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Revision Memo

- 12/02** Removed data from Properties of commercially available acids and bases tables.
Added chemicals in [Table 1](#).
Added detail in [Table 2](#).



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SCOPE

This section presents guidelines for the use of chemicals in wastewater, cooling water, and boiler water treatments. The chemical applications, the injection points, and control and monitoring issues are discussed. Information on the applicability of the most commonly used water / wastewater chemicals is provided along with general guidelines for handling and feeding the chemicals.

REFERENCES

DESIGN PRACTICES

Section XXVI-A	Boiler Feedwater Treating Systems
Section XXVII	Cooling Water Systems
Section XIX-A	Guidelines for Selecting Wastewater Treatment Systems
Section XIX-A2	Flotation Units
Section XIX-A3	Media Filtration
Section XIX-A4	Coagulation / Flocculation / Clarification Equipment
Section XIX-A5	Biological Treatment of Wastewater
Section XIX-A11	Chemical Oxidation
Section XX-A1	Dissolved Air Flotation Sludge Thickening
Section XX-A3	Mechanical Sludge Dewatering

GLOBAL PRACTICES

GP 8-1-1	Cooling Towers
GP 9-4-2	Additional Requirements for Atmospheric Storage Tanks for Acids
GP 19-6-1	Facilities for Corrosion Monitoring in Process Equipment

WATER AND WASTEWATER DESIGN GUIDE (EMRE Manual No. TMEE 080)

DG 11-2-1	Fixed Bed Ion Exchange Water Treating Units
DG 11-2-2	Aqueous Membrane Systems
DG 11-3-1	Gas Chlorinators for Water Treating Service
DG 11-4-1	Hot Process Water Treaters
DG 11-4-2	Cold Process Water Treaters
DG 11-6-1	Chemical Feeders for Boilers and Deaerators
DG 11-6-2	Chemical Feeders for Cooling Towers (Leased or Purchased)
DG 11-6-3	Chemical Feeders for Wastewater Treating
DG 11-7-1	Wastewater Dissolved-Air Flotation System
DG 11-7-2	Wastewater Induced Gas Flotation System
DG 11-8-1	Gravity Belt-Filter Press System

OTHER REFERENCES

1. Betz Handbook of Industrial Water Conditioning, 7th Edition (1976).
2. Devine, T. A., *Guidelines for Safety Evaluation of Chemical Injection Facilities*, EE.92E.94 (December 1994).
3. Franco, R. J., *Environmentally Acceptable Cooling Water Treatment*, EE.34E.86 (March 1986).
4. Kemmer, F. N., ed., *The Nalco Water Handbook*, 2nd Edition, McGraw-Hill Book Company (1988).
5. Kilpert, R., et al, *Cooling Tower Water Treatment Guidelines*, EE.102E.78 (November 1978).
6. Robertaccio, F. L., *Polyelectrolyte Guide*, EE.20E.84 (February 1984).
7. Smith & Loveless, Inc., *Engineering Data*, Water & Wastewater Treatment Systems Chem-Tower Notes on Design (1989).
8. Water Environment Research Foundation, Project 91-ISP-5, *Guidance Manual for Polymer Selection in Wastewater Treatment Plant*, (1993).
9. Wolfe, E. I., et al., *New Guide to Boiler Water Treatment*, EE.2E.86 (January 1986).

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10. Metcalf & Eddy, Inc., Wastewater Engineering Treatment, Disposal, and Reuse, 3rd Edition (1991).
11. *Refinery Construction Materials Manual*, EMRE Manual No. EETD 028.

DEFINITIONS

Alkalinity - A measure of water's capacity to neutralize acids. Includes the total carbonate, bicarbonate, and hydroxide ion concentration in the water expressed in ppm (mg/l) as calcium carbonate (CaCO₃) equivalent. Alkalinity is measured by double titration with acid and Phenolphthaleine (P) and Methyl Orange (MO or M) indicators. The M-alkalinity includes carbonate, bicarbonate and hydroxyl ions and the P-alkalinity includes all hydroxyl and 1/2 of the carbonate ions.

Anions - Negatively charged ions in the water (e.g., sulfates, chlorides, nitrates, bicarbonates, etc.).

Baumé (Bé) - This unit is often followed by "Am. Std." which signifies "American Standard Baumé Scale." For liquids heavier than water, this scale is defined by the formula:

$$\text{Degree Baumé} = 145 - \frac{145}{\text{Specific Gravity at } 60^{\circ} / 60^{\circ}\text{F}} \quad \text{Eq. (1)}$$

Brine - A solution of sodium chloride in water.

Bulking - A condition in the settling basin of a biological oxidation system where the sludge doesn't settle, or settles slowly, and may lead to floc carryover with the effluent.

