Operation of Nutrient Removal Facilities

wef Manual of Practice No. 37

OPERATION OF NUTRIENT REMOVAL FACILITIES

WEF Manual of Practice No. 37

2013

Chapter 8

Chemical Precipitation of Phosphorus

Jurek Patoczka, Ph.D., P.E.; Maria Inneo; and Susan Hansler, M.A.Sc., P.Eng.

1.0   INTRODUCTION

Chemical precipitation of phosphorus is a method frequently used as a primary phosphorus removal process or in conjunction with biological removal processes as a supplemental, polishing, or backup process. Chemical addition is often the phosphorus removal method of choice for small- and medium-size facilities, where implementation of a dedicated, enhanced biological phosphorus removal (EBPR) process is not practical or economical. This is particularly the case when an existing treatment facility has to meet new phosphorus limits and the configuration of the existing biological treatment process does not lend itself easily to an EBPR conversion. Because the EBPR process can be subject to periods of inferior performance or upsets, it is almost always supported by standby or polishing chemical addition facilities. In practice, whenever an effluent phosphorus limit has to be consistently met, chemical addition is almost always practiced, at least in a standby mode.

An advantage of chemical precipitation is that the phosphorus removed in this fashion remains fixed in the waste sludge as inorganic precipitate and is not readily released during sludge storage, thickening, or anaerobic digestion. At facilities with EBPR, phosphorus release from the sludge is common, particularly in oxygen-deficient conditions. Consequently, recycle streams from sludge processing operations can return a significant phosphorus load to the head of the facility, particularly when anaerobic digestion is practiced. At such facilities, the sludge processing train and return streams must be carefully designed and operated because uncontrolled releases of phosphorus can offset the purpose of the

EBPR process. When chemical phosphorus precipitation is practiced, chemically bound phosphorus in sludge is not subject to such release.

Use of chemicals for phosphorus removal has a number of disadvantages, which are discussed in more detail in the subsequent sections. Some of these are increased sludge generation (Section 6.1), alkalinity depletion (Section 6.3), an increase in total dissolved solids (TDS) (Section 6.4), increased inert concentration in mixed liquor with related potential effects on ultimate biosolids disposal (Section 3.2), and potential effects on other processes such as UV disinfection (Section 6.7).

2.0 PHOSPHORUS FORMS IN RAW WASTEWATER AND IN THE EFFLUENT

The principal form of phosphorus removed by chemical addition is soluble orthophosphate ions. These ions represent the significant form of phosphorus in raw municipal wastewater. Biological treatment processes will convert most of the remaining phosphorus forms (polyphosphates, or condensed phosphates, and organic phosphorus) into orthophosphates while assimilating and incorporating some of the available phosphorus to the biomass (approximately 1 mg/100 mg of 5-day biochemical oxygen demand [BOD_5] removed in the biological process). Effluent from the activated sludge, or from any other biological process, will contain residual, soluble phosphorus primarily in the orthophosphate form, with a relatively minor contribution from refractory or recalcitrant dissolved organic phosphates (rDOP). For practical purposes, the contributions from rDOP are only of concern where stringent limits (at the level of 0.1 mg/L total phosphorus or less) are required (Section 5.1). Consequently, soluble phosphorus in the effluent from biological processes, including in the mixed liquor as it exits the aeration basin, is amenable to almost complete removal by chemical precipitation. In addition to soluble phosphorus, effluent from any treatment process will contain phosphorus in particulate form, either as inorganic precipitate or as part of biological cells. In a typical situation in which chemical is added to the activated sludge system, the effluent suspended solids will contain phosphorus in both forms enmeshed together into the floc (see Section 3.3 for a more detailed discussion of this topic).

Facility recycle streams from solids processing operations, particularly when anaerobic digestion is used and particularly for facilities practicing EBPR, could be rich in phosphorus released from sludge, as discussed in more detail in Section 4.0 of Chapter 2. The effect of the phosphorus load from recycle streams should be considered when designing and operating chemical phosphorus removal processes.

Chemical addition to the primary clarifier, which is known as *chemically enhanced primary treatment* (CEPT), or *pre-precipitation*, is frequently used for enhanced particulate and colloidal BOD_5 and total suspended solids (TSS) removal in the primary clarifiers to lower organic and solids loading on the downstream

biological process. Chemicals commonly used in CEPT treatment (aluminum and iron salts) are the same ones used for orthophosphate precipitation. Consequently, most of the phosphorus present in raw wastewater in soluble, particulate, or colloidal form can be removed by chemical precipitation in the primary clarifier, potentially leading to phosphorus deficiency in downstream biological treatment processes. (For a detailed discussion of phosphorus sources and forms of phosphorus present in the influent and effluent, refer to Chapter 2 of this manual or Section 2.0 of Chapter 7 of Water Environment Federation's [WEF's] *Nutrient Removal* [WEF, 2010]).

3.0   PRINCIPLES OF CHEMICAL PHOSPHORUS REMOVAL

3.1   Mechanism of Phosphorus Removal

The basic mechanism of chemical phosphorus removal is precipitation followed by a solids separation step such as sedimentation and/or filtration. Phosphorus precipitation is the transformation of the soluble phosphorus present in wastewater as orthophosphate anion (PO_4^{3-}) to an insoluble chemical compound (salt) and the removal of these insoluble precipitates by sedimentation or filtration. Such a transformation occurs when a chemical agent bearing a proper cation, such as aluminum (Al^{3+}) or ferric (Fe^{3+}), is added to the wastewater and reacts with the soluble phosphorus to form an insoluble orthophosphate salt. In practice, more complex reactions are taking place, which involve co-precipitation and surface adsorption. These mechanisms are discussed in more detail in *Nutrient Removal* (WEF, 2010).

Precipitate formed in this way, together with other forms of particulate phosphorus present in the wastewater, can be separated from the wastewater by clarification or filtration. The phosphorus precipitated using chemicals is removed from the wastewater with sludge (i.e., either combined with waste primary or biological sludge or as a separate chemical sludge).

3.2   Fate of Chemicals Added During Treatment

The application dosages of chemicals needed to remove phosphorus to low levels are typically in excess of a stoichiometric requirement, as discussed in more detail in Section 4.0. When chemical is added to the mixed liquor at the effluent from the aeration basin (or influent to the final clarifier), which is the most common application point, any excess chemical that does not bind with orthophosphates will precipitate nevertheless. This precipitate will be in the form of aluminum hydroxide (for aluminum-based chemicals) and ferric hydroxide (for ferric-based salts), although, in reality, more complex hydrated-oxides mixtures will also be formed. These inorganic precipitates, only partially saturated with orthophosphates, will

be enmeshed with biological floc and settle in the final clarifier. Thus, the excess, unused chemicals will be incorporated to the mixed liquor and returned to the head of the facility with the return activated sludge (RAS). Here, these chemicals will be available to react with phosphorus entering the aeration basin with raw wastewater, reducing overall chemical use.

The precipitate accumulating in aeration basins will result in an increase in the basin inert solids concentration. The effect of an increased inert content of mixed liquor should be taken into account when designing and operating the activated sludge system. In particular, when operating the system at a given sludge age (such as that required for nitrification), inert solids from chemical addition will increase the equilibrium mixed liquor suspended solids (MLSS) concentration necessary to maintain the target sludge age. Conversely, if the same MLSS concentration is being maintained, the resulting sludge age will be lower after initiation of chemical addition. Refer to Section 6.1 for calculations of different chemicals' contribution to the inert content of MLSS.

3.3   Role of Solids Separation

Because effluent permit limits for phosphorus are commonly expressed as total phosphorus, precipitation of soluble phosphorus (orthophosphates) into a particulate form is only part of the job of phosphorus removal. Indeed, the solids separation step (clarification and/or filtration) must be capable of removing effluent TSS with associated particulate phosphorus forms to levels consistent with the effluent phosphorus limit.

The contribution of particulate phosphorus is particularly important for facilities with low effluent limits because even seemingly low effluent TSS can carry a significant phosphorus contribution (Figure 8.1). An additional consideration is that, in systems with a dedicated phosphorus removal process either by chemical addition to the activated sludge or by EBPR, the phosphorus content in MLSS and effluent TSS are increased. While the phosphorus content of MLSS is approximately 2% in a municipal conventional activated sludge facility, the content increases to 4 to 5% for a facility with a stringent phosphorus limit, regardless of whether the phosphorus is incorporated to the sludge by precipitation or by EBPR. For facilities operating at a low sludge age and with an influent phosphorus concentration higher than that for typical municipal wastewater, this could even be much higher.

Figure 8.1 shows that, for total phosphorus limits of 0.1 mg/L, effluent TSS should be no more than 1 mg/L. Presently, this can only be consistently achieved by membrane filtration (as in a membrane bioreactor [MBR]), multistage filtration, or by well-performing conventional filtration supported by polymer use. For limits of 0.5 to 1 mg/L total phosphorus, conventional filtration or even well-performing clarification (possibly supported by polymer addition) will be adequate, assuming that soluble orthophosphates are kept to a minimum by
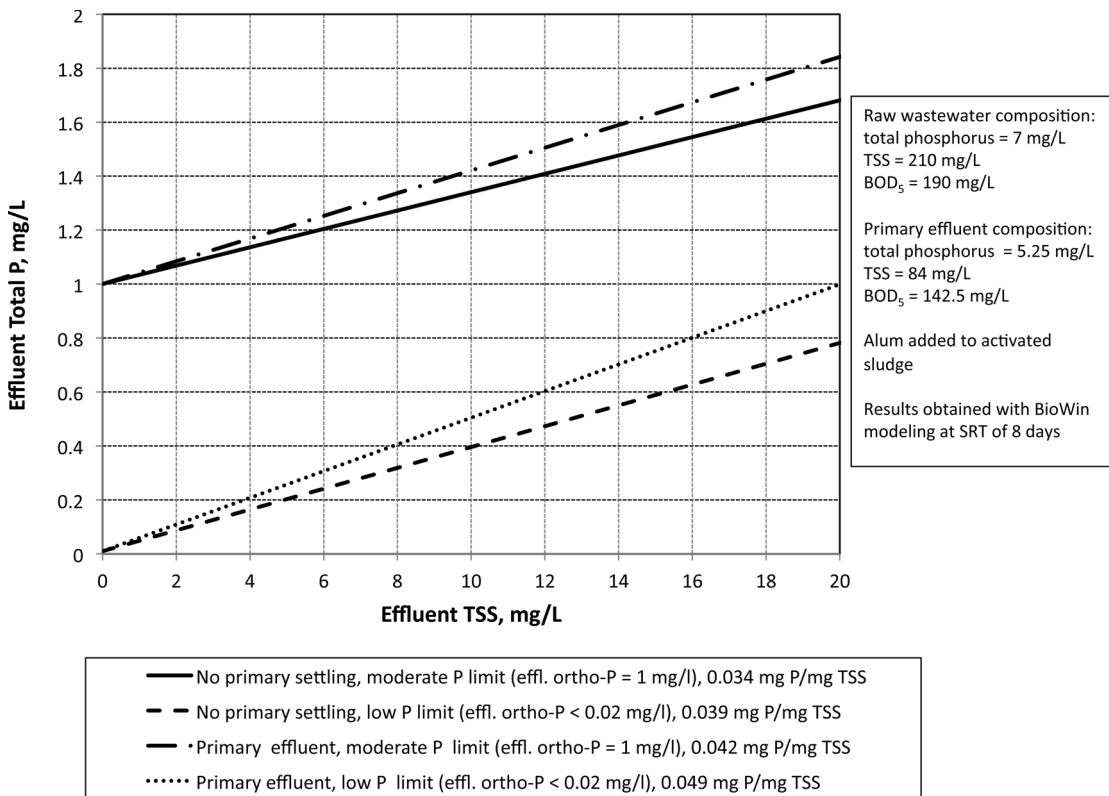
FIGURE 8.1 Contribution of effluent TSS to total phosphorus in the effluent for different treatment scenarios.

adequate chemical dose (or a well-functioning EBPR). As Figure 8.1 illustrates, for systems with primary clarification, which increases the mixed liquor volatile suspended solids (VSS) fraction of the MLSS, the phosphorus content in the MLSS and effluent TSS is even higher.

4.0   CHEMICALS USED FOR PHOSPHORUS PRECIPITATION

4.1   Introduction

In general, cations of the following metals can be used for the precipitation of phosphorus (orthophosphates) from wastewater:

- Aluminum,
- Iron,
- Calcium, and
- Magnesium.

