

Chapter 1

Particle and Natural Organic Matter Removal in Drinking Water

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INTRODUCTION

One of the most basic processes in the treatment of raw source waters to meet drinking water standards is the solid/liquid separation process to remove particulate material. Particulate material originating in raw water or contributed by addition of treatment chemicals is physically separated from source water during drinking water treatment by clarification and filtration processes. These processes target not only removal of particulate material itself but also contaminants that are associated with the particulate material. Clays, sands, colloids, and so on all may comprise typical particulates to be removed; however, removal of other particle classes, such as microorganisms and particulate forms of natural organic matter (NOM), is beneficial for efficient treatment. Further, other contaminants (e.g., arsenic, iron, manganese, or dissolved NOM) may be associated with particulate matter via coprecipitation, sorption, or other physico-chemical mechanisms. Disinfection by-products (DBPs) have been a primary driver for specific focus on NOM removal. In fact, although much research has been devoted to the coagulation of inorganic particles, coagulant dosages for many surface waters are controlled by the NOM concentration rather than by turbidity. During coagulation, dissolved-phase NOM is converted into a solid phase, allowing removal in subsequent clarification/filtration processes. Finally, chemical and/or physical disinfection is also dependent on effective removal of particulate matter that may shield microorganisms from disinfectant contact and/or reduce the effectiveness of disinfection chemicals.

This chapter provides an overview on the removal of particles and NOM by coagulation and filtration processes. These fundamentals serve as a basis for compliance with multiple treatment objectives and prepare the reader for additional detail introduced later in this manual. Specifically, the following are included in this chapter:

- A review of particles and NOM, including the characteristics of these constituents important in their removal
- A discussion of particle surface charge and coagulant chemistry
- An overview of the physical and chemical aspects of coagulation and filtration processes
- A brief discussion of management of multiple processes for effective treatment, including the multiple barrier approach, process control, and membrane filters

PARTICLES

Particles are ubiquitous in all natural waters. Their origins, compositions, and concentrations vary widely. They can be contaminants (as defined here as substances of natural, anthropogenic, or microbiological origin that may be harmful to the public health, adversely affect water quality, and/or affect the aesthetic properties of the finished water) or associated with contaminants and therefore need to be removed. Of the many ways that particles can be characterized, size and surface properties are two of the most important keys related to removal by coagulation and filtration processes. Further, different techniques exist that can be used to quantify or characterize particles. In this section, particle characteristics, quantification, and water quality are discussed.

Origin and Composition of Particles

Based on their underlying composition, particles can be considered as organic, inorganic, or biological (a subset of organic). Particles are introduced into natural waters (i.e., our water supplies) either through natural processes or as a result of anthropogenic (human) activities. An overview of the three major compositions of particles is provided below:

- The majority of organic particles in natural water are the result of degradation of plant and animal materials. These organic constituents may be classified as natural organic matter. However, NOM in natural water consists of more than suspended particles; it also includes dissolved NOM molecules. A separate section of this chapter focuses on NOM and its removal because of its increasing importance to water utilities.
- The majority of inorganic particles in natural water are mineral particles. Most of these particles are derived from the natural weathering of minerals. Examples include clays, iron oxides, aluminum oxides, and calcites. Inorganic particles often enter source water by means of erosion and runoff.
- Biological particles include microorganisms such as viruses, bacteria, and protozoa. These microorganisms enter the water through direct discharge of wastewater, runoff from the watershed, or animal excrement, and some may grow and prosper in the water body. Microorganisms may also be attached to suspended particulate matter. Another type of biological particle is algae, which use mineral nutrients (nitrogen and phosphorus) and photosynthesis to grow.

Particles may result from specific human activity, for example, discharge of municipal or industrial wastewater effluent into a source water. Runoff from land-disturbing activities and property development also introduce particulate matter, into water sources. The composition of these particles is case-specific. The influx of particles into a water body may be driven by natural events such as runoff from snowmelt and precipitation. Depending on the nature of the watershed, particles coming from these events may contain organic, inorganic, and/or biological matter.

In addition to natural particles that occur in water, particles are often added or created in water treatment processes to remove other particles and contaminants. Metal-based coagulants added to water to destabilize particles (as discussed in a later section) may also precipitate as metal hydroxides. These precipitates can then flocculate with particles from the source water and be removed by the solid/liquid separation processes in treatment plants. Bentonite may be added to low turbidity waters to enhance the contact opportunity between particles so that larger and denser flocs are formed for better removal in the settling process. Chlorine may be added to water to oxidize soluble iron (II) species into insoluble iron (III) particles so that these particles can be removed by settling and filtration processes.

Because of their reactivity, pure inorganic or organic particles seldom exist in natural water; that is, all inorganic particles have some kind of organic properties and vice versa. Most inorganic particles have an affinity to and can sorb organic chemicals such as synthetic organic chemicals onto their surfaces. Most inorganic particles in water also react with NOM and form an organic coating on their surfaces. This organic coating plays a significant role on the surface properties of particles, as will be discussed later. Furthermore, NOM, regardless of whether it is in dissolved or particulate form, can chemically bind with many inorganic contaminants such as metals.

The Need to Remove Particles

Particles must be removed from water for both aesthetic and health reasons. The presence of particles may impart color, taste, and/or odor to water, making it less palatable for the customer. More importantly, particles can also be pathogenic or toxic and must be removed to protect public health. Further, particles can shield microbes from disinfectants and reduce the efficiency of the disinfection process. For these reasons, it is essential that coagulation, flocculation, sedimentation, and filtration processes are properly designed and operated to optimize the removal of particles.