Calcium Hardness - The concentration of calcium ion in the water, expressed in ppm (mg/l) generally as calcium carbonate (CaCO₃) equivalent.

Cations - Positively charged ions in the water (e.g., calcium, magnesium, sodium, ammonium, etc.).

Caustic or Caustic Soda - The chemical compound sodium hydroxide (NaOH).

Coagulants - Materials added to the water / wastewater or water / wastewater treatment sludge to allow agglomeration of small particles into larger particles to facilitate their separation from the water.

Coagulation Aids - Materials added to the water / wastewater or water / wastewater treatment sludge after a coagulant (primary coagulant) has been added to increase the speed of floc formulation and the floc size and strength. Polymers (also called polyelectrolytes) are the most commonly used coagulant aids.

Coagulation - The term coagulation is applied to the overall process of particle charge neutralization and physical combination (with the aid of chemicals) of small particles into masses sufficiently large to be settled or floated.

Colloid - A substance made up of very small, insoluble particles less than one micron in size. These particles are small enough so that they remain suspended in a liquid without settling to the bottom.

Conductivity - The ability of water to conduct electricity due to the presence of ionized material within the solution. Conductivity is expressed in micromhos/cm (or micro Siemens/cm), and is directly proportional to the amount of dissolved matter in the water / wastewater. As a rule of thumb, for wastewater streams at pH 7 the Total Dissolved Solids (TDS) of that stream in ppm (mg/l) can be approximated by multiplying the conductivity in units of micromhos/cm or microSiemens/cm by 0.7.

Flash Mix Tank or Rapid Mix Tank - An agitated drum or tank in which chemicals are rapidly mixed with the water / wastewater in order to improve the effectiveness and speed of reaction.

Floc - Suspended particles formed by the agglomeration of smaller suspended particles.

Flocculation - The term flocculation is applied to the process of particle charge neutralization and physical combination (with the aid of chemicals) of small particles into masses sufficiently large enough to be settled or floated. The word flocculation is often interchangeably used with the word coagulation.

Flocculation Tank - A process whereby suspended particles and colloidal particles, which cause turbidity and color in water, are combined by physical means (with the aid of chemicals) into masses sufficiently large to be settled or floated.

Hardness - The concentration of calcium and magnesium ions in water, expressed in ppm (mg/l) as calcium carbonate (CaCO₃) equivalent.

Hardness Alkalinity - The concentration of calcium and magnesium bicarbonate and carbonate salts in water, expressed in ppm (mg/l) as calcium carbonate (CaCO₃) equivalent.

Hydroxide Alkalinity - The free hydroxide ions in water, expressed in ppm (mg/l) as calcium carbonate (CaCO₃) equivalent.

Ion - Electrically charged particle formed when a molecule dissociates into positive and negative particles in water (e.g., salt into sodium + and chloride - ions).

Makeup or Makeup Water - The water required to replace circulating water which is lost by evaporation, drift, blowdown, and leakage. It is expressed in percent of water circulated.

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Nutrients - Chemical elements such as nitrogen, potassium, phosphorous, etc., which are essential for bacterial growth in biological wastewater treatment systems.

Once-Through Cooling System - A system in which cooling water passes through heat exchange equipment once and is then discharged directly, with no recycle or circulation.

Polymer or Polyelectrolyte - A polymeric organic compound commonly added to water / wastewater to promote coagulation and flocculation of suspended material. It is also added to water / wastewater treatment sludges to enhance thickening and dewatering. The following are the three basic types and uses of polymers:

1. Anionic (negative charge) - generally serve as coagulant aids to inorganic or organic primary coagulants by increasing the rate of coagulation and the size and roughness of floc particles.
2. Cationic (positive charge) - serve as primary coagulant alone or in combination with inorganic coagulants or with anionic or nonionic polymers. Some cationic polymers with very high molecular weights may also be used as coagulant aids.
3. Nonionic (no net charge) - serve as coagulant aids in a manner similar that of both anionic and cationic polymers.

Recirculated Cooling System - A system in which water is circulated to coolers in a loop and the heat absorbed from this cooling operation is dissipated by a cooling tower or some other type of heat exchanger.

Recirculation - An undesirable condition in which part of the cooling tower discharge vapor stream is recirculated through the tower resulting in increased inlet air wet bulb temperature.

Sludge - The accumulated semi-liquid suspension of settled solids deposited in tanks or basins from raw or treated water / wastewaters. Dissolved-Air Flotation and Induced-Air Flotation floats and Granular-Media Filter backwash are also included in this definition for the purpose of this Design Practice.

Sludge Conditioning - The addition of inorganic or organic chemicals to increase the efficiency of sludge thickening and/or dewatering.