Most commonly utilized are various chemicals containing aluminum (mainly alum) and iron (mainly ferric chloride), with calcium and magnesium being much less common. The following sections will discuss the different chemicals available, the precipitation process, and sample calculations.

4.2   Aluminum Salts

4.2.1   Overview of Aluminum-Based Chemicals

There are several aluminum compounds that are used in the wastewater industry for phosphorus removal, including aluminum sulfate, polyaluminum chloride (PACl), and sodium aluminate. The most widely used chemical is aluminum sulfate, commonly known as *alum*, although PACl is gaining popularity because of its ease of handling and lowering effect on pH. Polyaluminum chloride was originally used in water treatment when enhanced solids removal was a treatment objective. Because the strength and composition of sodium aluminate and PACl products vary considerably, efficacy of a specific product considered for an application should be established and compared to alternative products in jar tests, as discussed in Section 4.6. Sodium aluminate in a dry form or in solutions of various strengths was also originally developed for water treatment applications and is typically used when additional alkalinity is required.

Solid alum could be supplied as a dry, powdery chemical ("filter alum"), with an average molecular composition of $Al_2(SO_4)_3 \cdot 14H_2O$. This is a hydrated aluminum sulfate salt that indicates the presence of a defined number of water molecules in the structure of the dry salt crystal under normal conditions. However, alum for wastewater treatment is commonly delivered as a 49% solution (indicating that 49 parts of dry alum are combined with 51 parts of water, by weight). By convention, the alum dose applied in the treatment process is expressed in equivalent units of weight of dry alum (including water of crystallization) per volume of water (wastewater). Properties of alum and other aluminum-based chemicals are summarized in Table 8.1. The effect of aluminum-based chemicals on sludge generation, alkalinity consumption, and the increase in TDS are discussed in Sections 6.1, 6.3, and 6.4, respectively.

Regardless of the chemical, the active precipitating agent is aluminum ion, which combines with orthophosphate ions to form aluminum phosphate, as follows:

$$Al^{3+} + (PO_4)^{3-} \rightarrow AlPO_4 \tag{8.1}$$

In reality, precipitation of phosphorus with aluminum and iron salts is a more complex process involving co-precipitation with aluminum hydroxide, hydrated aluminum oxides, and surface adsorption. This makes stoichiometric (based on chemistry of the reaction) calculations approximate; however, eq 8.1 will be used as the basis of dose calculations for illustrative purposes.

TABLE 8.1 Properties of aluminum-based chemicals used for phosphorus precipitation.

Name	Chemical formula	Molecular weight	Aluminum metal contents, % by weight	Specific density kg/L	Specific density lb/gal	Weight ratio of dry chemical ($Al_2(SO_4)_3 \cdot 14H_2O$) for stoichiometric phosphorus precipitation (g of chemical/g of P)
Alum, dry	$Al_2(SO_4)_3 \cdot 14H_2O$	594	9.1	0.6 to 1.1	5 to 9.5	9.6
Alum, 49% solution*	$Al_2(SO_4)_3 \cdot 14H_2O$	594	4.4	1.33	11.1	9.6
Sodium aluminate, anhydrous (powder)	$NaAlO_2$	82	33	0.72	6.0	2.64
Sodium aluminate, trihydrate (granular)	$Na_2O \cdot Al_2O_3 \cdot 3H_2O$	218	25	1.02	8.51	3.52
Sodium aluminate, 20 to 45% solution (could vary significantly)	$NaAlO_2$	82	Varies	Varies	Varies	
Polyaluminium chloride, solutions of various strengths	$Al_nCl_{(3n-m)}(OH)_m$ example: $Al_{12}Cl_{12}(OH)_{24}$	Varies	Varies	Varies	Varies	

*49% alum solution has a dry alum ($Al_2(SO_4)_3 \times 14H_2O$) content of 0.647 kg/L (5.4 lb/gal) and an aluminum metal content of 0.059 kg/L (0.492 lb/gal).

216

Equation 8.1 indicates that it will take 1 mol of aluminum ion to react with 1 mol of phosphate and, thus, a 1-to-1-mol ratio of aluminum to phosphorus is required for this reaction. Because the molecular weight of aluminum is 27 and the molecular weight of phosphorus is 31, the weight ratio of aluminum to phosphorus in eq 8.1 is 0.87 to 1, as shown in the following calculation:

$$(27 \text{ g Al}/1 \text{ mol Al})/(31 \text{ g P}/1 \text{ mol P}) = 0.87/1 \text{ or } 0.87{:}1$$

With aluminum sulfate, there are two molecules of aluminum per molecule of alum; therefore, the stoichiometric weight ratio is

$$594 \text{ g Al}_2 (SO_4)_3 {\cdot} 14 \text{ H}_2O/2/31 \text{ g P} = 9.6{:}1.$$

A larger amount of aluminum salt is required for actual operation than the chemistry of the reaction (stoichiometry) predicts. The amount of excess chemical required increases as the target residual phosphorus concentration decreases. The excess aluminum salt will precipitate as aluminum hydroxide, with a simplified reaction as follows:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{8.2}$$
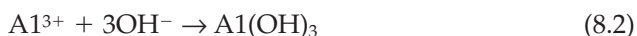
Therefore, sludge that is generated at the point of chemical application will include a mixture of aluminum hydroxide and aluminum phosphate generated according to eqs 8.1 and 8.2. Equation 8.2 also illustrates the consumption of alkalinity (pH reduction) encountered when applying alum. These effects are discussed in more detail in Section 6.3.

An alternative aluminum-based chemical available for phosphorus removal is PACl, with a general composition of $Al_nCl_{(3n-m)}(OH)_m$. Polyaluminum chloride products also include an admixture of polyaluminum chlorohydrate and vary in the degree of acid neutralization (amount of caustic added, or basicity) and polymerization and aluminum content. In the water treatment industry, PACl is used as a more effective coagulant for TSS removal than alum and is also being used for phosphorus removal from wastewater. Polyaluminum chloride use generally does not depress wastewater pH, although its effects on pH depend on the exact formulation. Polyaluminum chloride use for phosphorus removal is gaining popularity, particularly at smaller facilities, because it could eliminate the need for use of caustic to increase pH when straight alum is used.

Sodium aluminate can also serve as a source of aluminum for the precipitation of phosphorus. It is generated by reacting aluminum hydroxide with caustic soda. The chemical formula for sodium aluminate is $Na_2Al_2O_4$ or $NaAlO_2$. One commercial form of sodium aluminate is granular trihydrate, which may be written as $Na_2O{\cdot}Al_2O_3{\cdot}3H_2O$ and contains approximately 46% Al_2O_3 or 25% Al. It is also being sold as a solution in various strengths. In contrast to alum, which reduces wastewater pH, a rise in pH may be expected upon addition of sodium aluminate to wastewater. Consequently, in situations where caustic

addition would be required to counter pH depression caused by alum addition, application of sodium aluminate may eliminate the need for handling and dosing two different chemicals.

4.2.2   *Determination of Dose for Aluminum-Based Chemicals*

An approximate dose of alum (or other aluminum-based chemicals) required for a particular application can be calculated based on calculations presented in this section (including eqs 8.4 and 8.5 in Section 4.2.3). Refinement of the chemical application rate could then be performed in full scale based on the results obtained because the system response is fairly quick (Section 5.6).

Jar tests may also be performed to determine the chemical dosage for phosphorus removal in atypical applications (e.g., unusual wastewater composition) and to assess alkalinity destruction and pH depression from dosing of aluminum-based chemicals (and iron-based chemicals). Jar testing will also aid in determining requirements for supplemental alkalinity addition that may be necessary to maintain the required pH for nitrification (see also Section 6.3 for a discussion of the effects of pH and alkalinity). Jar test results may only be an approximation of the dose requirements and the chemical's effect on pH because many aspects of full-scale, continuous chemical addition may not be well duplicated in jar tests. However, jar tests are well suited for comparative testing of efficiency and costs of alternative chemicals (see also Section 4.6). Because of the inherent variability of wastewater, jar tests should be repeated on several different samples.

A design dose curve for chemical phosphorus removal using aluminum ions was developed using literature and pilot-facility data (Figure 8.2). Data in the literature include laboratory-scale test data and data from sites that are operating with chemical phosphorus removal (Gates et al., 1990). The full data set includes results for a range of pH values (mostly 6.5 to 7.5), temperatures, and wastewater characteristics. The effluent soluble phosphorus concentration is labeled "residual soluble P" on the logarithmic x-axis. The molar ratio for metal ion dose to soluble phosphorus removed is labeled "M_{dose}/soluble $P_{removed}$ (mol/mol)" on the y-axis. It is important to note that the curves apply to the soluble portion of the phosphorus only. The curve used to fit the data is based on the following equation:

$$y = a/(1 + be^{-cXe}) \quad (8.3)$$

Where

y = moles aluminum required per mole soluble phosphate removed,
a = 0.8,
b = −0.95,
c = 1.9, and
Xe = target effluent soluble phosphorus concentration (mg/L).

Chemical P Removal Dose Curve
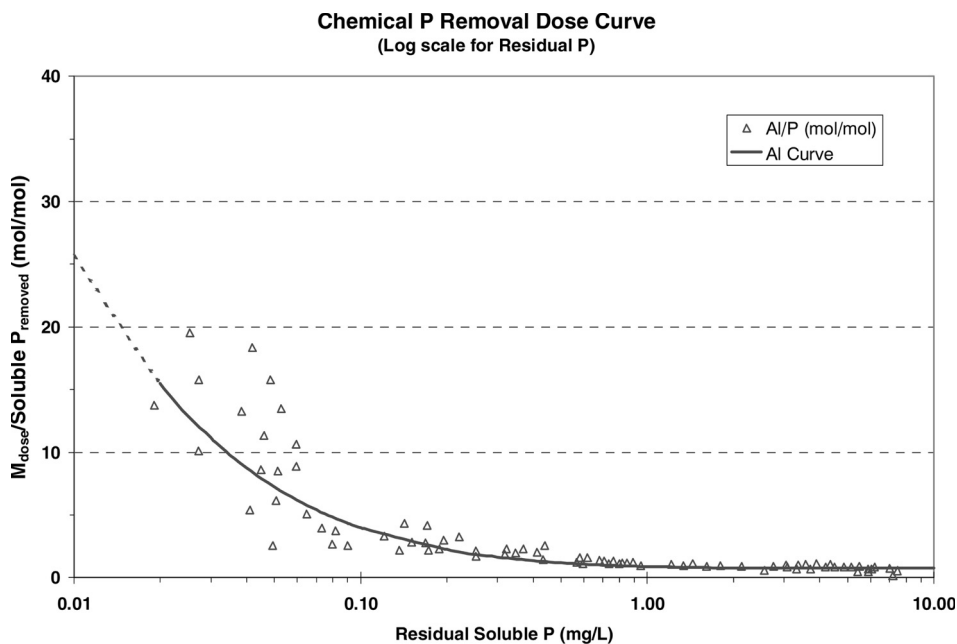**(Log scale for Residual P)**

FIGURE 8.2 Ratio of aluminum (Al^{3+}) dose to phosphorus removed as a function of residual orthophosphate concentration (Gates et al., 1990).

Because eq 8.3 was derived as a best-fit formula for empirical data, it is valid only for a limited range of residual soluble phosphorus concentrations (approximately 0.1 to 0.8 mg/L). For residual phosphorus concentrations above 0.8 mg/L, the value of "y" should be assumed to be 1.0 (i.e., no excess over the stoichiometric amount indicated).

In general, the dose response found in the literature is quite variable and the data scatter increases at residual soluble phosphorus concentrations below 0.1 mg/L. Because of this variability, pilot-scale testing is recommended to determine the actual chemical dose required to reach a low-targeted effluent soluble phosphorus concentration. While jar tests will provide the approximate dose required and are effective for comparison of efficacy of alternative chemicals, the actual dose required in the full-scale application, particularly when applied to an activated sludge process, could be different. This is attributable to the full-scale effects and recirculation of the excess chemicals, as discussed in Section 3.2, which are not duplicated in jar tests. The solids separation step, which plays a critical role in achieving a low effluent phosphorus concentration (Section 3.3), cannot be well simulated in jar tests, emphasizing the need for pilot (or full-scale) testing.

Table 8.1 includes the molecular weight for the different chemicals mentioned in this section. A sample calculation is provided in this section to determine the

dose required to precipitate soluble phosphate. Following the detailed, step-by-step derivation, simplified formulas for both International System of Units and U.S. customary units are provided. The following conditions are assumed:

- Influent facility flowrate is 37 850 m³/d (10 mgd),
- A residual (influent) soluble phosphorus concentration at the point of chemical application is 3.0 mg/L, and
- A residual (effluent) soluble phosphorus concentration of 0.4 mg/L is required.

