of PACl are available from different chemical suppliers. PACl has the advantage that it is hydrated and does not suppress pH when added to water. It is therefore attractive for poorly buffered waters. When dosing PACl, the chemical dose must be converted to an equivalent Al or  $\text{Al}_2\text{O}_3$

concentration. Dosage of chemical needs to be distinguished from dosage of the trade product in calculations.

Alum doses for scientific discussion or fundamental presentations are expressed in terms of the Al(III), and typically on a molar basis. Engineering and treatment plant applications, however, typically express doses in terms of “alum.” One should therefore exercise care when reporting, interpreting, and expressing alum dose. The relationships in the box above show the conversion.

A molar ratio of 1:1 mol aluminum/mol P is, therefore, equivalent to ~0.87 g Al/g P; or ~9.6 g alum/g P.

*Which Iron Based Chemicals are Typically Used?*

Ferric chloride (a.k.a. “ferric”) is the most commonly used trade chemical for ferric iron (Fe(III)). Ferrous chloride and sulfate is used for adding ferrous iron (Fe(II)).

Liquid ferric chloride is an orange brown aqueous solution that is acidic and very corrosive. There is opportunity for confusion since the trade chemical is called “ferric” as is the iron (III) ion. The two are quite distinct, though. Commercial ferric is typically specified as “dry ferric chloride” (ANSI/AWWA STANDARD B407-05).

When added to precipitate phosphorus, the following equivalents exist for ferric:

1 mol ferric chloride = 162 g ferric chloride = 56 g Fe(III)

100 g/L ferric (chloride) = 617 mM ferric (chloride) = 617 mM Fe(III)

100 mg/L ferric (chloride) = 35 mg/L Fe

100% ferric = 35% Fe

Ferric doses for scientific discussion or fundamental presentations, are expressed in terms of the Fe(III), and typically on a molar basis. Engineering and treatment plant applications, however, typically express doses in terms of “ferric.” One should therefore exercise care when reporting, interpreting, and expressing alum dose. The relationships in the box above show the conversion. Dosage of chemical needs to be distinguished from dosage of trade product in calculations.

A molar ratio of 1:1 mol Fe/mol P is therefore equivalent to ~1.8 g Fe/g P; or ~5.2 g ferric chloride/g P.

*What is the “Surface Complexation Model” and what does that mean?*

Surface complexation models (SCM) attempt to examine the molecular level electrostatic and chemical bonding forces that determine the retention of cations and anions on mineral surfaces such as oxides. SCM determines surface potential and the influence of sorbates, and the electrostatic behavior of water and ions for 2 or 3 layers. Integrating the influence of the mineral surface acidity constants,  $K_{a1}$  and  $K_{a2}$ , SCM can be used to develop a model to understand ion adsorption on a mineral surface across a pH range. This allows determination of the zero point of charge (ZPC) when the negatively charged surface sites are balanced with an equivalent proton balance, thus providing a transition point for anionic or cationic adsorption. For example, the ZPC of hydrous ferric oxide (HFO), freshly formed in contact with air has been shown to be about 6.6, whereas the ZPC of Goethite ( $\alpha$ -FeOOH) exceeds 8. SCM is widely used to better understand contaminant transport phenomena in soils, radioactive waste, mining impacted areas and

in engineered adsorption related processes, such as water treatment (Dzombak et al., 1990; James et al., 1977; Nowack et al., 1997).

### *Research Needs*

Reactions of iron has been studied and verified with some laboratory data. Aluminum reactions remain to be studied.

### *How do I perform a jar test?*

Despite its apparent simplicity, jar testing requires skill and careful planning. Many good texts and protocols are available to guide the analyst.

Jar tests are used to establish the relationship between chemical doses or combinations of chemicals, under various conditions (mixing, pH, temperature, etc.). It is a useful method to determine the impact of chemical addition under controlled conditions. The goals of the testing will determine the exact method followed in terms of mixing intensity, time, and sequencing of chemical addition.

The key to jar testing is to maintain the same physical test conditions. The mixing intensity, duration, method of adding chemicals, etc., should remain consistent from test to test. Also, the sample added to the individual jars should be well mixed, so that each jar has the same material. This goal is difficult to achieve for jar tests developed to study chemical addition to raw wastewater. Excellent mixing during chemical addition is used to disperse the chemical rapidly when studying the fundamental chemical reactions. However, when using jar testing to optimize chemical addition, flocculation and separation of a full scale facility, the mixing and flocculation conditions are selected to match those of the full scale facility. Similar, reaction and flocculation times will be selected to match the field conditions.