Sludge Dewatering - The removal of water from a sludge or slurry, usually by mechanical means, to greater than 10 wt% solids.

Sludge Thickening - Thickening is a process which aims to increase the solids content of a dilute slurry by removing some of the water content by gravitational or flotation means. Typically, gravity thickeners can produce sludges with 4-6% solids by weight. Flotation thickeners typically conditions sludges to between 4 and 8% solids by weight.

Softening - The process of removing calcium and magnesium ions from water.

Specific Gravity (SG) - The specific gravity of a liquid is the ratio of the weight of a given volume of the liquid to the weight of an equal volume of water. Thus the specific gravity of a solution of chemical at 60°/60°F refers to the weight of a given volume of chemical at 60°F as compared with the weight of an equal volume of water at 60°F.

Turbidity - A term referring to the lack of clearness in a water due to the presence of suspended or colloidal matter and expressed in Nephelometric Turbidity Units (NTU).

BACKGROUND

Chemical addition facilities are an integral part of many grassroots water / wastewater treatment process unit designs. They are necessary for the proper operation and performance of the facility. However, chemical addition may also be retrofitted on existing process units to improve the unit's functional performance, decrease its operating cost, or extend its capability to process larger than design flow rates of water / wastewater and/or water / wastewater treatment sludges.

The designer of the chemical feed systems should provide as much flexibility as possible in the design of the chemical injection system to allow optimum selection of the application point(s) and take advantage of different chemicals offered by vendors. This flexibility is particularly important for coagulant and coagulant aid addition points.

[Reference 2](#), *Guidelines for Safety Evaluation of Chemical Injection Facilities*, should be used when designing or receiving a chemical feeding and handling system. The application guide is especially written to facilitate a safety evaluation of vendor provided chemical injection facilities. The guidelines cover the storage container, injection pump, and injection point.

[Table 1](#) provides a summary of the chemicals which are most commonly used in water / wastewater treatment applications. [Table 2](#) provides detailed information such as chemical formulas, available forms, storage considerations, and safety considerations for the commonly used chemicals in [Table 1](#). [Figures 1 to 6](#) illustrate the various types of chemical feeding systems used in water / wastewater treatment. A water / wastewater analysis (see [Table 3](#)) can be very useful in determining the required chemical application.

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WASTEWATER TREATMENT

COAGULATION / COAGULATION AID

General - Chemical coagulation is accomplished by one or a combination of the following two basic mechanisms:

1. **Particle Charge Neutralization** - Most suspended matter in wastewater has an apparent negative surface charge. This negative surface charge on the particles creates a net repulsive force between particles, thereby inhibiting agglomeration of the suspended matter. The addition of positively charged metal ions or cationic polymers can neutralize these surface charges and allow particle agglomeration either with or without a coagulant aid.
2. **Particle Bridging** - The addition of metal salts can form metal hydroxides under the proper set of pH and dosage conditions. These metal hydroxides form large sets of molecules that attach themselves to the suspended particles, thereby bridging the gap between particles and drawing them together into a strong floc lattice structure. Polymers can also be effective particle bridging chemicals.

Particle Charge Neutralization using polymer chemicals is the preferred mechanism for coagulation because it generally requires less chemical and produces less sludge than Particle Bridging.

Primary Coagulant - Cationic polymers are the preferred primary coagulant for coagulation. In the past, Bentonite, Diatomaceous Earth, and metal salts were commonly used as primary coagulants. Some manufacturers provide blended products which contain both a metal salt and a polymer. However, due to improved polymer technology, polymers are now recommended for new applications. Cationic polymers have advantages over other primary coagulants as follows:

- Easier to store and handle.
- Used as neat polymers, eliminating mixed / diluted solution tank.
- Produce less sludge (which ultimately must be disposed of).
- Resulting sludge contains less water, is less acidic, and can be more easily dewatered.
- Performance is less pH dependent.
- Do not add to the total dissolved solids concentration.

Coagulant Aid - In cases when different types and large doses of primary coagulant fail to produce a satisfactory floc, a polymeric coagulant aid should be added after the primary coagulant. Very high molecular weight ($> 1 \times 10^6$) polymers like the nonionic polymers and low molecular weight ($< 20,000$) polymers like the anionic polymers have proven successful and are recommended coagulant aids.

Applications - Chemical coagulation is applied for suspended solids and free oil removal during wastewater treatment to enhance separation of solids and oil from the wastewater, in clarification and thickening, in sludge dewatering, and in metals removal.

1. **Flotation Processes (DP XIX-A2)** - Chemical coagulation is almost always required to attain even moderate degree of free oil and suspended solids removal from flotation processes. By chemically agglomerating the small diameter particles, impingement and attachment of air bubbles on the larger floc particles is enhanced, thereby improving the efficiency of the flotation process. Normally, chemical coagulation will also help increase the concentration of oil and solids in the float from these processes.