The amount of soluble phosphorus to be removed in kilograms (pounds) per day is as follows:

$$\text{Phosphorus} = (3 \text{ to } 0.4 \text{ mg/L}) \times 37\,850 \text{ m}^3/\text{d} \times 1\,000 \text{ L/m}^3 \times$$
$$1 \text{ kg}/1\,000\,000 \text{ mg} = 98.4 \text{ kg/d}$$

or

$$(3 \text{ to } 0.4) \text{ mg/L} \times 10 \text{ mgd} \times 8.34 \text{ (lb/mg} \times \text{L/mg)} =$$
$$217 \text{ 1b/d of soluble phosphorus to be removed.}$$

This is equivalent to (98.4 kg/d)/(31 kg/kg-mol P) = 3.17 kg-mol or (217 lb/d)/(31 lb/lb-mol P) = 7.0 lb-mol phosphorus to be removed.

The amount of aluminum ions required is calculated from eq 8.3 as follows:

$$Y = 0.8/(1 - 0.95e^{(-1.9)(0.4)}) = 1.44 \text{ kg-mol Al/kg-mol soluble}$$
$$\text{phosphorus removed (or lb-mol Al/lb-mol P).}$$

Consequently, the amount of aluminum ions required per day is

$$3.17 \text{ kg-mol P} \times 1.44 \text{ kg-mol Al/kg-mol P} = 4.57 \text{ kg-mol Al}$$
$$\text{or } 7.0 \text{ lb-mol P} \times 1.44 \text{ lb-mol Al/lb-mol P} = 10.1 \text{ lb-mol Al.}$$

As the molecular weight of the Al ion is 27, this is converted to mass of aluminum ions per day, as follows:

$$4.57 \text{ kg-mol Al} \times 27 \text{ kg Al/kg-mol Al} = 123 \text{ kg of aluminum ions per day}$$
$$\text{or } 10.1 \text{ lb-mol Al} \times 27 \text{ lb Al/lb-mol Al} = 272 \text{ lb of aluminum ions per day.}$$

As indicated in Table 8.1, dry alum contains 9.1% aluminum. Consequently, the amount of dry alum required for this application will be

$$123 \text{ kg Al/0.091kg Al/kg alum} = 1\,356 \text{ kg alum}$$
$$\text{or } 272 \text{ lb Al/0.091 lb Al/lb alum} = 2\,988 \text{ lb of dry alum per day.}$$

If 49% alum solution is used, it contains 0.059 kg/L (or 0.492 lb/gal) of aluminum ions (Table 8.1). Thus, the amount of liquid alum required for this application will be

$$123 \text{ kg Al}/0.059 \text{ kg Al/L} = 2\ 092 \text{ L}$$
$$\text{or } 273 \text{ lb Al}/0.492 \text{ lb Al/gal} = 553 \text{ gal of solution per day.}$$

The liquid alum required per day to reduce soluble phosphorus from 3.0 to 0.4 mg/L in the aforementioned example is 2092 L/d (553 gpd). The alum dose equivalent to this alum use rate may be calculated from a factor of 0.647 kg/L (5.4 lb/gal) of alum in the 49% solution, as listed in Table 8.1, as follows:

$$2092 \text{ L/d} \times 0.647 \text{ kg/L}/37\ 850 \text{ m}^3/\text{d} = 0.0358 \text{ kg/m}^3$$
$$0.0358 \text{ kg/m}^3 \times 1\ 000\ 000 \text{ mg/kg}/1000 \text{ L/m}^3 = 35.8 \text{ mg/L alum dose.}$$

In U.S. customary units, calculation for this 10-mgd facility will be as follows:

$$553 \text{ gpd} \times 5.4 \text{ lb/gal}/8.34 \text{ (lb/mg} \times \text{L/mg)}/10 \text{ mgd} =$$
$$35.8 \text{ mg/L alum dose.}$$

4.2.3   Summary Dose Formulas for Alum

The aforementioned calculations can be abbreviated to the following overall formula for calculation of the application rate of 49% alum solution in International System of Units:

$$A = (0.0118)(Xi - Xe)(Q)/[1 - 0.95 \times \exp(-1.9 \times Xe)] \qquad (8.4)$$

Where

A = 49% alum solution application rate (L/d),
Xi = soluble phosphorus concentration at the application point (mg/L),
Xe = target effluent soluble phosphorus concentration (mg/L), and
Q = facility flow (m³/d).

In U.S. customary units, the formula is as follows:

$$A = (11.8)(Xi - Xe)(Q)/[1 - 0.95 \times \exp(-1.9 \times Xe)] \qquad (8.5)$$

Where

A = 49% alum solution application rate (gpd),
Xi = soluble phosphorus concentration at the application point (mg/L),
Xe = target effluent soluble phosphorus concentration (mg/L), and
Q = facility flow (mgd).

The aforementioned dose calculations are approximate. Many site-specific factors such as mixing conditions (Section 5.3), application point (Section 5.4),

and wastewater chemistry and temperature will affect the actual dose of chemical required to accomplish treatment objectives. This is particularly true at residual soluble phosphorus concentrations below 0.1 mg/L.

The aforementioned calculations were based on a single application point; however, the optimum operating mode may involve dual application points (i.e., chemical addition to the primary clarifiers and to the secondary treatment process), which could result in overall savings in chemical consumption and cost (Section 5.4).

4.2.4   Other Considerations for Aluminum-Based Chemicals

A significant amount of sludge is produced when aluminum salts are added to the process to remove phosphorus. The quantity of sludge and handling considerations are discussed in Sections 6.1 and 6.2. Alkalinity and pH effects of aluminum sulfate addition are discussed in Section 6.3. Aluminum sulfate and, to a lesser extent, sodium aluminate and PACl, will increase TDS in the system. These effects are discussed in more detail in Section 6.4.

Aluminum compounds (and ferric compounds, discussed later) are mildly acidic and, therefore, storage and handling issues are of concern. Fiber-glass-reinforced plastic or polyethylene tanks can be used to store any of the aluminum compounds. Recommended metering pumps include solenoid, peristaltic, and diaphragm types. Carrier water should be avoided, if possible, because it will result in a more neutral pH; in addition, aluminum hydroxide may precipitate, causing plating in the chemical feed lines. If it is necessary to add carrier water for mixing or dilution, then it should be added as close to the injection point as possible to minimize plating effects. The point of addition of chemical should be in an accessible location above the water level so the delivery rate can be verified with a "bucket and stopwatch" method. For mixing recommendations, refer to Section 5.3. Pump heads should be constructed of polyvinyl chloride (PVC). Piping, valves, and fittings should be PVC or chlorinated PVC. Where feasible, chemical storage and handling equipment should be designed to be compatible with alternative chemicals to provide flexibility when availability and prices change. Storage and delivery piping should be heat-traced, where necessary, to prevent crystallization (49% alum will start to crystallize at $-1\ °C$ [30 °F]).

Facility personnel should wear personal protection equipment (PPE) when handling chemicals. The PPE should include, but not be limited to, gloves, respirators, goggles, aprons, and face shields, and should be worn when working or handling any aluminum salt solutions.

4.3   Iron Salts

4.3.1   Overview of Iron-Based Chemicals

The most common iron compounds used for phosphorus precipitation from wastewater are trivalent ferric (Fe^{3+}) salts, chiefly ferric chloride ($FeCl_3$), and,

sometimes, ferric sulfate [$Fe_2(SO4)_3$]. Because ferric salts addition to preliminary treatment facilities or to primary clarifiers is sometimes used for odor control, ferric may be a chemical of choice for phosphorus removal as it could serve dual purposes at facilities with a need to control odor in the liquid train. Table 8.2 includes general information for the different chemicals mentioned in this section. Chemistry of phosphorus precipitation with ferric salts is similar to that of aluminum compounds. Bivalent ferrous (Fe^{2+}) salts, primarily in the form of spent pickle liquor from metal surface cleaning with acids, are sometimes used as an inexpensive alternative, when locally available. Because pickle liquor can contain metal contaminants, it is important to ensure that these contaminants do not have an adverse effect on the sludge generated or facility effluent quality. It is not clear if the use of spent pickle liquor will continue to be a common practice in wastewater treatment because alternative methods of metal surface cleaning have recently been developed.

Ferrous salts (such as those found in pickle liquor) react with phosphates and precipitate rather poorly (WEF, 2010); therefore, they should only be added to the aeration basin, where they will first be oxidized to ferric salts. It should be noted that some additional oxygen demand will be created in the aeration basin to oxidize ferrous ions to ferric ions. Ferrous ions should never be added to the final clarifier for phosphorus removal because excess or unreacted ferrous ions will carry over into the disinfection system to consume chlorine and form a precipitate, contributing to effluent TSS. Furthermore, if a UV disinfection system is used, iron added to final clarifier may interfere with UV absorbance and foul the lamp sleeves, increasing the frequency of lamp cleaning (Section 6.7).

Effects of iron-based chemicals on sludge generation, alkalinity consumption, and TDS increase is discussed in Sections 6.1, 6.3, and 6.4, respectively (see also Table 8.3). Ferric salts can be added at various treatment facility locations, similar

TABLE 8.2 Properties of iron-based chemicals used for phosphorus precipitation.

Name	Chemical formula	Molecular weight	Iron metal contents, % by weight	Weight ratio of dry chemical for stoichiometric phosphorus precipitation (g of chemical/g of P)
Ferric chloride, dry	$FeCl_3$	162.5	34.5	5.24
Ferric chloride, 37% solution*	$FeCl_3$	162.5	12.8	5.24
Ferric sulfate, dry	$Fe_2(SO_4)_3$	400	28	6.45
Ferrous chloride, dry	$FeCl_2$	127	79	6.14
Ferrous sulfate, dry	$Fe(SO_4)_2$	152	37	7.36

*37% ferric chloride solution has a specific density of 1.36 kg/L (11.4 lb/gal), a dry $FeCl_3$ content of 0.504 kg/L (4.2 lb/gal), and an iron metal content of 0.173 kg/L (1.44 lb/gal).

TABLE 8.3   Sludge generation and TDS increase factors from the use of selected chemicals (Patoczka, 2006).

Chemical*/process	TSS increase factor (F), kg per kg (or mg/L per mg/L) of chemical added	TDS increase factor, kg per kg (or mg/L per mg/L) of chemical added
Alum for stoichiometric phosphorus precipitation (as alum orthophosphate), without neutralization	0.411	0.165
Excess alum (precipitating as aluminum hydroxide), without neutralization	0.263	0.485
Typical alum application for chemical phosphorus removal (at 3:1 alum to phosphorus stoichiometric rate), without neutralization	0.312	0.378
Typical alum application for chemical phosphorus removal (at 3:1 alum to phosphorus stoichiometric rate), with full neutralization with caustic	0.312	0.533
Ferric chloride precipitating as ferric orthophosphate	0.929	0.071
Excess ferric (precipitating as ferric hydroxide)	0.658	0.655
Typical ferric application for chemical phosphorus removal (at 3:1 ferric to phosphorus stoichiometric rate), without neutralization	0.748	0.460
Typical ferric application for chemical phosphorus removal (at 3:1 ferric to phosphorus stoichiometric rate), with full neutralization with caustic	0.748	0.745
pH adjustment with caustic	0	0.575
pH adjustment with sulfuric acid	0	0.980

*Alum dose expressed as $Al_2(SO_4)_3 \times 14H_2O$; ferric as $FeCl_3$.

to aluminum-based chemicals. Ferric ion combines with orthophosphate ions to form ferric phosphate, as follows:

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \tag{8.6}$$

The reaction between ferrous ions and phosphate ions can be written as follows:

$$3\ Fe^{2+} + 2\ PO_4^{3-} \rightarrow Fe_3(PO_4)_2 \tag{8.7}$$
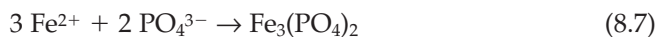
In reality, precipitation of phosphorus with ferric salts is a more complex process (as is the case with aluminum compounds) involving co-precipitation with ferric hydroxide and hydrated ferric oxides and surface adsorption. This makes stoichiometric calculations approximate; however, eq 8.6 will be used as the basis of dose calculations for illustrative purposes.