Current regulatory requirements for particle removal are based primarily on improved control of microbial pathogens. These requirements are summarized in Table 1-1 and discussed below:

- Removal of particles is regulated indirectly under the Surface Water Treatment Rule (SWTR) and its various revisions. These requirements apply to utilities using surface water or groundwater under the direct influence of surface water.
- Compliance with particle removal criteria is determined by filtered water turbidity, with regulatory limits ranging from 0.3 to 1.0 ntu, depending on the type of filtered water, percentile value, and location of measurement (see Table 1-1).

A utility meeting the turbidity requirements demonstrates that it can consistently provide good removal efficiency of particles and microbes through its coagulation and filtration processes. This, together with properly managed disinfection, ensures that the finished water leaving the treatment plant is of such quality that it minimizes microbial pathogens, has a physical appearance (low turbidity) that is palatable to the consumer, and is safe to drink.

Table 1-1 Regulatory requirements for particle and NOM removals

| Constituents | Regulation | Compliance Indicator | Requirements | | | |
|--------------|---|---|--|--|---------|-------|
| Particles | IESWTR ⁽¹⁾⁽³⁾ LT1SWTR ⁽²⁾⁽³⁾ | Filtered Water Turbidity | CFWT ⁽⁴⁾ <0.3 ntu 95% of the time | | | |
| | | | <1 ntu any time | | | |
| | | | IFWT ⁽⁵⁾ <0.5 ntu ⁽⁶⁾ <1.0 ntu ⁽⁷⁾ | | | |
| NOM | Stage 1 D/DBPR ⁽⁸⁾ | Removal Percentage of Total Organic Carbon (TOC) ⁹ | Removal Requirements, % | | | |
| | | | Source Water TOC, mg/L | Source Water Alkalinity, mg/L as CaCO ₃ | | |
| | | | | 0–60 | >60–120 | >120 |
| | | | >2.0–4.0 | 35.0% | 25.0% | 15.0% |
| | | | >4.0–8.0 | 45.0% | 35.0% | 25.0% |
| >8.0 | 50.0% | 40.0% | 30.0% | | | |

Courtesy of Kwok-Keung Au.

- (1) Interim Enhanced Surface Water Treatment Rule
- (2) Long Term 1 Enhanced Surface Water Treatment Rule
- (3) These requirements apply to utilities using surface water or groundwater under the direct influence of surface water
- (4) Combined filtered water turbidity
- (5) Individual filtered water turbidity
- (6) In any two consecutive measurements taken 15 min apart at the end of the first 4 hr of continuous filter operation after backwash
- (7) In any two consecutive measurements taken 15 min apart
- (8) Stage 1 Disinfectants and Disinfection By-products Rule
- (9) These requirements apply to conventional treatment facilities that use surface water or groundwater under the direct influence of surface water

Particle Quantification

Analytical methods related to the number and size of particles in water are turbidity, particle count, and suspended solids concentration measurements. Each method has advantages and limitations and is used to achieve a different objective. These quantification techniques are discussed below, and turbidity and particle counting are described in detail in chapter 3.

- Turbidity measurement is the most widely used method for assessing particles in water. It does not give a quantitative measure of particles in water but instead indicates the relative clarity of water samples by measuring the amount of light scattered by particles in water samples. The result is reported in nephelometric turbidity units (ntu). The turbidity level of a water sample depends on the physical properties (such as concentration, size, and shape) and the optical properties of the particles contained in the sample. Although the actual relationship among these characteristics is very complicated, the result is sufficient to describe turbidity as a composite measurement based on these properties. Turbidity has been used successfully as a regulatory indica-

tor to assess the removal efficiency of particles and microbes by treatment processes. Turbidity measurements can be performed with grab samples or continuous online instruments.

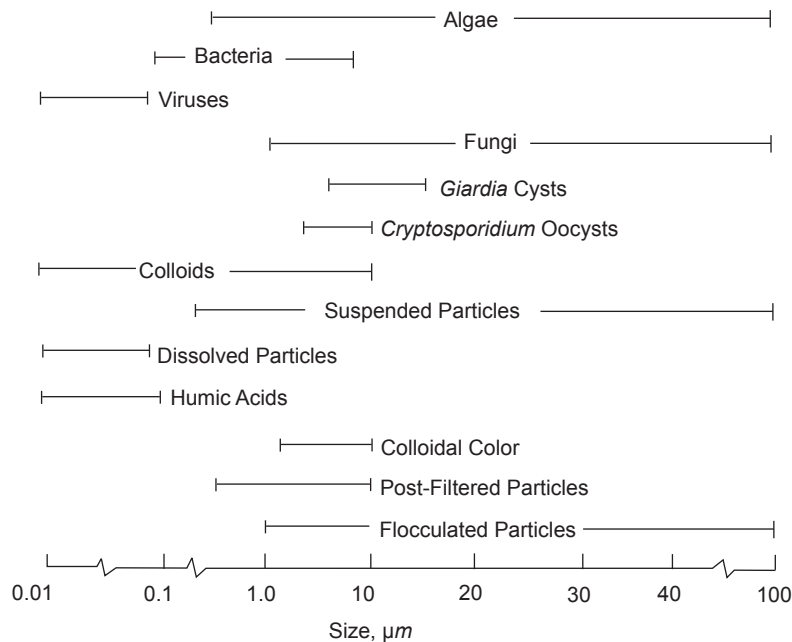
- Particle counts (particle counting) represent the numerical concentration of particles within finite particle diameter ranges. The results are usually reported as cts/mL at different size ranges. Particle counting can be used as a tool to monitor the performance of removal processes. However, because of several limitations in the application of this technique, particle counts are currently not used for regulatory compliance in drinking water. Particle count can be measured by grab samples or continuous online instruments.
- The mass of particles in a water sample can be quantified as the concentration of suspended solids, which is defined as the total mass of particles retained on a glass fiber filter disc through which a measured volume of water sample has been filtered. The result is reported as mg/L. Materials passing through the filter are defined as dissolved solids. Suspended solid measurement is typically not used to assess the removal efficiency of drinking water treatment processes. Instead, because of the exceedingly small mass of suspended solids in filtered drinking water, this analytical method is used by water utilities to estimate the amount of sludge or waste produced from clarification and filtration processes.