The most important key when conducting a jar test is to keep the experimental conditions consistent (unless that it the study variable!). Maintain the same mixing intensity and contact times.

### *What are the factors that impact the chemistry of phosphorus removal?*

This question is in preparation

### *What are the principal phosphorus precipitants that form?*

Chemical precipitants form from reactions with various chemical compounds. ([What chemicals are used to precipitate phosphorus?](#)) These chemical form a variety of precipitants, most complex precipitants that change depending on the chemistry, pH, composition, type of chemical, age, and other factors.

Phosphate is found as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  species in solution at circumneutral pH, with  $\text{H}_2\text{PO}_4^-$  being found in more acidic solution and  $\text{HPO}_4^{2-}$  being found in more basic solution. Phosphate can adsorb on reactive iron oxy-hydroxide surfaces by forming the complexes  $\equiv\text{FeH}_2\text{PO}_4$ ,  $\equiv\text{FeHPO}_4^-$ , and  $\equiv\text{FePO}_4^{2-}$ . For ferrihydrite there is direct X-ray spectroscopic evidence for removal of phosphate from solution by inner-sphere surface complexation. Surface complexation will result in a monolayer of phosphate ions on the metal oxide surface. With solution concentrations of ferric ions and phosphate that exceed  $K_{sp}$  there is a potential for precipitation from solution as  $\text{FePO}_4(s)$  or as a surface precipitate at a reactive iron oxide surface site with the potential to form embedded layers of iron and phosphate (Willett et al., 1988; Arai et al., 2001; Khare et al., 2004).

### *How does the organics in wastewater affect phosphorus removal chemical reactions?*

Wastewater treatment processes can produce dissolved polyanionic humic and fulvic acid polymers that are degradation products of biopolymers naturally present in municipal wastewater streams. With their polyanionic electrolytic properties, humic substances are important in the dissolution, transport, and precipitation of positively charged inorganic ions. When iron and aluminum metal salts are used as coagulants, flocculants, or adsorptive media for phosphorus removal, excess humic substances can form insoluble complexes with metal ions and their mineral oxides, thereby blocking sites for reactive phosphorus removal. Alternatively, phosphate is known to form mixed complexes with fulvic acid and trace metal ions. This presents the potential for quantitative complexation of phosphate in water with humic substances, thus making removal using chemical processes more difficult (Stumm and Morgan, 1962; Black and Christman, 1963; Wilson, 1959; Ramamoorthy and Manning, 1974; Steelink, 1977).

#### *Research Needs*

The reactions and impact of organic compounds on chemical phosphorus removal needs to be quantified to determine the types and degree of interference expected from organics normally present in the wastewater. Organic molecules themselves can also contain phosphorus and may not react with the iron or aluminum compounds in the water.

#### *Aluminum Reactions*

This section is still in preparation.

#### *Iron Reactions*

##### *What is the chemical reactions of ferric and phosphate?*

Ferric ion released into solution at sufficient concentrations rapidly hydrolyzes and precipitates as a hydrous ferric oxide (HFO) with high surface area and reactive surface functional groups. Phosphate has a high adsorptive binding strength to ferric oxides and will compete with and displace  $\text{AsO}_4^{3-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{Cl}^-$  given sufficient time.

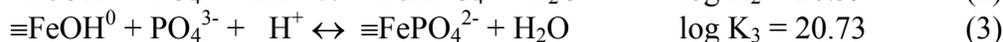
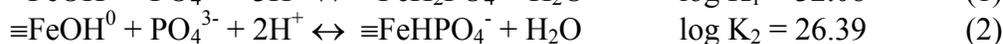
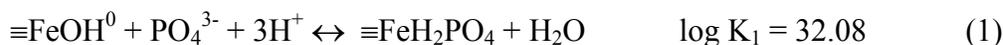
Chemical precipitation of  $\text{FePO}_4(s)$  based on solubility product calculations does not occur above pH 5 and at the relatively low concentrations typically found in most wastewater. It is now recognized that the mechanism of orthophosphate removal from wastewater using ferric iron treatment is adsorption on iron oxides.