Equation 8.6 indicates that it will take 1 mol of ferric ion to react with 1 mol of phosphate and, thus, a 1-to-1-mol ratio of iron to phosphorus is required for this reaction. Because the molecular weight of iron is 56 and the molecular weight of phosphorus is 31, the weight ratio of iron to phosphorus in eq 8.6 is 1.8 to 1, as shown in the following calculation:

$$(56 \text{ g Fe}/1 \text{ mol Fe})/(31 \text{ g P }/1 \text{ mol P}) = 1.81/1 \text{ or } 1.8{:}1$$

With ferric chloride, there is one molecule of ferric per molecule of ferric chloride; therefore, the stoichiometric weight ratio of ferric chloride to phosphorus is

$$(162.5 \text{ g FeCl}_3)/31 \text{ g P} = 5.24{:}1.$$

Similarly calculated chemical stoichiometric weight ratios for other ferric chemicals are provided in Table 8.2.

Bench-, pilot-, and full-scale studies have shown that considerably higher stoichiometric quantities of chemicals are typically necessary to meet phosphorus-removal objectives as a result of competing hydroxide and sulfide reactions. If iron salts are added to the primary clarifier, any sulfides presents will first react with the ferric or ferrous ion. Consequently, if a facility influent has significant levels of sulfide, then the iron dosing must be higher for the same amount of phosphorus removed in the primary clarifier.

The excess chemical required increases as the target residual phosphorus concentration decreases. The excess ferric salt will precipitate as ferric hydroxide, with a simplified reaction as follows:

$$Fe^{3+} + 3 \text{ OH}^- \rightarrow Fe(OH)_3 \qquad\qquad (8.8)$$
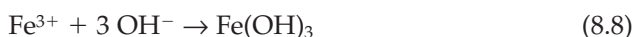
Therefore, sludge that is generated at the point of ferric application will include a mixture of ferric hydroxide and ferric phosphate generated according to eqs 8.6 and 8.8. Equation 8.8 also illustrates the consumption of alkalinity (pH reduction) encountered when applying ferric. These effects are discussed in more detail in Section 6.3.

4.3.2   Determination of Dose for Iron-Based Chemicals

An approximate dose of ferric salt required for the particular application can be determined based on calculations presented in this section, including eqs 8.10 and 8.11 presented in Section 4.3.3. Refinement of the chemical application rate can then be performed in full scale based on the results obtained because the system response is fairly quick (Section 5.6).

For comments on performing jar tests to determine chemical dose, refer to the beginning of Section 4.2.2 and to Section 4.6. A design dose curve for chemical phosphorus removal using ferric ions was developed using literature and pilot-facility data (Figure 8.3). Literature data include laboratory-scale test data and

Chemical P Removal Dose Curve
(Log scale for Residual P)
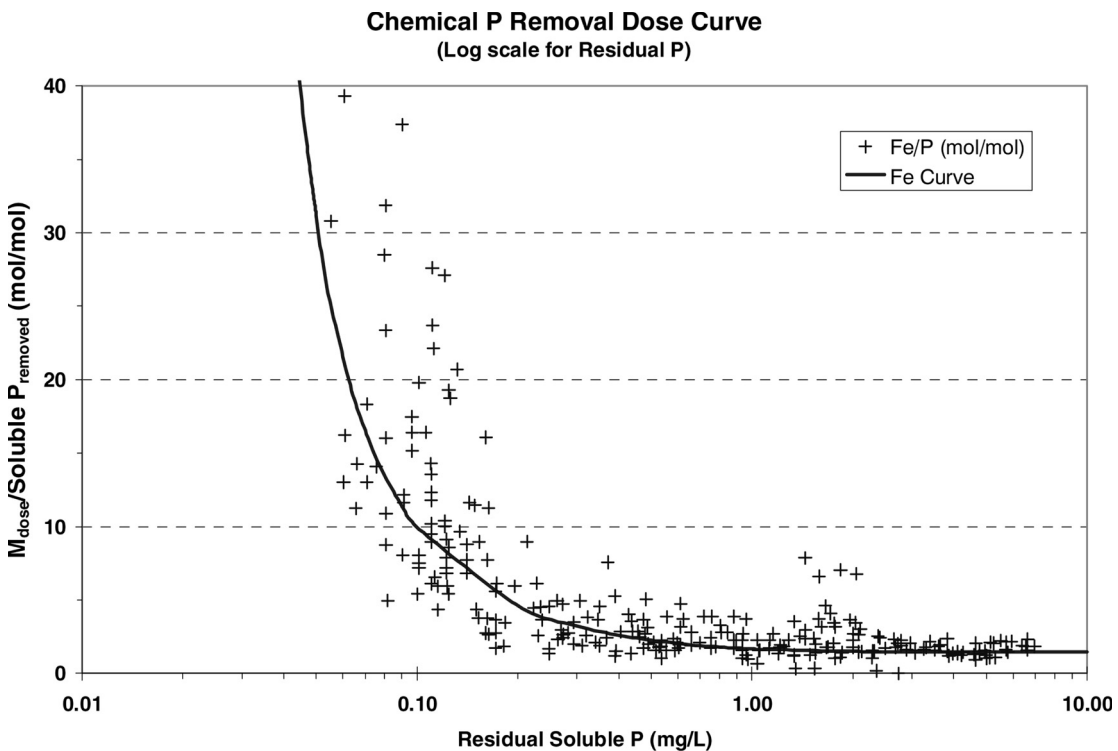
FIGURE 8.3 Ratio of iron (Fe^{3+}) dose to phosphorus removed as a function of residual soluble orthophosphate concentration (Luedecke et al. [1988], and data from the Blue Plains Wastewater Treatment Plant, Washington, D.C.).

data from sites that are operating with chemical phosphorus removal (Luedecke et al., 1988). The data set includes results for a range of pH values (mostly 6.5 to 7.5), temperatures, and wastewater characteristics. The effluent soluble phosphorus concentration is labeled "residual soluble P" on the logarithmic x-axis. The molar ratio for metal ion dose to soluble phosphorus removed is labeled "M_{dose}/ soluble $P_{removed}$ (mol/mol)" on the y-axis. It is important to note that the curves apply to the soluble portion of the phosphorus only. The curve used to fit the data is based on the following equation:

$$y = a/(1 + b \times e^{-cXe}) \tag{8.9}$$

Where

y = mole iron required per mole soluble phosphate removed,
a = 1.48,
b = −1.07,
c = 2.25, and
Xe = target effluent soluble phosphorus concentration at the chemical application point (mg/L).

In general, the data at lower residual soluble phosphorus concentrations are more scattered. Because of this variability, bench- or pilot-scale testing is recommended at each facility to determine the actual molar dose required to reach the targeted effluent soluble phosphorus concentration.

The molar dose for phosphorus precipitation is based on the desired final effluent soluble phosphorus concentration rather than the starting phosphorus concentration. For example, to meet a 0.5-mg/L soluble phosphorus concentration, a 2.7-mol ratio of ferric ion to phosphorus or a weight ratio of 4.1 g Fe^{3+}/g P is required. To remove 2.5 mg/L P (from 3 to 0.5 mg/L), an iron dose of 10.25 mg/L Fe^{3+} is required. It is important to determine if a value greater than the influent soluble phosphorus concentration should be used because of the potential for solubilization of the particulate phosphorus, which would increase the soluble phosphorus concentration above measured influent concentrations.

As noted previously, using dual application points may yield the optimum operating point with respect to chemical dose and sludge production. Using the same concentrations as those previously cited, if the phosphorus concentration were to be reduced to 1 mg/L in the primary clarifier, with additional iron added to the aeration basin to achieve a final effluent of 0.5 mg/L soluble phosphorus, less iron will be used in total. To achieve 1 mg/L of soluble phosphorus out of the primary clarifier requires a molar ratio of 1.67 to 1 or a weight ratio of 3 g Fe^{3+}/g P. Therefore, to remove 2 mg/L of phosphorus across the primary clarifier, an iron dose of 6 mg/L is required. To remove the remaining 0.5 mg/L of soluble phosphorus across the secondary treatment system requires a molar ratio of 2.27 to 1 or a weight ratio of 4.1 g Fe^{3+}/g P, which equates to an iron dose of 2.05 mg/L Fe^{3+}. The total iron dose to meet a residential soluble phosphorus concentration of 0.5 mg/L is, therefore, 6 + 2.05 = 8.05 mg/L Fe^{3+} as opposed to 10.25 mg/L Fe^{3+} if all of the phosphorus is removed at one time. There is a 20% savings in chemical use and a reduction in the overall chemical sludge production. It should be noted that this example has neither taken any credit for phosphorus that would be removed biologically across the secondary treatment system nor has it accounted for potential solubilization of particulate phosphorus. Actual dosages must be fine tuned in the field to account for these issues. A similar relationship exists when aluminum is used for phosphorus precipitation.

A sample calculation is provided in this section to determine the ferric chloride dose required to precipitate soluble phosphorus. Following the detailed, step-by-step derivation, simplified formulas for both International System of Units and U.S. customary units are provided. The following conditions are assumed:

- Influent facility flowrate is 37 850 m^3/d (10 mgd),
- Soluble phosphorus influent concentration to the facility is 3.0 mg/L, and
- A residual primary effluent phosphorus concentration of 1 mg/L is required.

The amount of soluble phosphorus to be removed in kilograms per day (pounds per day) is as follows:

$$\text{Phosphorus} = (3 - 1 \text{ mg/L}) \times 37\,850 \text{ m}^3/\text{d} \times 1000 \text{ L/m}^3 \times$$
$$1 \text{ kg}/1\,000\,000 \text{ mg} = 75.7 \text{ kg/d}$$

or

$$(3 - 1) \text{ mg/L} \times 10 \text{ mgd} \times 8.34 \text{ (lb/mg} \times \text{L/mg)} =$$
$$167 \text{ lb/d of soluble phosphorus to be removed.}$$

This is equivalent to (75.7 kg/d)/(31 kg/kg-mol P) = 2.44 kg-mol P or (167 lb/d)/(31 lb/lb-mol P) = 5.38 lb-mol of P to be removed.

The amount of ferric ions required can be calculated from eq 8.9 as follows:

$$y = 1.48/(1 - 1.07e^{(-2.25)(1)}) = 1.67 \text{ kg-mol Fe/kg-mol}$$
$$\text{(or 1.67 lb-mol Fe/lb mol) of soluble phosphorus removed.}$$

Consequently, the amount of ferric ions required per day is

$$2.44 \text{ kg-mol P} \times 1.67 \text{ kg-mol Fe/kg-mol P} = 4.07 \text{ kg-mol Fe}$$
$$\text{or 5.38 lb-mol P} \times 1.67 \text{ lb-mol Fe/lb-mol P} = 8.99 \text{ lb-mol Fe.}$$

The molecular weight of the Fe ion is 56, which can be converted to mass of ferric ions per day, as follows:

$$4.07 \text{ kg-mol Fe} \times 56 \text{ kg Fe/kg-mol Fe} = 228 \text{ kg}$$
$$\text{or 8.99 lb-mol Fe} \times 56 \text{ lb Fe/lb-mol Fe} = 503 \text{ lb/d of ferric ions.}$$

As indicated in Table 8.2, dry ferric chloride contains 34.5 % ferric. Consequently, the amount of dry ferric required for this application will be

$$228 \text{ kg Fe}/0.345 = 661 \text{ kg, or 503 lb Fe}/0.345 =$$
$$1459 \text{ lb/d of dry ferric chloride.}$$

If 37% ferric chloride solution is used, it contains 0.173 kg/L of ferric ions (Table 8.2). Thus, the amount of ferric solution required for this application will be

$$228 \text{ kg Fe}/0.173 \text{ kg/L} = 1318 \text{ L}$$
$$\text{or 503 lb Fe}/1.44 = 349 \text{ gpd of solution.}$$

The 37% ferric chloride solution required per day to reduce the soluble phosphorus from 3.0 to 1.0 mg/L in the aforementioned example is 1318 L/d

(349 gpd). The ferric dose equivalent to this ferric chloride use rate can be calculated from the factor listed in Table 8.2 of 0.504 kg/L (4.2 lb/gal) of ferric chloride in 37% solution, as follows:

$$1318 \text{ L/d} \times 0.504 \text{ kg/L/37 850 m}^3/\text{d} = 0.0176 \text{ kg/m}^3$$
$$0.0175 \text{ kg/m}^3 \times 1\ 000\ 000 \text{ mg/kg/1000 L/m}^3 = 17.6 \text{ mg/L}$$

In U.S. customary units, calculation for this 10-mgd facility will be as follows:

$$349 \text{ gpd} \times 4.2 \text{ lb/gal/8.34 (lb/mg} \times \text{L/mgd)/10 mgd} = 17.6 \text{ mg/L}$$

4.3.3   Summary Dose Formulas for Ferric Chloride

The aforementioned calculations can be abbreviated to the following overall formula for calculation of the application rate of 37% ferric chloride solution in International System of Units:

$$A = (0.0155)(Xi - Xe)(Q)/[1 - 1.07 \times \exp(-2.25 \times Xe)] \qquad (8.10)$$

Where
   A = 37% ferric chloride solution application rate (L/d),
   Xi = soluble phosphorus concentration at the application point (mg/L),
   Xe = target effluent soluble phosphorus concentration (mg/L), and
   Q = facility flow (m³/d).