Particle Size

The size of particles is an important characteristic affecting their removal in water treatment plants. Particle size may vary by several orders of magnitude. Most inorganic particles have sizes ranging from 0.1 to 5 micrometers (one-millionth of a meter, or μm). Figure 1-1 shows a comparison of sizes that may be encountered in water supplies. Biological particle size is dependent on the classification of the microorganism. Viruses, for example, are the smallest biological particles and have sizes of 3–100 nanometers (one billionth of a meter, or nm). Bacteria are larger than viruses and have sizes from slightly less than 1 μm to over 10 μm . Algae and protozoan cysts are even bigger and have sizes from a few μm to a several hundred μm .

Operators are often familiar with the terms *colloidal / suspended particles* and *suspended / dissolved solids*. These terms are based on particle size and sometimes can be confusing. Colloidal particles are particles with at least one of their dimensions less than about 1 μm or 0.5 μm and generally are not filtered out in the suspended solids test. Dissolved solids contain both colloidal particles and the impurities that are in dissolved form. By definition, colloidal particles do not include constituents that are in true dissolved or molecular form, which typically have sizes of less than 1 nm.

Particle size is important in water treatment because it is one of the key factors in determining the settling characteristics of the particle. For example, the settling velocity of a particle is directly proportional to the square of its diameter. Natural particles in the colloidal size range do not settle quickly enough to be removed in sedimentation basins, so they must be agglomerated together into larger particles, i.e., floc. The size of the floc particle is important for effective settling. Particles passing through the sedimentation process (and flocculated particles in direct filtration treatment plants) may be removed in the filtration process. Again, the size of the particle determines whether the particle will be removed in the top layer of the filter or will penetrate deeper into the filter bed.



Source: McTigue and Cornwell 1988.

Figure 1-1 Particulates present in source and finished water

NATURAL ORGANIC MATTER

Origin and Composition of NOM

Natural organic matter, or NOM, is a complex mixture of natural constituents. The primary sources of NOM are the degradation of vegetation in the watershed area and the growth and decomposition of aquatic organisms such as algae and weeds within the water body. NOM is generally classified into two components: humic substances (HSs) and nonhumic substances (nHSs). HSs are usually the major components of NOM in water with humic acids (HAs) and fulvic acids (FAs) as the major fractions. The major fractions of nHSs are proteins, polysaccharides, and carboxylic acids.

Both humic acids and fulvic acids represent a broad class of heterogeneous organic materials. Because of their complexity and heterogeneity, they cannot be well characterized in terms of a specific chemical structure. The most important properties of these substances are molecular weight, functional groups, and charge behavior. HAs and FAs are macromolecules with molecular weights of several hundred or higher. HAs and FAs carry weakly acidic functional groups such as carboxylic and phenolic groups. Dissociation of these functional groups induces negative charges of HS. The macromolecular nature and charge behavior of HAs and FAs play a significant role in increasing the colloidal stability of particles that bind with NOM and in the removal of NOM from water. The presence of NOM in water will induce an additional demand for coagulant dose. Two mechanisms are usually considered for coagulation of NOM. The first is the neutralization of negative charges of NOM followed by precipitation of the NOM. The second is adsorption of NOM onto precipitates formed from coagulants.

The Need to Remove NOM

Although NOM itself does not impose a direct health threat, removal of NOM from water is becoming more important for aesthetic, health, and operational reasons. The initial driving force for removing NOM was its adverse effect on aesthetic water quality because the color, taste, or odor caused by NOM can make water much less palatable for the consumer. For example, the presence of NOM molecules can make water appear yellow or brown. More importantly, however, NOM is now known to be the major precursor for many disinfection by-products (DBPs). The chemical compounds known as DBPs are formed when an oxidant such as chlorine is added to water that contains organic matter. Removal of NOM to reduce the formation of DBPs has become a major focus for water utilities in the past two decades. A coagulation process that is optimized for both particle removal and NOM reduction is known as enhanced coagulation (EC).

NOM also has adverse impacts on the operation of other treatment processes. By reacting with chemical disinfectants to form DBPs, NOM induces a disinfectant demand. Some NOM molecules contain chemical functional groups that can absorb light in the ultraviolet (UV) range and thus reduce the efficiency of UV disinfection facilities. NOM can foul membranes, reducing flux or increasing operating pressure. Short-chain molecules of NOM (e.g., as a result of oxidation) can serve as a food source for microbial growth in filter beds or the distribution system.

Current regulatory requirements for particle removal and NOM reduction are based on a balance between adequate inactivation of microbial pathogens and minimizing the production of DBPs. These requirements were summarized in Table 1-1 earlier in this chapter and are discussed below:

- NOM is regulated under the Disinfectants and Disinfection By-products Rule (D/DBPR), with reduction related to requirements for minimum removal percentages of TOC between the source and finished water. These removal levels range from 15 percent to 50 percent and are based on TOC levels in the source water and the source water alkalinity (Table 1-1).
- Compliance with NOM removal requirements typically indicates that a utility is effectively using its coagulation and filtration processes to significantly reduce the concentrations of DBP precursors and the formation of DBPs.
- Alternative compliance criteria for NOM removal exist (although not shown Table 1-1). These criteria are designed to provide flexibility to water utilities that use source water either with a proven low potential to form DBPs (indicated by low concentrations of TOC, specific ultraviolet absorbance [SUVA], and DBPs) or that have source waters that are not amenable to significant TOC removal as indicated by site-specific bench-scale jar test results.