[Ryden et al., 1977; Ryden et al., 1977; McBride, 1994; Geelhoed et al., 1997; Newcombe et al., 2008]

##### *What is the equilibrium constant for phosphorus and ferric?*

At the low concentrations of phosphate-P typically found in wastewaters, the dominant removal mechanism upon addition of Fe(III) salts will be the formation of hydrous ferric oxides (HFO) and the subsequent formation of stable surface complexes with anionic phosphate [Dzombak and Morel, 1990; Gustafsson, 2003].

The HFO surface reactions and intrinsic constants for trivalent phosphate anions are:



*How much ferric is needed to remove phosphorus?*

Traditionally the ferricphosphate precipitant  $\text{FePO}_4(\text{s})$  was thought to be the primary precipitant in wastewater treatment. However, recent research (Smith et al., 2008) showed a complex structure, with several fundamental reactions occurring simultaneously as iron reacts to form ferric hydroxides and phosphates.

The amount of phosphate that binds to the metal hydroxide is still a topic of discussion. Current research suggest that the stoichiometric ratio of metal:phosphorus (Me:P) in the precipitant depends on many factors, including the phosphate concentration in the liquid, chemical dose, age of the hydroxyl complex, mixing, and many other factors (Szabo et al., 2008, de Haas et al., 2000, Yang et al., 2006).

The ratio of Fe:P on a molar basis range from approximately 1:1 mol Fe/mol P to greater than 10:1 mol Fe/mol P. Hermanowicz (2006) showed full scale and laboratory data relating the residual phosphorus to the Fe/P dose.

*Research Needs*

The practical dose expressed as Fe/P remains uncertain, mainly as a result of the uncertainty in the ferric phosphate chemistry and an understanding of the factors that contribute to the precipitant/adsorption reactions. As the chemistry is better understood, the dose requirements will become clear.

*Does ORP affect phosphate-ferric reactions?*

Solution pH, followed by dissolved oxygen (DO) and redox potential (ORP), all affect P removal approaches that use iron salts. Reduction of ferric iron to ferrous iron can happen at low redox potentials and through the action of dissimilatory iron reducing bacteria (DIRB). Ferric hydroxide addition has been shown to have a favorable effect on phosphate elimination during anaerobic digestion of activated sludge. This has been shown to result from enhancement of DIRB activity and the concomitant reduction of ferric iron to ferrous iron in DIRB respiration. Ferrous iron can react to form  $\text{FeHPO}_4$  however high DO (e.g. 1.0–5.7  $\text{mg l}^{-1}$ ), mid-range redox potential (e.g. 57–91 mV) and high pH (e.g. 7.5–8.0) available in some wastewaters can oxidize the majority of added ferrous iron (Stabnikov et al., 2004; Thistleton et al., 2001).

*What is the optimal pH for phosphorus removal using ferric?*

Recent work by Szabo et al (2008) showed that there is an optimum pH for phosphorus removal, but that the optimum is relatively wide – ranging from pH 5 to pH 7 – with deterioration outside this pH range. At acidic pH, soluble phosphate complexes form and, at higher pH, some soluble iron-hydroxide complexes start to form with a resulting decrease in the phosphorus removal efficiency.

*How much alkalinity is removed when adding ferric?*

Question under review.

*How fast does ferric react to form ferric hydroxides?*

Ferric iron is a strong Lewis acid and, when released into solution, it rapidly hydrolyzes forming a basic salt with a hydroxyl group and subsequently precipitates as an oxide. Depending on reaction conditions and time, hydrous ferric oxides (HFO) formed when ferric salts are added to water can consist of amorphous ferric hydroxide ( $\text{am-Fe}(\text{OH})_3(\text{s})$ ), ferrihydrite ( $\text{Fe}_p\text{O}_r(\text{OH})_s \cdot n\text{H}_2\text{O}$ ), goethite ( $\alpha\text{-FeOOH}$ ),

lepidocrocite ( $\gamma$ -FeOOH), and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). Since ferric iron is a strong Lewis acid, low solution pH and alkalinity can limit hydrolysis and the subsequent production of oxy-hydroxide precipitants. Given sufficient alkalinity, the formation of ferric iron precipitants in most waters and wastewaters is very rapid; usually within milliseconds (Schwertman and Cornell, 2000).

*How fast does phosphorus react with ferric hydroxides?*

The rate of reactive removal of phosphate from solution using iron metal salt addition depends on many factors, including water chemistry (e.g. competitive reactions such as siderite formation), reactant concentrations, energy of mixing, and temperature. In typical wastewater applications with sufficient mixing and alkalinity, the removal reaction appears to have a fast stage that removes the majority of the dissolved phosphate (~90%) in less than a minute, followed by a slow step that occurs at a significantly slower rate (McLaughlin et al., 1977; Parfitt, 1989).