In U.S. customary units, the formula is as follows:

$$A = (15.5)(Xi - Xe)(Q)/[1 - 1.07 \times \exp(-2.25 \times Xe)] \qquad (8.11)$$

Where
   A = 37% ferric solution application rate (gpd),
   Xi = soluble phosphorus concentration at the application point (mg/L),
   Xe = target effluent soluble phosphorus concentration (mg/L), and
   Q = facility flow (mgd).

It should be recognized that the aforementioned dose calculations are approximate. Many site-specific factors such as mixing conditions (Section 5.3), application point (Section 5.4), wastewater chemistry, and temperature, discussed in more detail later in this chapter, will affect the actual dose of chemical required to accomplish treatment objectives. This is particularly true at low residual soluble phosphorus concentrations (below 0.1 mg/L).

The aforementioned calculations were based on a single application point; however, the optimum operating mode may involve dual application points (i.e., chemical addition to the primary clarifiers and to the secondary treatment process), which could result in savings in chemical consumption and cost (Section 5.4).

4.3.4   *Other Considerations for Iron-Based Chemicals*

As with aluminum-based compounds, there will be a significant amount of sludge produced when iron salts are added to the process to remove phosphorus. The quantity of sludge and handling considerations are discussed in Sections 6.1 and 6.2, respectively. Alkalinity and pH effects of ferric salts are discussed in Section 6.3. Metal salts will also increase TDS in the system. These effects are discussed in more detail in Section 6.4. A potentially significant drawback of using ferric is its potential effect on UV disinfection, as discussed in Section 6.7. Tank and pipe material, pump type, and safety considerations are all similar to the aluminum-based options discussed in Section 4.2.4.

4.4   Lime

Lime has historically been used to increase alkalinity, remove phosphorus, and improve removal efficiencies across primary clarifiers. More recently, use of lime at water resource recovery facilities for phosphorus removal has become less common, presumably because of lime-handling difficulties and the availability of more effective chemicals.

Because high pH (>10) is needed for phosphorus precipitation with lime, lime addition for the purpose of phosphorus removal is not compatible with biological treatment as the required pH is too high for microorganisms. However, lime-treated primary effluent may potentially be accepted by the subsequent biological treatment step without neutralization (or with minimal neutralization) because carbon dioxide generated during aerobic treatment will lower the pH. Nitrification, if practiced, could consume alkalinity (i.e., lower the pH) as well.

In addition to the aforementioned use in primary clarifiers, lime addition for phosphorus removal may potentially be used in sidestream treatment (such as in the Phostrip process) or as a post-treatment step with a subsequent pH adjustment. However, use of lime for phosphorus removal is rare. The residual phosphorus concentration typically achieved with lime treatment is approximately 1 mg/L. The dose of lime required for phosphorus removal is typically governed by the alkalinity of the wastewater because lime will first react with bicarbonate before precipitating as hydroxyapatite. That dose is approximately 1.5 times that of total alkalinity in milligrams per liter as $CaCO_3$ (Sedlak, 1991). The hydroxyapatite has a variable composition; however, an approximate equation for its formation can be written as follows, assuming, in this instance, that the phosphate present is the hydrogen phosphate ion (HPO_4^{2-}):

$$3\ HPO_4^{2-} + 5\ Ca^{2+} + 4\ OH^- \rightarrow Ca_5\ (OH)(PO_4)_3 + 3\ H_2O \qquad (8.12)$$

Use of lime for phosphorus removal results in generation of inert solids, the quantity of which is governed mainly by wastewater alkalinity. The following two issues should also be considered when lime is added to the treatment

process: (1) relatively high calcium concentrations in the process water can inhibit VSS destruction in digesters and (2) high calcium content in the final sludge may not be advantageous to certain soils if the sludge is ultimately used for soil amendments.

Lime is either gravity fed or pumped to the point of application. Materials of construction for lime systems are carbon steel or PVC. Personnel should wear PPE when handling chemicals; the PPE should include, but not be limited to, gloves, respirators, goggles, aprons, and face shields and should be worn when working or handling chemical solids or slurries.

4.5   Magnesium Hydroxide

Another alternative chemical available to precipitate phosphorus is magnesium hydroxide, although its use in the main liquid train is presently limited because of its high cost. Magnesium hydroxide raises the pH to precipitate phosphorus and, therefore, yields similar results as lime addition, although chemical handling issues are not as significant as those for lime.

In anaerobic digesters, magnesium in the presence of ammonia and orthophosphate promotes formation of magnesium ammonium phosphate (struvite), which is known to cause severe clogging of digester piping. Magnesium addition is used in dedicated treatment processes recently developed for removal and recovery of phosphorus and ammonia from sludge recycle streams (e.g., the Pearl® process by Ostara). This is discussed in more detail in Chapter 12.

Magnesium hydroxide is received in liquid form and can be used similar to ferric or aluminum addition. Tank materials are typically constructed of fiberglass reinforced plastic (FRP) or polyethylene. Piping, valves, and fittings are typically constructed of PVC or other compatible plastic material.

4.6   Proprietary Formulations

A number of proprietary formulations for phosphorus removal have been marketed in recent years. While the exact composition of these products is typically not known, they are likely based on a combination of some of the chemicals previously discussed in this chapter. The products variously claim to be easier to handle, generate less sludge, be less sensitive to lower wastewater temperatures, and/or have a lesser effect on facility pH. While claims of lower sludge generation should be treated with skepticism, the other claims may be valid. This is attributable to the fact that these formulations typically contain some form of neutralizing alkali agent, which increases pH and alkalinity and makes the chemicals less corrosive, as in the case of sodium aluminate and PACl discussed earlier in this chapter.

However, this convenience typically comes at a higher chemical cost. The recommended method of evaluating the expected benefits of using alternative chemicals is to determine the dose of each chemical needed to achieve the required

phosphorus removal in side-by-side jar tests. Such jar tests should include evaluation of the required dose of a neutralizing agent. The dose requirements established in the comparative jar tests can then be combined with unit costs of alternative chemicals to determine overall application costs. Only then can the relative costs of using different chemicals be compared to other factors, such as ease of handling and need for any additional neutralizing chemicals, and an informed decision be made. For small facilities, use of specialized or proprietary formulations may sometimes be justified; however, at larger facilities, chemical costs will likely be an overriding consideration.

4.7   Water Treatment Sludge

Water treatment residuals typically contain a large fraction of aluminum or ferric salts, which may have residual capacity to bound and adsorb phosphorus. Such sludges can be used as cost-effective materials to reduce soluble phosphorus in wastewater. Although fresh alum was found to be more efficient at phosphorus removal than spent alum sludge (Georgantas et al., 2006), alum sludge may be a reasonable substitute for alum because of its low cost and high availability. It should also be noted that the efficiency of alum sludge to remove phosphorus decreases through aging. More than 90% phosphorus removal from wastewater has been observed at sufficiently high spent-water-treatment sludge application doses (Asada et al., 2010; Ippolito et al., 2011; Mortula and Gagnon, 2007). Naturally, use of spent water treatment facility sludge for wastewater treatment transfers the burden of water treatment residual handling to the wastewater facility and could result in a large increase of waste sludge generated at the facility.

4.8   Role of Polymers

Organic polymers do not remove or precipitate soluble phosphorus on their own to any significant extent. However, their use can significantly improve the solids separation process by coagulating colloids and increasing the size and compactness of the chemical and biological solids, thus increasing their settling velocity.

Use of metal salts for phosphorus removal can create, at least initially, fine precipitate (floc) or even colloids. Flocculation and settling of such particulates can be greatly improved by the application of a polymer. The use of polymer can be particularly effective when low-effluent phosphorus levels are required. In some high-rate applications used for phosphorus removal, such as several patented sand-ballasted flocculation and sedimentation processes, the use of polymer at a proper dose is critical to process performance.

When used, the polymer addition point should be as far downstream from the point of addition of the metal salts as practical and should be located in a place where adequate mixing is available or can be created. In many typical configurations of the activated sludge process, metal salts are added at the outlet of the aeration basin, with polymer addition at the final clarifier splitter box.

Adequate mixing, which is critical to polymer effectiveness, can be provided by simple air agitation.

When added to mixed liquor, the polymer dose required is typically in the range of 0.5 to 1 mg/L for dry polymers, which typically have approximately 90% active content. For emulsion polymers, with only 30 to 40% active content, the required dose will be about 2.5 to 3 times higher (as expressed in the weight of the emulsion, as supplied).

It should be noted that, at some activated sludge facilities, polymer addition is continually added to final clarifiers to improve their performance. Other facilities use polymer addition to final clarifiers in a standby mode during storm flows.

When metal salts are added to the primary clarifier (CEPT), polymer addition can significantly increase phosphorus, TSS, and particulate biochemical oxygen demand (BOD) removal compared to that obtained by coagulant alone. The optimal polymer dose in CEPT treatment, or when applied in a tertiary phosphorus removal process, will typically be lower for a mixed liquor application than mentioned previously.

Typical polymer systems require stainless steel or FRP storage or aging tanks. Polyvinyl chloride piping, valves, and fittings are typically used for polymer service. Because polymers are sensitive to shear and have higher viscosity than most metal salts, progressive cavity pumps are often recommended for polymer service.

Polymer does not have the chemical handling issues associated with most other chemicals. Generally, slips and falls are the most common hazard when handling a polymer solution. Care should be taken when changing the type of the polymer from anionic to cationic based (or vice versa) because a thorough cleaning of polymer storing and handling equipment with solvents may be needed to prevent formation of scale-type deposits.

5.0   PROCESS CONSIDERATIONS

5.1   Limits of Technology

The minimum achievable effluent phosphorus concentration depends on a number of factors, including efficiency of the solids separation process, as discussed in Section 3.3. In general, soluble orthophosphate concentrations in wastewater can be reduced to below 0.01 mg/L with a sufficiently high chemical dose (Smith et al., 2008; U.S. EPA, 2007). Dual-step filtration processes are particularly suited to achieving low concentrations because they provide extended contact time for precipitation, coagulation, and separation of fine particulates initially generated after chemical addition. Microfiltration or ultrafiltration (e.g., in an MBR) while achieving a reliable separation of suspended matter may not be as effective in lowering soluble orthophosphate concentration to the limits of solubility because contact time in the filtration step is limited (WEF, 2010). In some effluents, a

measurable concentration (as much as 0.05 mg/L) of non-reactive rDOP may be present (refer to Chapter 11).

In practice, taking into account process and wastewater chemistry variability, the potential presence of measurable rDOP, the effect of any residual particulate phosphorus, and any imperfections in the solids separation step, a monthly average effluent total phosphorus concentration below 0.05 mg/L is generally achievable at a well-designed and operated full-scale facility. In a survey of advanced treatment facilities (U.S. EPA, 2007), the range of monthly average phosphorus concentrations for facilities having a phosphorus limit of 0.1 mg/L or less typically was approximately 0.03 to 0.09 mg/L.

It should be noted that analyzing residual phosphorus at low levels by the standard colorimetrical method is uncertain. Concentration readings from a spectrophotometer calibration curve should be verified manually (as opposed to relying on a regression equation), with calibration data developed at the low end of the concentration range.

5.2   Effect of pH

The minimum solubility of ferric and aluminum orthophosphates in wastewater is in the acidic pH range of 3 to 5 (WEF, 2010), with the exact optimum pH likely being site specific depending on a number of factors, including wastewater chemistry. At pH greater than 7, the residual dissolved orthophosphate concentration starts to increase for the same chemical dose applied. Considering that most facilities must maintain their effluent pH above 6, the optimal pH for minimizing residual soluble phosphorus concentration will be approximately 6.5 to maintain a safety margin. However, maintaining a particular target pH may not be practical or necessary because low effluent phosphorus concentrations were achieved at facilities operating at a pH as high as 7.5 (Takacs et al., 2006).