The key to meeting the challenges set by new regulations will often be maximizing the removal of NOM while ensuring adequate microbial control by both particle removal and disinfection. For many surface waters, coagulant dosages are controlled by NOM concentration rather than by turbidity (Edzwald and Van Benschoten 1990, Pernitsky and Edzwald 2006). NOM can be removed by coagulation through complexation with positively charged coagulant species forming Al-NOM precipitates or by the adsorption of NOM onto the surface of floc particles, allowing removal in subsequent solids separation processes. The charge density of these NOM functional groups is typically 10 to 100 times greater than the charge density of inorganic particles. For example, a water with 10 mg/L of clay turbidity having a negative charge of 0.5 $\mu\text{eq}/\text{mg}$ will have a positive charge demand of 5 $\mu\text{eq}/\text{L}$. In contrast, a water containing only 3 mg/L dissolved organic carbon (DOC) with a negative charge of 10 $\mu\text{eq}/\text{mg}$ will

have a positive charge demand of 30 $\mu\text{eq/L}$, which is six times that of the 10 mg/L clay turbidity example (Edzwald and Van Benschoten 1990). The conversion of dissolved NOM to a solid phase happens quickly and is complete prior to the clarification and filtration process.

As mentioned previously, NOM is a mixture of various organic compounds that are present in water as a result of decay of vegetation, runoff from organic soils, and biological activity. As such, NOM from different water sources will have different characteristics. The concept of specific UV absorbance has been developed as an operational indicator of the nature of NOM and the effectiveness of coagulation for removing NOM, DOC, and DBP precursors (Edzwald and Van Benschoten 1990, Edzwald and Tobiason 1999). SUVA values offer a simple characterization of the nature of the NOM, based on measurements of the UV absorbance at 254 nm and DOC. SUVA is defined as the UV absorbance of a water sample normalized with respect to the DOC concentration. SUVA is normally calculated on samples of raw water prior to the addition of any treatment chemicals. Samples must be filtered in the lab to remove turbidity interferences as described in Standard Method 5910 (APHA et al. 2005). It is expressed in units of m^{-1} of absorbance per mg/L of DOC, or $\text{L/mg C} \cdot \text{m}^{-1}$ and also expressed using the units notation of L/mg-m .

$$\text{SUVA (L/mg C} \cdot \text{m}^{-1}) = [\text{UV}_{254}(\text{cm}^{-1}) \times 100 (\text{cm/m})] / \text{DOC (mg/L)}$$

Guidelines for the interpretation of SUVA values are presented in Table 1-2. For supplies with low SUVA (2 or lower), DOC will not control coagulant dosage. For water supplies with SUVA greater than 2, the amount of NOM typically exerts a greater coagulant demand than the amount of particles. For these waters, the required coagulant dosage increases with increasing DOC concentration.

Optimizing treatment processes to remove NOM and particles and also to control microbiological contaminants may involve setting coagulant doses to achieve NOM removal, reducing coagulation pH, improving mixing conditions, and/or using alternative approaches for oxidation of NOM and inactivation of microorganisms. Water treatment operators need effective tools for quick and accurate assessment of treatment performance and evaluations of alternatives. These tools are described in chapters 2 and 3 of this manual.

Table 1-2 Guidelines on the nature of NOM and expected DOC removals

| SUVA | Composition | Coagulation | DOC Removals |
|------|---|--|---|
| <2 | Mostly nonhumics; low hydrophobicity, low molecular weight | NOM has little influence Poor DOC removals | <25% for alum Potentially higher removals for ferric |
| 2–4 | Mixture of aquatic humics and other NOM; mixture of hydrophobic and hydrophilic NOM; mixture of molecular weights | NOM influences DOC removals should be fair to good for these categories | 25–50% for alum Potentially higher removals for ferric |
| >4 | Mostly aquatic humics; high hydrophobicity, high molecular weight | NOM controls Good DOC removals | >50% for alum Potentially higher removals for ferric |

Source: Edzwald and Tobiason 1999.

PARTICLE STABILITY AND COAGULANT CHEMISTRY

Surface Properties and Colloidal Stability

The surface characteristics of natural particles and their reactions with water and with other solutes in water result in an electrical surface charge being carried by most particles in water. More importantly, the sign of the net charge is usually negative under most conditions in water. The following mechanisms are usually used to explain the charge behavior of particles in water:

Lattice imperfection or isomorphic replacement (intrinsic properties of particles). Lattice imperfection refers to the replacement of atoms in the crystalline lattice (structure) by atoms with different valences. This mechanism is often used to explain the charge behavior of many clay minerals. Clay has a layered structure of silica (SiO_2). During the formation of the structure, if an Al^{3+} atom replaces an Si^{4+} atom, a negative charge develops. Similarly, negative charge develops when an Mg^{2+} atom replaces an Al^{3+} atom in an aluminum oxide crystalline lattice (Al_2O_3).

Ionization of particle surface functional groups (reactions with water). Many particle surfaces contain ionizable functional groups. For example, mineral oxide particles contain surface hydroxyl groups. Biological particles may have surface proteins that contain carboxyl and amino groups. In the presence of water molecules, these surface functional groups can accept or donate protons (H^+), depending primarily on water pH. As a result, the surfaces of particles become charged. In this case, the surface charge is strongly pH dependent, being positive at low pH and negative at high pH. Most natural particles have a negative surface charge at the pH of most natural waters.