Dissolved Air Flotation (DAF) process units are generally preceded by chemical flocculation equipment (i.e., a flash mix and a flocculation tanks). The primary coagulant is generally added in the flash mix tank. If a coagulant aid is required, it is added in the flocculation tank or injected in the influent line just prior to the flotation unit.

Induced Gas Flotation (IGF) process units do not normally have a flash mix or a flocculation tank. The primary coagulant is injected directly into the influent line far enough upstream of the flotation unit to allow complete mixing with the wastewater. If a coagulant aid is required, it is injected in the influent line just prior to the flotation unit. Static or in-line mixers are generally used for direct injection.

2. **Filtration Processes (DP XIX-A3)** - Use of chemical coagulation, optimized with respect to both chemical type(s), dosage(s), and point(s) of injection, can improve effluent quality, extend the run length of Granular-Media Filtration (GMF) units, and increase the concentration of oil and solids in the backwash. The primary coagulant is injected directly into the influent line far enough upstream of the filtration unit to allow complete mixing with the wastewater.
3. **Clarification (DP XIX-A4 and XIX-A5)** - Primary coagulants, and sometimes coagulant aids, are used to help settle out suspended material in the clarifier. They also help chemically treat dispersed growth of biological solids. Both the primary coagulant and coagulant aid are added upstream of the clarifier.
4. **Sludge Thickening by Flotation (DP XX-A1)** - In sludge thickening by flotation or gravity filtration, cationic polymers are the preferred primary coagulant. A coagulant aid is not generally required. The cationic polymer is injected directly into

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the influent line far enough upstream of the thickener to provide complete mixing with the sludge. It may also be added in a feed mixing tank. However, care should be exercised in controlling the intensity of mixing in this tank to avoid excessive shearing of the sludge.

5. **Sludge Dewatering (DP XX-A3)** - For low shear sludge dewatering processes such as belt filter pressing, vacuum filtration, and centrifugation, the primary coagulant is usually injected in the influent pipe just prior to, or directly into a low intensity mixing tank which precedes the process unit. In some cases, it is also possible to eliminate the need for a gentle mixing tank by injecting the primary coagulant into the influent line upstream of an in-line mixer, or far enough upstream to allow complete mixing of the chemical with the sludge. If a coagulant aid is required, it is injected immediately before the dewatering process unit.

For high shear sludge dewatering processes, such as high-pressure filtration, the primary coagulant is added to the sludge in a batch mixing tank prior to the filter press. Diatomaceous Earth is sometimes useful as a precoat material on the pressure filter cloth. A precoat both enhances the concentrated sludge cake release from the cloth and prevents plugging of the cloth during the filtration process. Waste FCCU catalyst fines can also be used as a filter cloth precoat material. If a precoat is used on the filter cloth, it is generally applied directly to the filter cloth in slurry form prior to feeding the sludge to the filter.

6. **Metals Removal** - Depending on the metal, chemical coagulation followed by gravity separation, flotation, or filtration can remove undissolved and some dissolved heavy metals which may be chelated or coprecipitated by the chemicals, such as EDTA and Iron salts, respectively. Similarly, a small reduction in both the dissolved and undissolved heavy metals occurs by adsorption on biological solids and undissolved heavy metals are removed by incorporation into the biological solids floc.

The primary coagulant, which forces the precipitation of metals, is typically added in the flash mix tank. If required, a coagulant aid is usually added either in the flocculation tank or in the influent line just prior to the separation unit where the metal precipitate is removed from the wastewater.

Types and Dosages - The types and dosage rates of coagulant / coagulant aid required to provide the best performance for specific applications cannot be theoretically predicted and must be determined by bench laboratory tests and field trials. [Table 4](#) summarizes the bench scale tests that will help determine the best combination of chemicals and the optimum dosages for a particular wastewater. If pilot plant facilities are used to optimize new process unit design parameters, concurrent tests on these units may also be utilized to determine the optimum chemical type(s) and dosage(s).