The target pH of the precipitation reaction, as discussed in this section, should be measured at the point of the precipitate formation, that is, downstream of the chemical application point or at the solids separation point (clarifier effluent). The final effluent pH or aeration basin pH could be somewhat different.

An important consideration is that some commonly used chemicals, including alum and all iron salts, are acidic and will lower the wastewater pH to a degree depending on the alkalinity of the wastewater and the dose of chemical. For larger chemical doses and/or for wastewater with low alkalinity, use of neutralizing agents such as caustic may be necessary. In some instances, use of ferric or alum may actually lower the pH of the wastewater to around 6.5, at which point use of chemicals for phosphorus removal is likely to be optimal.

5.3   Effect of Mixing and Contact Time

Orthophosphate removal with metal salts significantly improves if vigorous mixing at the point of chemical addition is provided. The benefits of mixing seem

to be greater at a higher pH and are more pronounced for alum than for ferric (Sagberg et al., 2006; Szabo et al., 2008). Extending the contact time between the precipitated matter and wastewater allows for additional adsorption of soluble orthophosphates and increases the removal efficiency. Consequently, the recommended chemical addition location should be at a turbulent point as far upstream from the solids separation point (i.e., clarifier or filter) as practical. A convenient location for coagulant addition to an activated sludge train is to a turbulent area at the tail end of the aeration basin (e.g., effluent weir).

When chemical addition to the primary clarifier is contemplated, a suitable addition point may be a turbulent location at a preliminary treatment facility, such as at the screens, or to grit tanks (if available), with conveyance and flow distribution structures upstream of the primary clarifiers providing a good flocculating environment. Vigorous mixing desired at the point of chemical addition could also be enhanced by an additional mixing device, such as an air sparger.

5.4   Points of Addition

Metal salts addition points should be upstream of solids separation steps such as clarification of filtration. Figure 8.4 depicts typical available options. The use of chemicals is most efficient at a tertiary application point, where most primary or biological solids or other constituents that can bind with metal salts are already removed. However, most existing facilities are not equipped with a suitable tertiary treatment process.

Chemicals can be added in front of conventional sand filters; however, this decreases the filter run time (the higher the dose, the shorter the filter run) and the acceptable chemical dose in such an application can be too small for adequate phosphorus removal. In such instances, split-point addition may be most
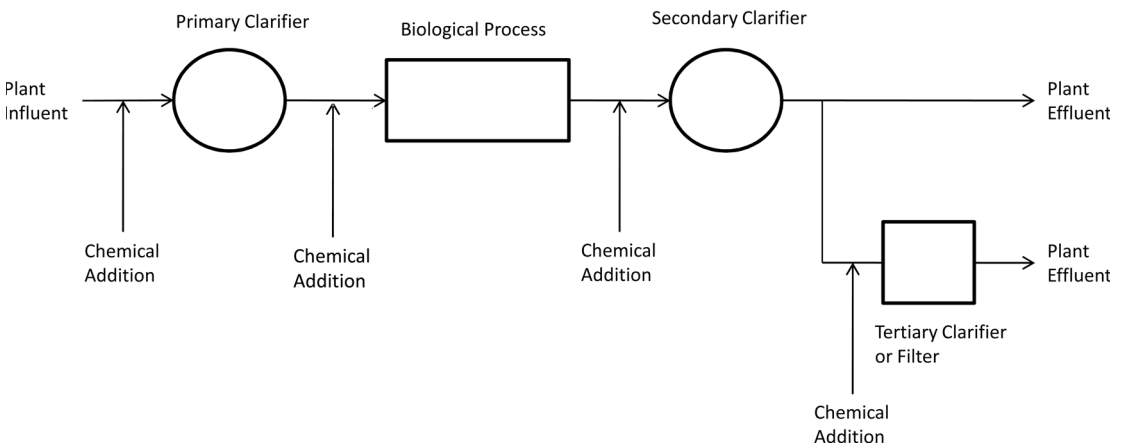

FIGURE 8.4   Chemical phosphorus removal dosing locations.

effective, with part of the chemical going to secondary clarifier influent (aeration basin effluent) and part going to secondary clarifier effluent (filter influent).

At conventional activated sludge facilities, and particularly at smaller, extended aeration facilities, common practice is to add chemicals to a turbulent location in front of final clarifiers such as the effluent weir of the aeration basin or to a clarifier's distribution box.

Application of chemicals for phosphorus removal to the primary clarifier (CEPT) is effective, particularly when biological processes could benefit from lower loading of organics, nitrogen, and TSS. Such practice also minimizes the inert fraction of the mixed liquor and, in case of ferric addition, minimizes the potential effects of chemicals on UV disinfection. Selection of the chemical application point at existing facilities may be limited by the need for good mixing previously discussed, which may not be easy to achieve at all potential locations.

A potentially significant reduction in chemical use could be accomplished by multipoint (or split-point) chemical addition. A commensurable reduction in waste sludge generation and the need for neutralizing chemicals and other process effects can also be realized. Multipoint addition is typically achieved by splitting chemical addition between primary clarifier and aeration basin effluent or between aeration basin effluent and final clarifier effluent (i.e., filter influent).

When phosphorus is removed by chemical addition to tertiary facilities (tertiary clarifiers and/or polishing filters), recycling the resulting chemical sludge to the primary treatment process should be considered, if feasible. Such practice will facilitate use of the residual phosphate bonding capacity of tertiary sludge and could substantially reduce the overall use of chemicals (Takacs et al., 2006).

5.5   Chemical Feed Control

Many smaller and medium-size facilities adding chemicals to the aeration basin operate at a constant chemical flowrate that is manually adjusted periodically, as needed. Diurnal variations in influent phosphorus loading are partially absorbed by large quantities of partially active chemical precipitate present in the aeration basin. Such facilities add chemicals in excess of what is required to meet the permit limit.

Because of the increasing availability and reliability of online probes measuring residual orthophosphate, real-time dose control is becoming feasible and cost effective, even at smaller facilities. A less efficient but simpler option would be to flow-pace the chemical addition with periodic adjustment of the feed ratio based on observed results. Implementation of phosphorus removal process monitoring and dose control is recommended because it lowers chemical costs and mitigates other negative aspects of chemical addition. Chapter 14 provides more details on online analyzers and dose control.

5.6   Response Time and Startup of Chemical Addition

Phosphorus removal by chemical addition can be initiated on demand without the prolonged acclimation period required for some biological processes, such as EBPR. This is typically the case for chemical processes. Some dedicated tertiary processes with a minimal hydraulic retention time (HRT) can lower the effluent phosphorus concentration within minutes of startup. For more conventional applications, the response is more measured and predictable because it depends on HRT in downstream treatment facilities.

Figure 8.5 illustrates results from a test performed at an oxidation-ditch facility without primary clarifiers or tertiary filters (Patoczka, 2008). The alum dose required for achieving the desired effluent total phosphorus level (below 0.5 mg/L) was determined before initiating the test; however, no chemical was added for more than 3 weeks before initiation of the test. As Figure 8.5 shows, the clarifier effluent total phosphorus, originally at 3.7 mg/L, started to decrease almost immediately upon activation of alum addition and dropped below 1 mg/L within 24 hours. In 3 days, the concentration stabilized at 0.35 mg/L.

The delay in system response to initiation of chemical addition to activated sludge is likely attributable to a combination of the followings factors:

- Travel time between the chemical application point and the effluent sampling location. If a final clarifier is only present, this delay will be marginal.
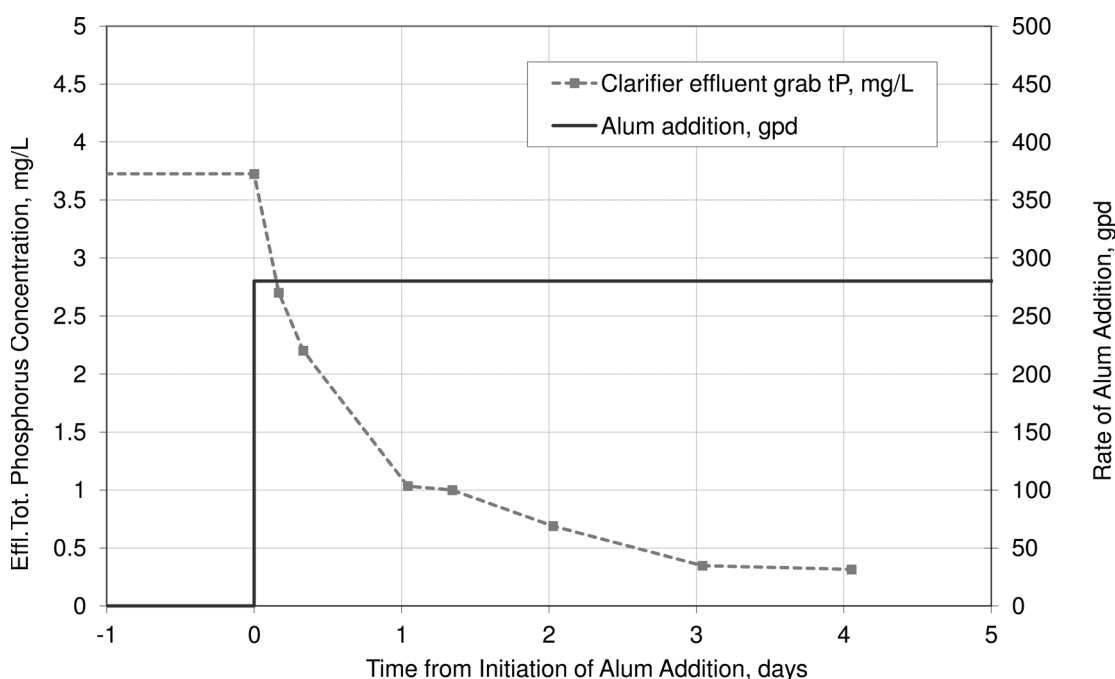

FIGURE 8.5   Response time to initiation of chemical addition.

Any tertiary facilities, chlorine contact tanks, and, particularly, a stabilization lagoon, will add delay commeasurable with HRT of these facilities;

- As discussed in Section 3.2, the excess, unused chemicals applied at the secondary clarifier influent will be returned with RAS to the aeration basin and will bind with phosphorus in the raw wastewater. The time required to reach an accumulation of these chemicals close to a saturation point (steady state) corresponds to several multiples (3 is a good number) of HRT. For an aeration basin with a nominal HRT of 1 day, the time to approach equilibrium conditions will thus be approximately 3 days;

- Metal salts are coagulating agents and will be partially used by biomass and colloids in the aeration basin for coagulation of mixed liquor flocs until a degree of saturation of the biomass inventory is achieved and the mixed liquor at the point of the chemical application is presaturated with chemicals and pre-coagulated; and

- Precipitates resulting from metal salt addition continue to adsorb orthophosphate for several hours or even days, delaying the time to achieve equilibrium.

6.0　EFFECT OF CHEMICAL ADDITION ON FACILITY OPERATIONS

6.1　Sludge Generation

The addition of chemicals for precipitation of phosphorus will generate additional inert chemical sludge at the point of addition, be it in a primary clarifier, activated sludge system, or tertiary application. The amount of additional sludge (on a dry-weight basis) generated by the addition of selected chemicals can be calculated based on the conversion factors provided in Table 8.3. For example, for a 3785-mL/d (1-mgd) facility adding 10 mg/L of alum, the expected additional sludge generation will be 4.11 mg/L, or 15.6 kg/d (33.9 lb/d), based on a 0.411-conversion factor. In many applications, particularly when levels of phosphorus below 1 mg/L are targeted with chemical addition, an excess of chemical over that required by the stoichiometric equation is needed. Because the excess chemical will precipitate in a different form, a different conversion factor will result, as indicated in Table 8.3. As discussed in Section 4.0, the stoichiometric amount of chemical for the removal of 1 mg/L of phosphorus is 9.6 mg/L for alum and 5.2 mg/L for ferric chloride (the chemical dose convention is noted in the footnote in Table 8.3).

Conversion factors listed in Table 8.3 are approximate because simplifying assumptions of precipitate composition were used in their derivation. The addition of coagulating chemicals will increase the capture of colloidal and particulate matter, which may further increase additional sludge generation.

This is particularly applicable when chemicals are added to primary clarifiers (CEPT), where enhanced removal of TSS and BOD will generate even more primary sludge. However, decreased TSS and organic loading to the secondary system will result in a lower waste biological sludge generation. Typical primary clarifier removal rates of 50% for TSS and 30% for BOD_5 may increase to 70 and 50%, respectively, or even more, particularly when polymer addition is also provided.