*Does pre-formed ferric hydroxide remove phosphorus?*

Pre-formed iron oxy-hydroxide and iron oxide solids will remove phosphate from water; however, their activity will vary according to the surface area of the formed mineral, the reactive sites available in that mineral form, and interaction of solution pH and the point of charge (ZPC) of the specific mineral that has formed. Aging of the iron oxide mineral, in general, will decrease the removal and increase the ZPC, often above pH 8. In general, concomitant formation of iron oxy-hydroxide solids and surface complexation of the phosphate moiety will yield higher rates of removal. This will occur when phosphorus containing wastewater is treated with Fe(III) solutions. (Madrid and DeArambarri, 1985; Denham, 2007).

*Does the ferric precipitant change over time?*

The structure of the iron oxide mineral change over time as shown by Szabo et al. (2008). The ferric hydroxide structure changes from an amorphous precipitant to a hard mineral structure over time (months).

The mineral structure appears to affect the phosphorus chemistry fundamentally: first, during the initial precipitation, phosphate is included in the structure of the surface complexation model structure. If present during the crystal growth phase, the phosphorus is included in the crystal. As the crystal ages and becomes harder, diffusion to bond with the metal is much more difficult and inefficient (from a metal dose/phosphorus removal perspective).

*Research Needs*

The kinetics, structure, implications and impact of the precipitant age is still largely a question. Research has shown that the crystal changes in structure, but the fundamental implications of these changes on phosphorus chemistry, and the significance of these factors in wastewater treatment operations, has yet to be determined.

*How does mixing affect phosphorus precipitation with ferric?*

Energy of mixing will allow for non-diffusion limited formation of iron oxy-hydroxide precipitants with the potential for simultaneous surface complexation of available solution phosphate to reactive surface sites. Hence, rapid mixing is favorable for P removal. Mixing at very high energy can result in high shear forces that limit floc size and this can have a negative impact on settling and filterability.

*What ferric residual remains in the liquid following phosphorus removal?*

Question under review.

*What is the conversion mechanism and rate from Fe<sup>2+</sup> to Fe<sup>3+</sup> ? And back (in low ORP environments)? Do biological or abiotic mechanisms play a role?*

Question under review.

*Does polymer improve phosphorus removal?*

Polymer does not react with phosphate to produce insoluble particulates but is used to enhance particulate phosphorus removal. Polymer is used to flocculate small particles and also to improve the capture efficiency of some solids separation devices.

Polymer is added as a flocculation aid to capture small colloidal solid phosphorus containing particles and enhance particle growth to form larger particles. The polymer acts to neutralize the particle charge and stabilize the colloidal particles that form when a metal salt is added to wastewater. In addition, the long chain organic molecule used as a building block for the polymer acts as a bridge to flocculate particles.

Polymers also enhance solids separation processes such as sand filters or ballasted sedimentation to attach the colloidal phosphorus containing particles to the sand and remove it.