As a general guide for initial lab tests or as a design guide for grassroots facilities where there is no wastewater available, chemical dosage ranges are as follows:

TREATMENT TYPE	POLYMER TYPE	TYPICAL DOSAGE RANGE
PRIMARY COAGULANT	Cationic	1 - 10 ppm (mg/l) as neat polymer
COAGULANT AID	Anionic or Nonionic	0.1 - 3 ppm (mg/l) as neat polymer

Design guidelines / parameters for coagulation / coagulation aid / flocculation are as follows:

- The chemical feed system for cationic polymers ([Figure 4](#)) typically includes a bulk storage tank (temporary semi-bulk storage tanks may be provided by supplier) and a spared pumping configuration.
- The chemical feed system for anionic or nonionic polymers ([Figure 3](#)), typically includes a bulk storage tank (temporary semi-bulk storage tanks may be provided by supplier), a mixing tank, a mixture storage tank, and two spared pumping configurations (one set for the bulk tank and the second for the mixing tank).
- The coagulant / coagulant aid should be injected via dosing pumps. Normally, 2-100% capacity pumps are provided for each pump configuration. Positive displacement metering pumps are used for rates up to 100 gph (0.1 L/s). Centrifugal pumps with flow control are used for higher rates. As with any pumps or equipment, area classifications should be considered in selecting and specifying them.
- The bulk storage tank should provide a minimum inventory of 15 days at the design consumption rate.
- The mixing tank and the mixture storage tank for anionic and nonionic polymer feed systems should not exceed 48 hours of inventory.
- The bulk tanks should contain a slow speed, blade type agitator. The intensity of mixing energy supplied depends on the emulsion tendency, the nature of the solids in the stream, and shearing intensity if in sludge service.
- The bulk storage tank should be equipped with a level gage that is visible from the unloading connection.
- Dilution water shall be clean condensate or equivalent water quality. Potable water must never be used.¹

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- A pressure relief valve should be provided downstream of each pump system even if built-in relief valves are provided with the pumps. The set pressure is to be 10% above the operating pressure at the pump discharge or 10% above the process equipment design pressure, whichever is greater.
- Sizing of the facilities may require consultation with the chemical(s) suppliers. Concentrations and activity of vendor supplied chemicals can vary and have an effect on storage volumes and pumping rates.
- Commonly used worldwide polymer suppliers are as follows. The company distribution area and internet web address are listed below.

Company	Web Address	Distribution Area
Ashland Specialty Chemical Company	www.ashchem.com	North America
Vulcan Chemicals	www.vul.com	North America
Baker Petrolite	www.bakerhughes.com/bakerpetrolite	International
GEBetz Chemicals	www.gebetz.com	International
ONDEO Nalco Chemical Co.	www.ondeonalco.com	International
US Filter - Stranco	www.stranco.com	International

** This list is provided as a convenience to the user and is not intended as an endorsement. Other suppliers should also be contacted; they may provide unique products unavailable from the suppliers on this list.

NUTRIENT ADDITION

Microorganisms require nutrients in addition to the primary carbon food source. Macronutrients consist of nitrogen (N) and phosphorus (P). Micronutrients, or trace elements, are also required by microorganisms. The micronutrients (K, Fe, Mg, Ca, Zn, Cu, Co, etc.) are typically found in refinery and petrochemical wastewaters in sufficient concentrations. However, the macronutrients are often insufficient. Because nitrogen and phosphorus are essential for microorganism growth and reproduction, they are also essential for waste degradation.

Nitrogen - There are several forms of nitrogen found in wastewater: organic nitrogen, ammonia, nitrate, and nitrite. Ammonia nitrogen exists in aqueous solution as either the ammonium ion or ammonia, depending on the pH of the solution.

As a rule of thumb:

$$\text{PPM (mg/L) of Nitrogen required for bio-growth} = \text{ppm (mg/l) of BOD}_5 \text{ in the wastewater}/20$$

If supplemental nitrogen is required, there are several sources of nitrogen that can be used. The recommended nitrogen source is ammonium salts due to their easier handling and mild corrosivity. The advantages and disadvantages for the most common sources of nitrogen are as follows:

NITROGEN SOURCE	ADVANTAGES	DISADVANTAGES
Ammonia² (NH ₃)	Requires small dosages due to high strength	- Gas toxic at concentrations over 100 ppm in air - Gives off pungent, irritating odor - Corrosive - Safety equipment required
Ammonium Hydroxide² (NH ₄ OH)	Available in bulk liquid	- Gives off pungent, irritating odor - Corrosive - Safety equipment required
Ammonium Salts² e.g., (NH ₄) ₂ SO ₄	- Relatively easy to handle - Only mildly corrosive	- Tends to cake - Safety equipment required
Urea² (NH ₂ CONH ₂)	Relatively easy to handle	Corrosive

¹: Unless isolation and backflow concerns are addressed to meet local and/or minimum ExxonMobil Requirements.

²: Refer to Table 2 for Safety Considerations

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Design guidelines / parameters for ammonium sulfate feed systems are described below. The preferred method of feeding ammonium salts is to prepare a bulk solution and follow the recommended procedures for bulk liquid chemicals.