As discussed in Section 3.2, chemical precipitates accumulating in the aeration basins will result in an increase in the basin inert solids concentration. This effect should be considered when designing a biological treatment system. The equilibrium concentration of inert chemical residue resulting from chemical addition to the activated sludge system can be calculated as follows:

$$\text{MLSSci} = D \times F \times \text{SRT}/\text{HRT} \qquad (8.13)$$

Where

   MLSSci = concentration of chemical inerts in the mixed liquor arising from chemical addition, mg/L;

   D = chemical dose applied to the activated sludge process, mg/L (based on the nominal, forward flow of wastewater);

   F = TSS conversion factor for the chemical applied, as listed in Table 8.3;

   SRT = solids retention time, days; and

   HRT = hydraulic retention time, days.

The following conditions are assumed for the sample calculations described herein:

- Flowrate, 3785 m³/d (1 mgd);

- Aeration basin volume, 1892 m³ (500 000 gal);

- Sludge age of the process, 12 days; and

- Ferric (37% solution) application rate, 300 L/d (79.3 gpd).

The HRT of this activated sludge system is equal to the aeration basin volume divided by flow, that is, 1892 m³/3785 m³/d = 0.5 days (or 12 hours). The ferric solution application rate is equal to the ferric chloride dose of 40 mg/L (refer to Section 4.3.2 for a calculation example). With 3-mg/L phosphorus concentration in the influent, this represents a stoichiometric ratio of Fe to P of approximately 3 to 1 (again, refer to Sections 4.2.2 and 4.3.2 for exemplary calculations). From Table 8.3, the TSS increase conversion factor (F) for $FeCl_3$ applied at a 3-to-1 ratio is 0.748. Consequently, the inert MLSS concentration is

$$40 \text{ mg/L} \times 0.748 \times 12 \text{ d}/0.5 \text{ d} = 718 \text{ mg/L}$$

The MLSSci calculated from eq 8.13 only accounts for the component of the inert fraction of the mixed liquor resulting from chemical dosing in addition, and above, the typically expected inert MLSS fraction resulting from inert TSS present in the influent or generated during the treatment.

Equation 8.13 can also be used to calculate the amount of additional waste sludge generated by chemical addition. If the facility operated without ferric addition at 3000 mg/L MLSS, the equilibrium MLSS concentration with ferric addition will be 3718 mg/L for the conditions in the aforementioned example. This corresponds to a 24% (3718 mg/L ÷ 3000 mg/L) increase in the dry mass of waste activated sludge generation.

An even more straightforward way of calculating the additional mass of dry-waste inert chemical sludge that is generated is to multiply the chemical use rate expressed in kilograms per day (pounds per day) (see Tables 8.1 and 8.2 for chemical content of typical technical solutions) by the applicable TSS conversion factor from Table 8.3. For example, 49% alum solution has 0.647 kg/L (5.4 lb/gal) of alum (Table 8.1). If a facility is using 200 L/d (52.8 gpd) of the 49% solution, the mass of alum used is 200 L/d × 0.647 kg/L = 129 kg/d (285 lb/d). Assuming a typical application with a 3-to-1 stoichiometric rate, the appropriate TSS conversion factor from Table 8.3 is 0.312. Consequently, this alum addition will result in generation of 129 kg/d × 0.312 = 40.3 kg/d (88.7 lb/d) of inert alum sludge.

When using iron-based coagulants, the presence of iron in the waste sludge disposed of off-site may be beneficial for using the sludge as a soil amendment. Aluminum has no advantage as a soil amendment; therefore, if the final sludge is blended with soil, there may be additional concerns with aluminum content in the sludge.

6.2   Sludge Settling, Thickening, and Dewatering

In addition to increasing the waste solids generation rate on a dry-mass basis, the addition of chemicals such as aluminum and ferric salts will affect sludge settling and dewatering properties. When added to activated sludge, these flocculating chemicals will generally improve solids separation in the secondary clarifier because of the increased capture of fine floc and colloids. Alum and, in particular, iron-based chemicals will increase activated sludge specific density, thereby improving its settling properties (lowering the sludge volume index). This could significantly improve performance of secondary clarifiers, allowing operation at a lower sludge blanket and/or higher MLSS concentration. Ferrous, ferric, and aluminum-based chemicals could also help control activated sludge foaming and possibly inhibit filamentous bulking.

The effect of chemicals is more difficult to predict in sludge thickening and dewatering operations. On several occasions, the Woodland Plant in Morris Township, New Jersey, has initiated and stopped adding alum to remove total phosphorus to approximately 0.7 mg/L. Each time, the facility experienced a decrease

in dry solids concentration during gravity belt thickening from approximately 5.5 to 4.5% solids when chemical was being added. Another New Jersey facility, the East Windsor Municipal Utilities Authority, observed a decrease from 3.2 to 2.8% solids concentration from gravity thickeners when alum was used for phosphorus removal.

6.3   Alkalinity and pH

Addition of alum and, particularly, iron compounds will lower the pH of wastewater because these agents are acidic and alkalinity is consumed during precipitation reactions (Section 4.0). As discussed in Section 4.2, some alternative aluminum-based products such as sodium aluminate and PACl will not depress pH or consume alkalinity.

The extent of pH reduction mainly depends on the alkalinity of the wastewater; the higher the alkalinity, the lower the reduction in pH for a given chemical dosage. In some instances of low wastewater alkalinity, addition of an alkaline substance such as sodium hydroxide, soda ash, or lime may be required to maintain acceptable pH. If the facility also nitrifies, alkalinity consumption by phosphorus precipitation must be added to the nitrification alkalinity demand to evaluate the overall effect on the system.

Alum addition consumes alkalinity at a rate of 0.505 mg (as $CaCO_3$) per milligram of alum added, which corresponds to a need for 0.404 mg of caustic (NaOH). Thus, a 3.785-mL/d (1-mgd) facility that applies a 60-mg/L alum dose (227 kg/d or 500 lb/d alum application rate, corresponding to 351 L/d or 92.7 gpd of 49% alum solution, respectively) would require 91.7 kg/d (202 lb/d) of dry caustic to completely recover alkalinity loss induced by alum. This amount of dry caustic corresponds to 120 L/d (31.8 gpd) of 50% caustic solution.

Similarly, ferric chloride addition consumes alkalinity at a rate of 0.923 mg (as $CaCO_3$) per milligram of ferric chloride added, which corresponds to a need for 0.738 mg of caustic (NaOH). Thus, a 3.785-mL/d (1-mgd) facility that applies 30 mg/L of ferric chloride dose (114 kg/d or 250 lb/d dry ferric chloride application rate, corresponding to 226 L/d or 59.5 gpd of 27% ferric chloride solution, respectively) would require 84.1 kg/d (184 lb/d) of dry caustic to completely recover alkalinity loss induced by ferric chloride. This amount of dry caustic corresponds to 111 L/d (29 gpd) of 50% caustic solution.

It is important to note that complete neutralization may or may not be necessary or desired, depending on wastewater alkalinity, effluent pH requirements, and other process considerations such as maintenance of optimum pH for phosphorus precipitation (typically below pH 7) or optimum pH for nitrification (above 7). All technical iron solutions and, in particular, pickle liquor, contain substantial amounts of free sulfuric acid or hydrochloric acid, which will additionally consume alkalinity and suppress the pH of the wastewater, depending on the acid content. As the effectiveness of chemical phosphorus precipitation increases

with the lowering of pH (in the typical range of treatment facility operations), some depression of the pH by chemicals may be desirable, providing that the nitrification process is not affected and the effluent remains within the acceptable range of pH.

6.4   Total Dissolved Solids Increase

Addition of chemicals will, in most instances, result in an increase in TDS concentration. Total dissolved solids represents a parameter of growing regulatory concern in many regions. In many areas, regulators are enforcing water quality standards for TDS, which, for fresh waters, typically are 500 mg/L (e.g., New Jersey Water Quality Standards). Discharging high TDS can also be of concern in instances where reclaimed water is used for irrigation purposes or as a cooling water makeup.

However, in most typical applications, an increase in TDS because of chemical addition will be relatively modest. Table 8.3 provides TDS increase factors for selected chemicals. For example, the addition of a relatively high (100-mg/L) dose of alum, which could be sufficient in producing 0.1 mg/L of effluent total phosphorus concentration according to eq 8.2, will increase TDS by 53.3 mg/L based on a factor of 0.533 from Table 8.3 (assuming a 3-to-1 stoichiometric rate). In most situations where chemical addition is lower, TDS effects from using chemicals for phosphorus removal will be relatively small. Table 8.3 also provides TDS increase factors for some other chemicals and processes commonly used in wastewater treatment.

6.5   Biological Phosphorus Removal

While the EBPR process can sometimes be effective in producing low-effluent phosphorus, consistently meeting low-effluent limits could be impaired by periods of substandard performance or upsets. For these reasons, chemical addition is commonly practiced at EBPR facilities as a tertiary polishing step, a backup process, or, more commonly, in a form of simultaneous biological and chemical phosphorus removal by coagulant addition to the activated sludge train (Gebremariam et al., 2011; Neethling et al., 2005). Although metal salts addition to an EBPR process has been shown to improve the overall phosphorus removal efficiency, there are concerns that continuous dosing of coagulants to an activated sludge facility may lower efficiency of the phosphorus release and uptake cycle by competition or inhibition. As chemicals added to activated sludge remain in the system for a period commensurable with sludge age, the effect of a chemical added at a high dose during a period of inferior EBPR performance could linger for a considerable time, delaying recovery of the EBPR system.

Consequently, metals addition to the EBPR process should be practiced carefully, at the lowest necessary dose, with the point of addition being at the effluent from the aeration basin. Where possible, chemical addition to the EBPR activated

sludge train should be avoided and, if necessary, chemicals should be applied to the primary clarifier and/or to the tertiary process.

6.6   Anaerobic Digestion

Because of the low solubility of ferrous sulfide (FeS), ferric salt addition directly to anaerobic digesters has been used to control H_2S in the digester gas and for odor control. Lee et al. (2009), Novak and Park (2010), and Yuan and Bandosz (2007) suggested that the addition of iron salts for phosphorus removal in the liquid train will have a similar effect on digester gas quality. Aluminum-based salts are not expected to have this effect.

When metal salts are used in the liquid train for phosphorus removal or ferric is added directly to the digester for odor control, struvite (magnesium ammonium phosphate) formation in the anaerobic digesters is typically prevented. This is because most of the orthophosphate in the waste sludge is bound in a stable precipitate, making it unavailable for struvite formation. There are some reports (e.g., Chen et al. [2008]; Dentel and Gosset [1982], and Monteith and Atkinson [2001]) that at certain aluminum concentrations anaerobic digestion could become inhibited. However, this does not appear to be a problem at metal addition rates typically used for phosphorus control because no instances of full-scale anaerobic digestion inhibition were found at a number of facilities using alum for phosphorus removal.

In summary, when anaerobic digestion is part of the treatment process, the effect of chemicals added for phosphorus removal should be carefully considered. Ferric salts may be preferred over aluminum-based products in such applications, mainly because of their side benefit in odor control. However, under some conditions, ferric addition at a high dose could cause formation of iron scales in digester piping. Separation of biological and chemical sludges should be considered, if practical, to avoid increased inert load to the digester. Additionally, when phosphorus is bound with aluminum or ferric in the waste (and digested) sludge, it becomes largely unavailable as fertilizer, potentially diminishing the value of biosolids derived from sludge. It is important to note that magnesium ammonium phosphate (struvite) is more soluble than aluminum or ferric sulfates. Consequently, this compound recovered from sidestreams by processes such as Pearl (see Chapter 12) may be more suitable as a long-release fertilizer.

6.7   Ultraviolet Disinfection

Effectiveness of UV disinfection is dependent on the delivered UV dose, contact time, liquid film thickness, wastewater absorbance, wastewater turbidity, wastewater chemistry (including hardness, alkalinity, pH, and oxidation–reduction potential), system configuration, and temperature. Fouling of UV lamp sleeves decreases the effective UV dose reaching the wastewater and is the main cause of decreased UV-system disinfection efficiency.