### **Solids Separation (Last updated November 4, 2008)**

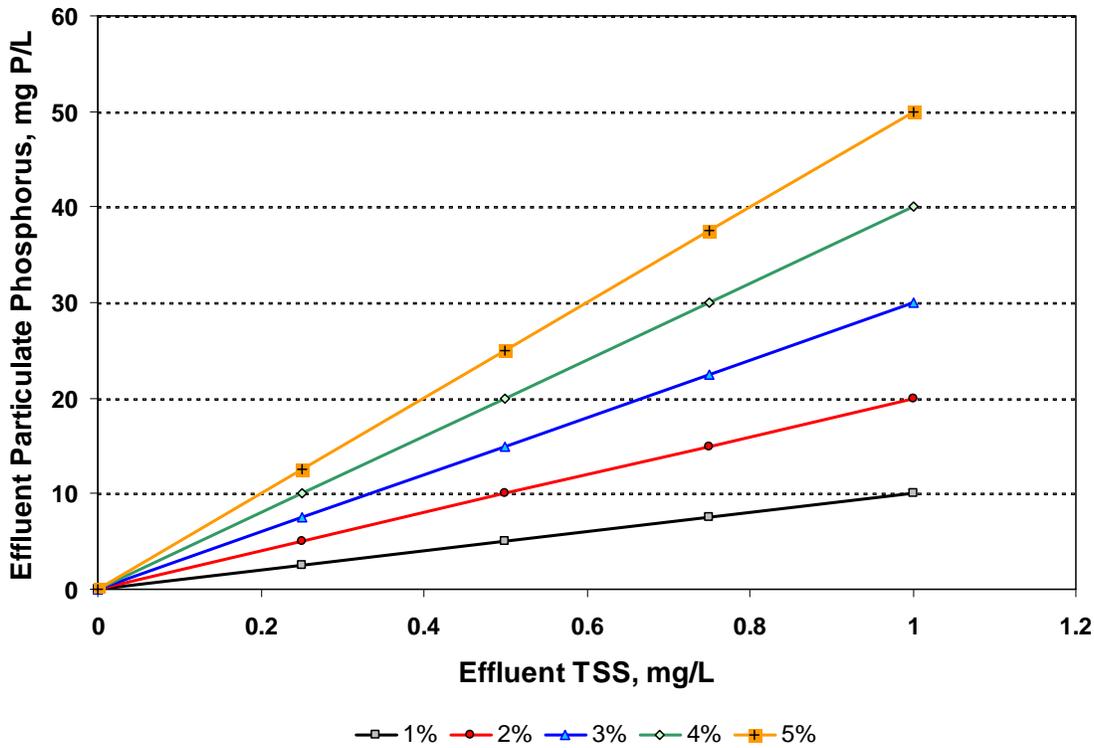
Effective solids separation is essential to achieve phosphorus removal. Chemical reactions are used to convert soluble phosphorus species into particulates, which must be removed from the liquid in order to eliminate the phosphorus. The resulting total phosphorus concentration from solids separation processes is a function of solids removal efficiency, phosphorus content of the solids, and the amount of soluble phosphorus.

The phosphorus content of the solids plays an important role in achieving low phosphorus concentrations. The phosphorus content of the solids depends on the type of solids retained and the pretreatment, for instance:

- Conventional Activated Sludge biomass: 1% – 3% P
- EPBR Activated MLSS: 2% – 8% P

The phosphorus content of tertiary solids are highly variable and is determined to a large extent by the Me/P (Metal/Phosphorus) dose ratio. Since almost all of the metal salt is precipitated as a metal hydroxide complex to produce particles, solids produced under a higher Me/P dose will have lower phosphorus concentration than the solids produced at a lower Me/P dose.

A lower phosphorus content in the solids is beneficial to achieve low effluent phosphorus concentrations. For example, if the solids contain 5 percent P, then the effluent TSS of 1 mg/L will contribute 50 ug P/L. The figure below shows the relationship between the effluent particulate phosphorus and effluent TSS as the phosphorus content of the solids change from 1 to 5 percent. This figure shows that in order to meet an effluent particulate phosphorus concentration of 10 ug/L, the effluent TSS must be reduced to 0.2 mg/L for a high (5 percent) phosphorus content. If the phosphorus content of the solids is low (1 percent), then the 10 ug/L limit can be met with as much as 1 mg/L.



The discussion above illustrates the two key features of the solids removal process:

1. Solids separation process must be very efficient, producing effluent TSS to non-detectable levels.
2. The solids separation device must be able to handle high chemical doses required for phosphorus removal.

*What processes are used to separate chemical precipitants?*

The following processes are typical of solids separation processes:

- Sedimentation/filtration facilities. Many different type of filters (dual media filters, trimedia filters, deep bed filters, others) have been used. Including sedimentation facilities (conventional or other solids removal facilities) provides a secondary barrier to improve performance. Examples of this approach are Clean Water Services in Portland, OR, where this type arrangement has consistently met a 70 ug/L effluent TP permit limit.
- Direct filtration (without sedimentation facilities) using different types of filters (dual media filters, trimedia filters, deep bed filters, others) have been used. This provides a single barrier for solids separation. An example of this approach is the City of Las Vegas, where this type arrangement has consistently met a 170 ug/L effluent TP permit limit.

- Two stage filtration has been used to improve separation of phosphorus containing particles. By using two filters in series, an additional removal barrier is provided to improve reliability and performance. This type of technology has been able to reduce total phosphorus below 50 ug/L in New York city watershed at Stamford, Delhi, and Walton.
- Microfiltration will theoretically remove all soluble phosphorus since the pore size of commercial membranes is typically less than the 0.45 um used in the laboratory analysis. In practical application though, defects in the membrane can cause colloidal particles to escape to the product water.

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