- The chemical feed system for ammonium salts ([Figure 1](#)) typically includes a bulk storage tank and a spared pumping configuration.
- The ammonium salt solution should be injected via dosing pumps. Normally, 2-100% capacity pumps are provided. Positive displacement metering pumps are used for rates up to 100 gph (0.1 L/s). Centrifugal pumps with flow control are used for higher rates.
- The bulk storage tank should provide a minimum inventory of 15 days at the design consumption rate.
- The bulk storage tank should contain an agitator.
- The bulk storage tank should be equipped with a level gage that is visible from the unloading connection.
- Dilution water shall be clean condensate or equivalent water quality. Potable water must never be used.¹
- A pressure relief valve shall be provided downstream of each pump system even if built-in relief valves are provided with the pumps. The set pressure is to be 10% above the operating pressure at the pump discharge or 10% above the process equipment design pressure, whichever is greater.
- Protective facilities, e.g., safety shower and eye wash, should be within 50 ft of the injection facilities (**GP 3-2-6**).

Phosphorus - The usual forms of phosphorous found in aqueous solutions include orthophosphate (PO_4^{-3} , HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-1}$, H_3PO_4), polyphosphate (molecules with two or more phosphorus atoms), and organic phosphate.

As a rule of thumb:

$$\text{PPM (mg/L) of Phosphorus required for bio-growth} = \text{ppm (mg/l) of BOD}_5 \text{ in the wastewater}/100$$

If an appropriate amount of phosphorus for bio-growth is not found in the wastewater for biotreatment, phosphorus may be added. Several sources of phosphorus are available, however typically phosphoric acid (H_3PO_4) is used. The phosphoric acid is a low strength acid and is added in relatively low dosages, hence there is no significant effect on the wastewater pH. The advantages and disadvantages for the most common sources of phosphorus are as follows:

PHOSPHORUS SOURCE	ADVANTAGES	DISADVANTAGES
Phosphoric Acid (H_3PO_4) ²	• Available in bulk liquid • Easy to pump and meter flow	• Corrosive • Safety Equipment Required
Phosphate ²	• Neutral Solution	• Low strength solution due to solubility limitations

Design guidelines / parameters for phosphoric acid feed systems are as follows:

- The chemical feed system for phosphoric acid addition ([Figure 1](#)) typically includes a bulk storage tank and a spared pumping configuration.
- The phosphoric acid should be injected via dosing pumps. Normally, 2-100% capacity pumps are provided. Positive displacement metering pumps are used for rates up to 100 gph (0.1 L/s).
- The bulk storage tank should provide a minimum inventory of 15 days at the design consumption rate.
- The bulk storage tank should be equipped with a level gage that is visible from the unloading connection.
- Dilution water, if required, shall be clean condensate or equivalent water quality. Potable water must never be used.¹
- A pressure relief valve shall be provided downstream of each pump system even if built-in relief valves are provided with the pumps. The set pressure is to be 10% above the operating pressure at the pump discharge or 10% above the process equipment design pressure, whichever is greater.
- Protective facilities, e.g., safety shower and eye wash, shall be within 50 ft of the injection facilities (**GP 3-2-6**).

pH ADJUSTMENTS

General - Refineries and petrochemical plant's wastewater often contain acidic or alkaline materials that may require pH adjustment prior to discharge to receiving waters, or prior to chemical or biological treatment.

¹: Unless isolation and backflow concerns are addressed to meet local and/or minimum ExxonMobil Requirements.

²: Refer to Table 2 for Safety Considerations

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Acids - Any strong acid can be used effectively to neutralize alkaline wastes, but cost considerations usually limit the choice to sulfuric or hydrochloric acid. The reaction rates are practically instantaneous. Some advantages and disadvantages for these two recommended acids are:

ACID	ADVANTAGES	DISADVANTAGES
Sulfuric	Normally Lower Cost	Corrosive Dangerous to handle May form CaSO ₄ precipitation in the presence of calcium
Hydrochloric	No Heated Dilution Most effective	Corrosive Dangerous to handle Gives off pungent irritating odor Volatile

Properties of commercially available forms are as follows:

SOLUTION TYPE	WT% OF CHEMICAL	WT OF CHEMICAL PER VOLUME OF SOLUTION		SG OF SOLUTION	BAUMÉ
		lb/gal	g/l		
Sulfuric Acid (H₂SO₄)	93	14.19	1700	1.8279	65.7
	98	15.02	1799	1.8361	66.0
Hydrochloric Acid (HCl)	32	3.096	371.0	1.1593	19.9
	36	3.542	424.4	1.1789	22.0

Bases - Sodium Hydroxide, also called caustic soda, is the most commonly used base due to its availability as an aqueous solution. The advantages of liquid caustic (< 50 wt% strength) over other bases are:

- It is easier to unload (tank trucks) and handle.
- Delivery cost is lower than any other dry bases.