Reactions between surface functional groups and other solutes in water (reactions with other solutes). Many cations (such as metals) and anions (such as NOM) in water can react with surface functional groups of particles, resulting in the binding of these ions to the particle surfaces. Interactions other than simple electrostatic interactions are often involved in these processes. Typical examples are hydrophobic interaction, hydrogen bonding, ligand exchange, and covalent bonding. As a result, even anions that have negative charges can bind to negatively charged particles. Binding of cations to a particle makes the particle's surface charge more positive, whereas binding of anions to a particle makes the particle's surface charge more negative. An important example is the binding of NOM onto particle surfaces. Recent research indicated that most particles in water carry some kind of NOM coating on their surfaces, one of the major reasons that most particles in water are negatively charged.

Interactions between particles with similar surface charge result in an electrical repulsive force between them, making them more difficult to aggregate. In colloidal chemistry, a *stable* solution or set of particles is defined as one in which most of the particles have similar charges and thus these particles tend not to aggregate or settle. Chemical pretreatment (coagulation) is therefore needed to reduce or eliminate this repulsion and enhance particle removal by sedimentation and filtration processes. This step is termed *destabilization*.

Use of oxidants to change surface properties of particles. Use of oxidants prior to filtration has been shown to benefit filter performance at numerous plants. Reported benefits include a reduction in filtered water turbidity or particle counts or both, a decrease in turbidity peak during the filter ripening period, and a shorter duration for filter ripening. Oxidants generally used for this purpose are free chlorine and ozone. However, other oxidants such as chlorine dioxide and potassium permanganate exhibit similar benefits. A recent study (Becker et al. 2004) indicated that one of the major mechanisms for these benefits is on the effect of oxidation on particle stability. As mentioned previously, most particles in water carry some kind of NOM coating on their

surfaces. The NOM coating increases particle stability by making the particle's charge more negative and also extending the particle's negative electric field further away from the particle. Mechanistic studies show that oxidation can detach part of the NOM coating from particle surfaces and thereby reduce particle stability. Typically, very low dosages of oxidant and short contact times are enough for these benefits to occur.

At plants where oxidation is an aid to filtration, interruption of oxidation can cause filter performance to deteriorate. Factors to consider related to using oxidants for improving filter performance are cost of the oxidation process, efficacy of the oxidant, and possible detrimental effects of oxidation products, such as formation of assimilable organic matter and bromate by ozone and formation of chlorinated disinfection by-products by chlorine.

Coagulant Chemistry

Aluminum and iron-based coagulants such as aluminium sulfate (alum), polyaluminum chloride (PACl), and ferric chloride react with water to form charged and dissolved metal-hydroxide species, as well as solid-phase metal-hydroxide precipitates (floc particles). These reactions consume alkalinity in the raw water and reduce the pH. Alum and ferric coagulants are more acidic than PACls and therefore result in greater pH depression after addition. For PACls, alkalinity consumption is related to basicity. Higher-basicity PACls will consume less alkalinity than low- or medium-basicity ones.

The charge on the dissolved coagulant species and the relative amount of floc formed are a function of pH. Therefore, the pH at which coagulation occurs is one of the most important parameters for proper coagulation performance. For alum and PACls, the best coagulation performance is generally seen at pH values that are close to the pH of minimum solubility of the coagulant. This controls dissolved Al residuals, as well as maximizing the presence of floc particles. Acid or base addition is often used after coagulant addition to control pH.

The solubility characteristics of various coagulants, and therefore the pH range at which they are most effective, are important properties of the coagulants. Solubility refers to the maximum concentration of dissolved species that can exist in solution before precipitation. This concentration varies with temperature and pH. The pH of minimum solubility represents the pH at which the concentration of dissolved coagulant species is a minimum. This is important from a treatment perspective, as this pH also corresponds to the point at which the maximum amount of solid floc species is formed.

Table 1-3 Summary of coagulant solubility

| Coagulant | Minimum Solubility 20°C | | Minimum Solubility 5°C | |
|---------------------------------------|-------------------------|---------|------------------------|---------|
| | pH | µg/L Al | pH | µg/L Al |
| Alum | 6.0 | 16 | 6.2 | 3 |
| Polyaluminum sulfate (PAS) | 6.0 | 28 | 6.4 | 6 |
| PACl low-basicity nonsulfated (LBNS) | 6.2 | 27 | 6.7 | 4 |
| PACl medium-basicity sulfated (MBS) | 6.3 | 29 | 6.5 | 4 |
| PACl high-basicity nonsulfated (HBNS) | 6.4 | 36 | 6.8 | 9 |
| PACl high-basicity sulfated (HBS) | 6.4 | 52 | 6.9 | 5 |
| Aluminum chlorohydrate (ACH) | 6.7 | 101 | 7.6 | 53 |
| FeCl ₃ | 8.7 | 0.006 | — | — |

Source: Pernitsky and Edzwald 2003.

The minimum solubility (concentration) and pH of minimum solubility for several common coagulants are shown in Table 1-3. As can be seen in this table, the minimum solubility and pH of minimum solubility differ for the various chemical coagulants. PACls are more soluble and have a higher pH of minimum solubility than alum. Polyaluminum sulfates have solubility characteristics similar to alum. Ferric coagulants are much less soluble than aluminium-based ones. This means that Fe-based coagulants can be used over a much greater pH range without worrying about dissolved metal concentrations in the finished water. The pH of minimum solubility for Fe(III) is near pH 8.8. However, unlike Al-based coagulants, FeCl_3 is not an effective water treatment coagulant at its pH of minimum solubility because of the weak positive charge of the $\text{Fe}(\text{OH})_2^+$ species present at that pH. Ferric coagulants have, however, been used successfully in secondary clarification of lime softening process basin effluent at softening plants that treat surface waters. More effective performance is seen at lower pH, as low as pH 5.5, where more positively charged species are present. A case study, "Conversion From Alum to Ferric Sulfate at the Addison-Evans Water Treatment Plant, Chesterfield County, Va." is presented in chapter 7.