Lu et al. (2012) observed that iron salts have a greater negative effect on UV transmittance in wastewater than other coagulants. The presence of iron in UV-system influent has been documented to be a significant factor in the overall decrease of the disinfection efficacy through the following mechanisms:

- Dissolved iron molecules can absorb UV radiation in critical wavelengths, preventing UV light from reaching target organisms. This may include cationic free iron or iron complexes adsorbed into the residual suspended solids and bacteria flocs (Kozak et al., 2011);

- Iron precipitates can add to the resulting suspended solids of a treated effluent, thereby causing enhanced shielding effects, blocking the transmittance of UV light. Ultraviolet radiation is believed to promote precipitation processes of residual dissolved iron as $Fe(OH)_3$ and other compounds (Kozak et al., 2011; Nessim and Gehr, 2006); and

- Residual iron, particularly at concentrations in excess of 0.5 mg/L, has been found to be the main constituent associated with fouling of UV lamps, although the presence of calcium, magnesium, phosphorus, and organic matter is also important for scale formation. Formation and deposition of precipitates on the lamp's quartz sleeves is promoted by the lamp's high temperature. The precipitate, in addition to ferric salts, could include $CaCO_3$, $CaSO_4$, $MgCO_3$, $MgSO_4$, $Al(OH)_3$, and $Al_2(SO_4)_3$ (Black and Veatch, 2010; Kozak et al., 2011; Nessim and Gehr, 2006; Peng et al., 2005; Sehnaoui and Gehr, 2001; Sheriff and Gehr, 2001).

Operation of the UV system could also be affected by fouling of UV light sensors, causing an unnecessary increase in power to compensate for the errant light-intensity measurements.

With increasing iron concentrations above 0.5 mg/L, particularly in the presence of other scale-forming constituents, scaling may be quite rapid, resulting in decreased effectiveness of UV disinfection in a matter of days or even hours, depending on the concentration of iron and other constituents (Sheriff and Gehr, 2001). It is important to note that the presence of residual ferric at such elevated concentrations is not typical (and not necessary) and the ferric application rate should be reduced. Chemical and mechanical cleaning of the sleeves could cause permanent fouling because of the scratches that trap foulants (Peng et al., 2005). On the other hand, addition of coagulants and/or polymer to the upstream treatment processes could significantly reduce the concentration of dispersed solids and colloidal matter in the UV influent, thus reducing turbidity and improving disinfection performance.

6.8   Potential Phosphorus Deficiency

It is well established that activated sludge bacteria need both nitrogen and phosphorus (sometimes called *macronutrients*) in addition to other microconstituents.

These are typically available in adequate concentrations in municipal wastewater. An aggressive phosphorus removal approach using chemical addition ahead of the biological process, like CEPT, could result in inadequate phosphorus supply for the bacteria.

As discussed in Section 3.3, a conventional activated sludge biomass has a phosphorus content of about 2% (and much more if EBPR is practiced). As a first approximation, a general rule can be used that for each 100 mg/L of BOD_5 consumed by the biological process, 1 mg/L of phosphorus will be needed for biological growth (in addition to 5 mg/L of nitrogen). Consequently, to avoid phosphorus deficiency in the downstream biological treatment process, effluent from a primary clarifier with 50 mg/L of BOD_5 should have residual phosphorus of no less than 0.5 mg/L in soluble orthophosphate form because other forms of phosphorus may not be bioavailable.

Another treatment process that could experience phosphorus deficiency is a separate-stage tertiary denitrification process at facilities required to also meet a tight effluent phosphorus limit. Some facilities, particularly in the Chesapeake Bay watershed, are required to simultaneously meet total nitrogen limits of 3 mg/L and total phosphorus limits as low as 0.18 mg/L. To ensure that denitrifying bacteria have an adequate supply of phosphorus, deBarbadillo et al. (2006) recommended maintaining an orthophosphorus-P (i.e., expressed as phosphorus to NO_x-N (i.e., nitrates and nitrites expressed as nitrogen) ratio of 0.02 or more.

6.9   Safety and Operational Considerations

All chemicals, whether they are a gas, solid, or liquid, require a feeding system to accurately and repeatedly control the amount applied. Effective use of chemicals depends on accurate dosages and proper mixing. The effectiveness of certain chemicals is more sensitive to dosage rates and mixing than that of others. Design of a chemical feed system must consider the physical and chemical characteristics of each chemical used for feeding; minimum and maximum ambient or room temperatures; minimum, average, and maximum wastewater flows; minimum average and maximum anticipated dosages required; and the reliability of feeding devices.

Operators and maintenance personnel should be aware of the hazards and characteristics of the chemicals that are used at a facility. Material safety data sheets and technical specifications provided by suppliers are a good source of this information. Additional resources for design and operation of chemical feed systems are cited in the Suggested Readings section of this Chapter.

7.0   REFERENCES

Asada, L. N.; Sundefeld, G. C., Jr.; Alvarez, C. R.; Filho, S. S.; Piveli, R. P. (2010) Water Treatment Plant Sludge Discharge to Wastewater Treatment Works:

Effects on the Operation of Upflow Anaerobic sludge Blanket Reactor and Activated Sludge Systems. *Water Environ. Res.*, **82** (5), 392–400.

deBarbadillo, C.; Rectanus, R.; Canham, R.; Schauer, P. (2006) Tertiary Denitrification and Very Low Phosphorus Limits: A Practical Look at Phosphorus Limitations on Denitrification Filters. *Proceedings of the 79th Annual Water Environment Federation Technical Exhibition and Conference* [CD-ROM], Dallas, Texas, Oct 21–25; Water Environment Federation: Alexandria, Virginia.

Black and Veatch Corporation (2010) *White's Handbook of Chlorination and Alternative Disinfectants,* 5th ed.; Wiley & Sons: Hoboken, New Jersey.

Chen, Y.; Cheng, J. J.; Creamer, K. S. (2008) Inhibition of Anaerobic Digestion Process: A Review. *Bioresour. Technol.*, **99** (10), 4044–4064.

Dentel, S. K.; Gosset, J. M. (1982) Effect of Chemical Coagulation on Anaerobic Digestibility of Organic Materials. *Water Res.*, **16** (5), 707–718.

Gates, D. D.; Luedecke, C.; Hermanowicz, S. W.; Jenkins, D. (1990) Mechanisms of Chemical Phosphorus Removal in Activated Sludge with Al(III) and Fe(III). *Proceedings of the 1990 Specialty Conference on Environmental Engineering*; American Society of Civil Engineers; Reston, Virginia; p 322.

Gebremariam, S. Y.; Beutel, M. W.; Christian, D.; Hess, T. F. (2011) Research Advances and Challenges in the Microbiology of Enhanced Biological Phosphorus Removal—A Critical Review. *Water Environ. Res.*, **83** (3), 195–219.

Georgantas, D. A.; Matsis, V. M.; Grigoropoulou, H. P. (2006) Soluble Phosphorus Removal Through Adsorption on Spent Alum Sludge. *Environ. Technol.*, **27** (10), 1081–1088.

Ippolito, J. A.; Barbarick, K. A.; Elliot, H. A. (2011) Drinking Water Treatment Residuals: A Review of Recent Uses. *J. Environ. Qual.*, **40** (1), 1–12.

Kozak, J. A.; Lordi, D. T.; Abedin, Z.; O'Connor, C.; Granato, T.; Kollias, L. (2011) The Effect of Ferric Chloride Addition for Phosphorus Removal on Ultraviolet Radiation Disinfection of Wastewater. *Environ. Practice*, **12** (4), 275–284.

Lee, Y.; Baker, S.; Wang L.; Gibson, D.; Amos, J.; Zaleski, A. (2009) Operational Impact of Phosphorus Removal Using Ferric Chloride on Anaerobic Digesters and Dewatering. *Proceedings of the Water Environment Federation Nutrient Removal Specialty Conference*; Washington, D.C., June 28–July 1; Water Environment Federation: Alexandria, Virginia; pp 7411–7418.

Luedecke, C.; Hermanowicz, S. W.; Jenkins, D. (1988) Precipitation of Ferric Phosphate in Activated Sludge: A Chemical Model and its Verification. *Water Sci. Technol.*, **21**, 325–338.

Lu, G.; Li, C.; Zheng, Y.; Deng, A. (2012) Effect of Different Coagulants on The Ultraviolet Light Intensity Attenuation. *Desalination Water Treat.*, **37** (1–3), 302–307.

Monteith, H.; Atkinson, D. (2001) By The Numbers: Process Data Review Reveals the Causes of Digester Inhibition. *Proceedings of the 74th Annual Water Environment Federation Technical Exhibition and Conference* [CD-ROM]; Atlanta, Georgia, Oct 13–17; Water Environment Federation: Alexandria, Virginia; pp 389–400.

Mortula, M. M.; Gagnon, G. A. (2007) Phosphorus Treatment of Secondary Municipal Effluent Using Oven-Dried Alum Residual. *J. Environ. Sci. Health.,* **42**, 1685–1691.

Neethling, J. B.; Bakke, B.; Benish, M.; Gu, A.; Stephens, H.; Stensel, H. D.; Moore, R. (2005) *Factors Influencing the Reliability of Enhanced Biological Phosphorus Removal*; Report No. 01-CTS-3; Water Environment Research Foundation: Alexandria, Virginia.

Nessim, Y.; Gehr, R. (2006) Fouling Mechanisms in a Laboratory-Scale UV Disinfection System. *Water Environ. Res.*, **78** (12), 2311–2323.

Patoczka, J. (2006) TDS and Sludge Generation Impacts from Use of Chemicals in Wastewater Treatment. *Proceedings of the 79th Annual Water Environment Federation Technical Exhibition and Conference* [CD-ROM], Dallas, Texas, Oct 21–25; Water Environment Federation: Alexandria, Virginia.

Patoczka, J. (2009) Unpublished Report Prepared for Bernards Township Sewerage Authority, New Jersey, by Hatch Mott MacDonald, Millburn, New Jersey.

Peng, J.; Qiu, Y.; Gehr, R. (2005) Characterization of Permanent Fouling on the Surfaces of UV Lamps Used for Wastewater Disinfection. *Water Environ. Res.*, **77** (4), 309–322.

Sedlak, R. (1991) *Phosphorus and Nitrogen Removal from Municipal Wastewater;* Lewis Publishers: New York.

Sehnaoui, K.; Gehr, R. (2001) Fouling of UV Lamp Sleeves: Exploring Inconsistencies in the Role of Iron. *Proceedings of the First International Congress on UV Technologies;* Washington, D.C., June 14–16; International UV Association: Ayr, Ontario, Canada.

Sheriff, M.; Gehr, R. (2001) Laboratory Investigation of Inorganic Fouling of Low Pressure UV Disinfection Lamps. *Water Quality Res.,* **36** (1), 71–92.

Smith, S.; Takacs, I.; Murthy.; Daigger, G. T.; Szabo, A. (2008) Phosphate Complexation Model and Its Implications for Chemical Phosphorus Removal. *Water Environ. Res.,* **80** (5), 428–438.

Takacs, I.; Murthy, S.; Smith, S; McGrath, M. (2006) Chemical Phosphorus Removal to Extremely Low Levels: Experience at Two Plants in the Washington, D.C. Area. *Water Sci. Technol.*, **53,** 21.

U.S. Environmental Protection Agency (2007) *Advanced Wastewater Treatment to Achieve Low Concentration of Phosphorus*; EPA 910-R/07-002; U.S. Environmental Protection Agency: Washington, D.C.

Water Environment Federation (2010) *Nutrient Removal*; Manual of Practice No. 34; McGraw-Hill: New York.

Yuan, W.; Bandosz, T. J. (2007) Removal of Hydrogen Sulfide from Biogas on Sludge-Derived Adsorbents. *Fuel*, **86** (17–18), 2736–2746.

8.0   SUGGESTED READINGS

Cabirol, N.; Barraga'n, E. J.; Dura'n, A.; Nayola, A. (2003) Effect of Aluminum and Sulphate on Anaerobic Digestion of Sludge from Wastewater Enhanced Primary Treatment. *Water Sci. Technol.*, **48** (6), 235–240.

Gehr, R.; Wright, H. (1998) UV Disinfection of Wastewater Coagulated with Ferric Chloride: Recalcitrance and Fouling Problems. *Water Sci. Technol.*, **38** (3), 15–23.

Stumm, W.; Morgan, J. J. (1970) *Aquatic Chemistry*; Wiley & Sons: New York.

Water Environment Federation; American Society of Civil Engineers; Environmental and Water Resources Institute (2009) *Design of Municipal Wastewater Treatment Plants,* 5th ed.; Manual of Practice No. 8; ASCE Manuals and Reports on Engineering Practice No. 76; McGraw-Hill: New York.

Water Environment Federation (2007) *Operation of Municipal Wastewater Treatment Plants*, 6th ed.; Manual of Practice No. 11; McGraw-Hill: New York.