The commercially available strengths for caustic are as follows:

SOLUTION TYPE	WT% OF CHEMICAL*	WT OF CHEMICAL PER VOLUME OF SOLUTION		SG OF SOLUTION	BAUMÉ
		lb/gal	g/l		
Sodium Hydroxide (NaOH)	20-25	2.035	243.8	1.2191	26.1
	50	6.364	762.7	1.5253	49.9

Note:

*For caustic with strength greater than 50%, special care must be provided. Consult EMRE's Water and Waste Section.

Applications - Wastewater typically requires pH adjustment in the following wastewater treatment areas.

1. **Prior to Secondary Oil and Suspended Solids Separation** - The primary purpose of adjusting the pH at this point is to assure that the proper pH range is maintained for optimum performance of inorganic coagulants and coagulant aids.
2. **Biological Treatment** - Aerobic biological treatment systems operate effectively within a relatively narrow pH window. The pH in the biological reactor should be controlled between 6.5 and 8.5 (optimum range is 7 to 8). Therefore, pH control is required to prevent upsets of the biological treatment system.

Aerobic treatment under non-nitrifying conditions uses H⁺ ions tending to increase pH. The increase in pH is only slightly because alkalinity is also produced.

Biological nitrification of ammonia consumes about 7 pounds of alkalinity for every pound of ammonia (expressed as CaCO₃) which is oxidized to nitrate. If the influent wastewater to the biological treatment plant does not have sufficient

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alkalinity, the pH can be significantly lowered and the biological process upset by alkalinity consumption through nitrification. It is recommended to control the pH of the basin, which is easier to control than the feed.

Anaerobic biological decomposition of organic matter may either produce or consume alkalinity depending on the organic composition of the feed. The alkalinity in the anaerobic biological treatment system should be maintained at a minimum of 1000 ppm (mg/l) as CaCO_3 equivalent to avoid process upsets which can be caused by extreme pHs (optimum pH range is 6.5 to 7.5).

3. **Prior to Final Discharge** - Generally, if the final discharge of the wastewater is preceded by biological treatment, additional pH adjustment is not necessary. Otherwise, it may be necessary to adjust the pH of the final discharge to comply with local regulations.

Dosages - The dosage rates for acids / bases have been traditionally predicted by bench-scale tests. More recently, computer modeling via the Environmental Simulation Program (ESP) has been successfully used in ExxonMobil to predict dosage requirements for acids and bases. This model is available through EMRE's Water & Waste Section. Pilot plant facilities can also be used to determine the optimum chemical dosages in certain cases.

Design guidelines / parameters for pH adjustment chemical feeders are as follows:

- The chemical feed system for liquid acid / base ([Figure 1](#)) typically includes a bulk storage tank (temporary storage tanks may be provided by supplier) and a spared pumping configuration.
- The acid / base should be injected via dosing pumps. Normally, 2-100% capacity pumps are provided. Positive displacement metering pumps are used for rates up to 100 gph (0.1 L/s). Centrifugal pumps with flow control are used for higher rates.
- Whether fixed or portable, the bulk storage tank should provide a minimum inventory of 15 days at the design consumption rate.
- The fixed bulk storage tank should be equipped with a level gage that is visible from the unloading connection.
- Dilution water, if required, shall be clean condensate or equivalent water quality. Potable water must never be used.¹
- A pressure relief valve shall be provided downstream of each pump system even if built-in relief valves are provided with the pumps. The set pressure is to be 10% above the operating pressure at the pump discharge or 10% above the process equipment design pressure, whichever is greater.
- Protective facilities, e.g., safety shower and eye wash, shall be provided within 50 ft of the injection facilities (**GP 3-2-6**).
- A feedback / feedforward control loop is recommended to compensate for the inherent short retention time of in-pipe injection.
- Use of feedback, feedforward, or both for pH control will depend on the application and control band. (Consult with EMRE's Environmental Section on specific applications)
- A pH analyzer with high and low alarm is generally provided to control the amount of acid / base feed.

OXIDANTS

Applications - Oxidants like hydrogen peroxide have been used to oxidize small quantities of sulfide, phenols, and other organics in wastewater, at their source such as tank bottoms, desalters, or in pre-treated wastewaters. Hydrogen peroxide is usually added in a flash mix tank or a junction of a flow splitter box with a high level of mixing, or a static mixer may need to be employed in a line.

Hydrogen peroxide has also been used to control severe cases of filamentous bacteria or bulking (poor settling) of biological solids in activated sludge clarifiers. The injection point is the biological sludge recycle line.