For all of the metal coagulants, it is important to note that the pH of minimum solubility increases as temperature decreases, as shown in Table 1-3. This is especially important in cold climates because of the wide range in raw water temperatures experienced. For example, the pH of minimum solubility for alum increases from 6.0 at 20°C to 6.2 at 5°C. Over that same range, the pH of minimum solubility for high-basidity PACl changes from 6.4 to 6.8.

Particles can be destabilized through the addition of coagulants/flocculants by three major mechanisms (shown in Figure 1-2).

Adsorption and Charge Neutralization

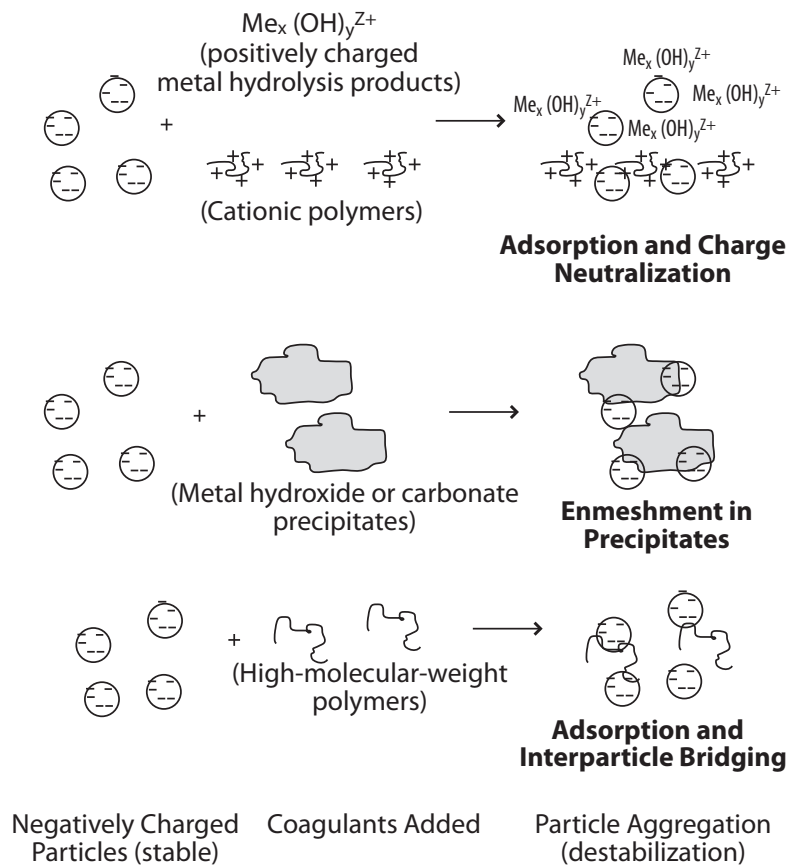
When metal coagulants are added to water, several hydrolysis species are formed. Some of these species are positively charged, depending primarily on water pH. These positively charged species will attach to negatively charged particles and reduce or neutralize the particles' negative charges. This charge neutralization results in a reduction or elimination of the electric repulsion between particles. Cationic polyelectrolytes also can reduce the negative charges and repulsive forces. Note, however, that if the dosage of a cationic polymer is substantially greater than that needed to neutralize the negative charges on particles, then the particles can become positively charged and restabilized, a condition that hinders particle removal.

Enmeshment in a Precipitate (Sweep Floc)

When metal coagulants are added to water, precipitates of metal hydroxide or metal carbonate may form, depending on the dose and water chemistry. Particles can be enmeshed into these amorphous precipitates (coagulant flocs) and subsequently removed by settling and filtration of the flocs. Thus for the sweep floc mechanism, as opposed to the charge neutralization mechanism, the use of dosages of metal coagulants larger than those needed to neutralize the surface charges of particles does not hinder particle removal, because the coagulant will precipitate and can enmesh the particles.

Adsorption and Interparticle Bridging

When high-molecular-weight polymers are added to water, part of the polymeric chains can attach to the surface of one particle with the remaining length of the chains extending into the solution. If these extended chains find other particles with vacant sites not



Courtesy of Kwok-Keung Au.

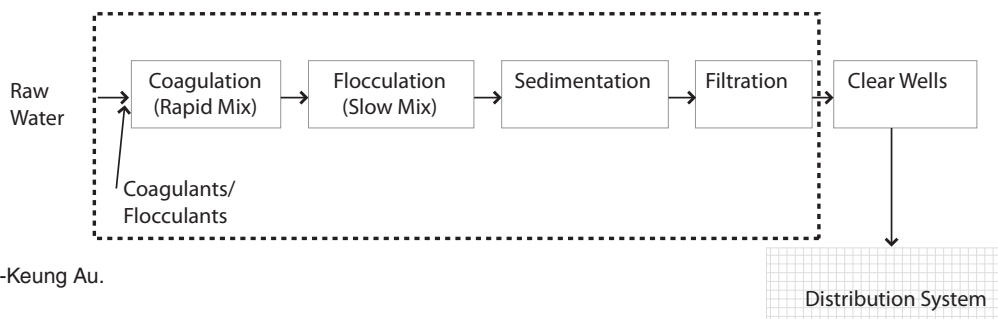
Figure 1-2 Coagulation (destabilization) mechanisms for particulate contaminants

yet attached by other polymeric chains, bridges between particles could form, resulting in particle destabilization and floc formation. Overdose of polymer may result in restabilization because it becomes difficult for the extended polymer molecule to find available vacant sites for adsorption.