The use of hypochlorite or other halogenated compounds for oxidation is generally recommended only for sulfide control in fairly clean or low organic contamination wastewaters (such as stagnant pond or lagoon waters). The use on organic laden wastewaters, especially those containing phenolic compounds, could potentially form halogenated organics, and therefore is not recommended. Use of hypochlorite for biological sludge bulking control should only be considered after use of peroxide has been tried. Hypochlorite use needs to be carefully controlled to avoid killing off desirable microbes in the activated sludge.

Dosage - The dosage rate of hydrogen peroxide generally ranges between 50 to 200 ppm (mg/l) for controlling biosolids bulking. The dosage should be started at a low level (50 wppm) and increased gradually in steps, until the bulking is controlled. For oxidation of sulfide and phenols contamination, a guideline of 3 wppm of H_2O_2 (100% basis) per 1 wppm of sulfide, and 4 wppm of H_2O_2 per 1 wppm of phenols is typical, but temperature, pH and reaction time need to be considered, especially for organic contaminants such as phenol.

¹: Unless isolation and backflow concerns are addressed to meet local and/or minimum ExxonMobil Requirements.

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Design guidelines / parameters on the use of hydrogen peroxide are given below. Refer to DP-XIX-A11 on Chemical Oxidation for more details on use of hydrogen peroxide for treatment.

- The chemical feed system for hydrogen peroxide ([Figure 1](#)) typically includes a bulk storage tank (permanent or temporary) and a spared pumping configuration.
- The oxidant should be injected via dosing pumps. Normally, 2-100% capacity pumps are provided. Positive displacement metering pumps are used for rates up to 100 gph (0.1 L/s). Centrifugal pumps with flow control are used for higher rates.
- For permanent facility, the bulk storage tank should provide a minimum inventory of 15 days at the design consumption rate.
- The bulk storage tank should be equipped with a level gage that is visible from the unloading connection.
- Dilution water, if required, shall be clean condensate or equivalent water quality.
- A pressure relief valve shall be provided downstream of each pump system even if built-in relief valves are provided with the pumps. The set pressure is to be 10% above the operating pressure at the pump discharge or 10% above the process equipment design pressure, whichever is greater.
- Protective facilities, e.g., safety shower and eye wash, shall be provided within 50 ft of the injection facilities. (**GP 3-2-6**).
- Peroxides are strong oxidants and should not be added directly to very oily waters or in plant sewer systems that can dry out. Consult plant safety personnel and supply vendors for safe application. Permanent systems will require a peroxide addition pump cut off, when there is no flow of wastewater in the lines being treated. Usually, commercial grades of 35% H₂O₂ are preferred to ensure there is enough dilution water, and a minimal temperature rise due to the exothermic reaction of the peroxide with the contamination.
- Due to oxidative nature of chemicals, materials of construction will require review.

FOAM CONTROL

The most typical application of defoamers in wastewater treatment is in biological treatment units. Usually, defoamers are only used on a sporadic basis to eliminate serious foaming problems. Defoamer type and dosage may be selected by placing influent water, or water from the biological treatment in a 2-L graduated cylinder which is moderately aerated with a sparger. The effectiveness of the chemical type and dosage in reducing the tendency of the water to foam is evaluated visually. Typically silicone based antifoams are used due to their low toxicity.

Design guidelines / parameters on the use of defoamers are given below.

- Defoamers are most commonly sprayed on the surface of the wastewater in the reactor basin rather than injected directly into the bulk wastewater. Spray application may be performed using a portable tank and spray system or a permanently installed spray system.
- For small volume, liquid defoamers, gravity feed directly from the drum using a needle valve.
- For large volume feed, more accurate dose control, and/or high viscosity defoamers, metering pumps are recommended.
- Prepare the defoamer as 5% solutions for feeding convenience. The solution should be continuously agitated to maintain a homogeneous solution.
- Because the products are non-corrosive, metal or plastic feed lines can be used. Avoid use of rubber gaskets or hoses which may dissolve in prolonged contact with defoamers.
- The best time to apply a defoamer is shortly before the foam becomes troublesome, such as when the foam layer is building in a biox basin/tank or clarifier, thus allowing for adequate mixing and reaction time. Although defoamers can collapse foam, they are more effective when applied before it develops.

COOLING WATER TREATMENT

BIOLOGICAL CONTROL

The operating conditions in recirculated cooling water are ideal for the growth of biological matter. To control the biological activities, a biocide chemical is added to the water treatment program. Oxidizing biocides such as chlorine, sodium hypochlorite, chlorine dioxide, or bromine-associated compounds are most commonly used with good results.

For either once-through or recirculation system, facilities should be provided for feeding the biocide into the back of the cooling tower basin. If chlorine is used, it must be present in the cooling water as free residual to be effective.