Double-layer compression is often cited as the fourth mechanism of coagulation. However, this process is not a dominant mechanism in the chemical coagulation of most raw waters.

PARTICLE AND NOM REMOVAL PROCESSES

The objectives of particle removal and NOM reduction typically cannot be accomplished in a single treatment step. Rather, several plant processes work together to achieve this goal. Specifically, coagulation/mixing, flocculation, sedimentation, and filtration, schematically shown in Figure 1-3, are all interdependent on each other to produce a water of high quality. This section provides a brief overview of each process and describes the mechanisms by which each contributes to particle and NOM removal. These processes are described briefly in this section and in greater detail in chapter 4 (Flocculation and Clarification Processes) and chapter 5 (Filtration).



Courtesy of Kwok-Keung Au.

Figure 1-3 Treatment train (from coagulation to filtration)

Mixing/Coagulation

As described previously, many of the particles that occur in raw water supplies have negative electrical charges and are of such size and density that they will not settle easily in the time available in water treatment plant clarification processes. Therefore, positively charged metal coagulants or polymers are used to decrease the extent of the negative surface charge on the particles so that when they come in contact with each other they can stick together and form larger particles (flocs).

Generally, the chemical reactions associated with coagulation occur very quickly and thus the coagulant must be mixed into the raw water as quickly and efficiently as possible. This initial mixing is often called rapid mixing or flash mixing. The hydraulic retention time in a flash mix process ranges from <1 sec to 30 sec. During this time, the coagulant and any other associated chemicals (e.g., pH and alkalinity control) are dispersed throughout the raw water. The dose of chemicals and the required mixing intensities for optimum coagulation can be determined using bench-scale experiments such as jar tests as described in chapter 2. Rapid mixing is discussed in chapter 4. One exception to the very rapid coagulation reaction is the slower action of alum in very cold water (about 5°C or colder). To accommodate the slower reactions, some water utilities use coagulants other than aluminum sulfate for coagulation of such water (Logsdon et al. 2002).

Flocculation

The next treatment process after coagulation typically is flocculation. The main objective of flocculation is to bring together the particle solids created and/or conditioned in the coagulation step, which ultimately changes the size distribution of the particles. Essentially, a large number of small particles are transformed into a smaller number of larger particles. Traditionally, the objective of flocculation has been to produce particles large enough and dense enough to settle in the clarifier (sedimentation basin). Since the 1980s, several plants have replaced conventional sedimentation with filtration without clarification (direct filtration) or dissolved air flotation (DAF). For these types of treatment processes, the goal of flocculation and floc size production is modified since both of these processes work well with flocs that are considerably smaller than the size of flocs needed for sedimentation. For direct filtration and DAF plants, shorter flocculation times are used as compared to the times employed at plants with conventional sedimentation basins.

Sedimentation/Clarification

After the particles have been preconditioned in the coagulation process and brought together into clumps (flocs) in the flocculation process, physical removal of the solids can be accomplished by sedimentation or by flotation. The hydraulic retention time of a conventional sedimentation basin ranges from 2 to 4 hr. Since the late 1960s, studies of the sedimentation process have led to a variety of approaches that can accomplish sedimentation in times considerably shorter than 2 to 4 hr. Clarification, whether by sedimentation or flotation, is necessary for effective filtration of many source waters because of the excessively high load of solids (particulate matter, including floc formed by coagulant chemical) that would be applied to the filters in the absence of a clarification process.

Filtration

After clarification, water is treated by filtration to remove those particles that were not removed in the clarification process. As water treatment was being developed in the United States, experimental work in Louisville, Ky., and Cincinnati, Ohio, in the late 1890s and early 1900s showed that turbid waters could be treated successfully by chemical coagulation, sedimentation, and rapid sand filtration. About the same time, studies at Pittsburgh, Pa., showed the importance of using an adequate dosage of coagulant chemical to attain successful treatment with rapid sand filters. Coagulation, clarification, and rapid sand filtration became known as conventional water treatment, and this process train was shown to significantly reduce both turbidity and bacteria in water. Today, the performance of granular media filters reflects both source water quality and the changes to the source water induced by added chemicals (pretreatment chemistry). Filtration in drinking water treatment is not just a physical straining process (like that in a coffee filter) by the granular media particles. Attachment of the particles to the filter media is the primary form of target constituent removal. Thus, filtration is a physical and chemical process in which the effectiveness of the particle removal is determined by several variables, including:

- Type of filter media (size, depth, material)
- Water chemistry
- Surface chemistry of the particles (as conditioned by coagulation and flocculation)
- Surface chemistry of the filter media.

During filtration, particles must be transported to the surfaces of the filter media, and the particles must attach to the media surface for removal to occur. Both hydrodynamics and chemistry are important determinants of success. Design criteria most often specify filtration rate, media size, and bed depth. Pretreatment (coagulation) chemistry is the most important factor affecting particle removal in granular media filters. Without proper coagulation, efficient particle removal will not occur.

Plant operators have direct control over the coagulation process (chemical selection and dosing), flocculation (mixing energy), filtration (filter run times, backwashing), and, to some extent, flow rates through each of these processes. Thus, operators have the ultimate responsibility to ensure effective particle and NOM removal.

MULTIPLE BARRIER APPROACH

Multiple treatment processes must be incorporated into a water treatment plant to achieve high-quality finished water. Combined with disinfection, clarification and filtration processes provide multiple barriers to the passage of particles, pathogens, and dissolved constituents into the public water supply. This multiple barrier approach was formally established in the Surface Water Treatment Rule for microbial control and removal of contaminants, and specifically referenced the coagulation/filtration processes, primary disinfection as defined by the CT concept, and maintenance of microbial control through the distribution system. The simple combination of coagulation, sedimentation, filtration, and disinfection constituted an early multiple-barrier approach to microbial control in drinking water technology.

As more contaminants, including pathogens other than bacteria, were discovered in raw water supplies, drinking water treatment objectives were expanded. The drinking water processes of coagulation, flocculation, sedimentation, and filtration must now be optimized to meet multiple treatment objectives. Further, new advanced technologies are being developed and may be incorporated within the conventional treatment process train.

One of the more effective methods of meeting new regulatory requirements is through a “systems approach” that recognizes that all unit processes are interrelated, so what impacts one will also impact the others. Analysis under this systems approach reveals that the conventional treatment processes work together to remove unwanted components from the water, including particles, NOM, color, microorganisms, iron, manganese, and objectionable tastes and odors. Coagulation and flocculation create flocs of suspended particles and convert organic and/or inorganic material from the dissolved phase into the particulate phase. These conditioned particles are subsequently removed by either clarification or filtration.

Much of the effort to optimize conventional treatment focuses on coagulation chemistry as the single most important factor affecting treatment plant performance. This principle is based on the fact that if the pretreatment chemistry is wrong, none of the other downstream processes will work well. Managing the coagulation process to remove both particles and NOM is an example of the challenges that may be encountered when it is necessary to adjust pretreatment chemistry to achieve multiple objectives.

PROCESS CONTROL STRATEGIES

Effective process control strategies are based on theory, experience, practical knowledge of the source water, and performance characteristics of the treatment plant. Water treatment plant operators should be familiar with routine plant operations, special operations (such as startup and shutdown of individual processes), and the preventive maintenance required for each treatment process. On a daily basis, operators may be responsible for monitoring process performance, analyzing water quality (raw, settled, and finished), adjusting process controls, and inspecting plant facilities. Finally, one of the most important operator tasks is record-keeping. Maintaining a daily operation log, including keeping a diary that provides an accurate day-to-day account of plant operations, provides a historical record of events for future reference. Recording all analytical results needed to complete reports that are required by local regulatory agencies supports the regulatory compliance effort and also enables the utility to have long-term records of its water quality. Water quality monitoring for process control is discussed in chapter 3.

Membrane Filtration

Membranes are considered an alternative filtration process and consist of polymeric layers with very small pores that physically strain particles, pathogens, and so on from the influent water. Membranes are classified according to both the pore size and the amount of pressure required to force the water through the membranes. Low-pressure membranes (microfiltration and ultrafiltration) have larger pore sizes and are used for filtration, while high-pressure membranes (nanofiltration and reverse osmosis) have much smaller pore sizes and are used to modify the chemical characteristics of water being treated. Because low-pressure membranes rely on a physical removal process, i.e., straining, the size of the pores determines what contaminants can be removed from the process. Ultrafiltration membranes can remove a portion of the smaller particles that could pass microfiltration membranes. These membranes can be used as a replacement for coagulation, flocculation, sedimentation, and filtration, or can be used as a polishing step behind any combination of these processes. Because microfiltration and ultrafiltration membranes do not remove dissolved constituents such as arsenic or iron in groundwater or NOM in the form of dissolved organic carbon, some form of pretreatment such as coagulation, and perhaps clarification, may be needed prior to microfiltration or ultrafiltration if removal of dissolved substances is necessary. In this situation, information contained in this manual can be helpful for optimizing the pretreatment processes.

REFERENCES

- American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). 2005. *Standard Methods for the Analysis of Water and Wastewater*. 21st ed. Washington, D.C.: APHA.
- Becker, W.C., C.R. O'Melia., K.-K. Au, and J.S. Young Jr. 2004. *Using Oxidants to Enhance Filter Performance*. Denver, Colo.: Awwa Research Foundation and AWWA.
- Edzwald, J.K., and J.E. Van Benschoten. 1990. Aluminum Coagulation of Natural Organic Matter. In *Chemical Water and Wastewater Treatment*, ed. H. Halan and R. Klute, 341–359. New York: Springer-Verlag.
- Edzwald, J.K., and J.E. Tobiason. 1999. Enhanced Coagulation: USA Requirements and a Broader View. In *Removal of Humic Substances From Water*. Trondheim, Norway: IAWQ/IWSA Joint Specialist Group on Particle Separation.
- Logsdon, G.S., A.F. Hess, M.J. Chipps, and A.J. Rachwal. 2002. *Filter Maintenance and Operations Guidance Manual*. Denver, Colo.: Awwa Research Foundation and AWWA.
- McTigue, N.E., and D. Cornwell. 1988. The Use of Particle Counting for the Evaluation of Filter Performance. In *Proc. AWWA Annual Conference, Orlando, Fla.* Denver, Colo.: AWWA.
- Pernitsky, D.J., and J.K. Edzwald. 2003. Solubility of Polyaluminum Coagulants. *Journal of Water Supply: Research and Technology-AQUA*, 52(6):395–406.
- Pernitsky, D.J., and J.K. Edzwald. 2006. Selection of Alum and Poly-aluminum Coagulants: Principles and Applications. *Journal of Water Supply: Research and Technology-AQUA*, 55(2):121–141.