

**Appendix B –
Background Information on Chemical Treatment**

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This information was obtained from the 2005 Stormwater Management Manual for Western Washington, including updates.

D.1 Coagulation and Flocculation

Coagulation and flocculation have been used for over a century to treat water. It is used less frequently for the treatment of wastewater. The use of coagulation and flocculation for treating stormwater is a very recent application. Experience with the treatment of water and wastewater has resulted in a basic understanding of the process, in particular factors that affect performance. This experience can provide insights as to how to most effectively design and operate similar systems in the treatment of stormwater.

Fine particles suspended in water give it a milky appearance, measured as turbidity. Their small size, often much less than 1 μm in diameter, give them a very large surface area relative to their volume. These fine particles typically carry a negative surface charge. Largely because of these two factors, small size and negative charge, these particles tend to stay in suspension for extended periods of time. Thus, removal is not practical by gravity settling. These are called stable suspensions. Polymers, as well as inorganic chemicals such as alum, speed the process of clarification. The added chemical destabilizes the suspension and causes the smaller particles to agglomerate. The process consists of three steps: coagulation, flocculation, and settling or clarification. Each step is explained below as well as the factors that affect the efficiency of the process.

Coagulation is the first step. It is the process by which negative charges on the fine particles that prevent their agglomeration are disrupted. Chemical addition is one method of destabilizing the suspension, and polymers are one class of chemicals that are generally effective. Chemicals that are used for this purpose are called coagulants. Coagulation is complete when the suspension is destabilized by the neutralization of the negative charges. Coagulants perform best when they are thoroughly and evenly dispersed under relatively intense mixing. This rapid mixing involves adding the coagulant in a manner that promotes rapid dispersion, followed by a short time period for destabilization of the particle suspension. The particles are still very small and are not readily separated by clarification until flocculation occurs.

Flocculation is the process by which fine particles that have been destabilized bind together to form larger particles that settle rapidly. Flocculation begins naturally following coagulation, but is enhanced by gentle mixing of the destabilized suspension. Gentle mixing helps to bring particles in contact with one another such that they bind and continually grow to form "flocs." As the size of the flocs increases they become heavier and tend to settle more rapidly.

Clarification is the final step, settling of the particles. Particle density, size and shape are important during settling. Dense, compact flocs settle more readily than less dense, fluffy flocs. Because of this, flocculation to form dense, compact flocs is particularly important during water treatment. Water temperature is important during settling. Both the density and viscosity of water are affected by temperature; these in turn affect settling. Cold temperatures increase viscosity and density, thus slowing down the rate at which the particles settle.

The conditions under which clarification is achieved can affect performance. Currents can affect settling. Currents can be produced by wind, by differences between the temperature of the incoming water and the water in the clarifier, and by flow conditions near the inlets and outlets. Quiescent water such as that which occurs during batch clarification provides a good environment for effective performance as many of these factors become less important in comparison to typical sedimentation basins. One source of currents that is likely important in batch systems is movement of the water leaving the clarifier unit. Given that flocs are relatively small and light the exit velocity of the water must be as low as possible. Sediment on the bottom of the basin can be resuspended and removed by fairly modest velocities.

Coagulants, such as polymers, are large organic molecules that are made up of subunits linked together in a chain-like structure. Attached to these chain-like structures are other groups that carry positive or negative charges, or have no charge. Polymers that carry groups with positive charges are called cationic, those with negative charges are called anionic, and those with no charge (neutral) are called nonionic.

Cationic polymers can be used as coagulants to destabilize negatively charged turbidity particles present in natural waters, wastewater and stormwater. Aluminum sulfate (alum) can also be used as this chemical becomes positively charged when dispersed in water. In practice, the only way to determine whether a polymer is effective for a specific application is to perform preliminary or on-site testing.

Polymers are available as powders, concentrated liquids, and emulsions (which appear as milky liquids). The latter are petroleum based, which are not allowed for construction stormwater treatment. Polymer effectiveness can degrade with time and also from other influences. Thus, manufacturers' recommendations for storage should be followed. Manufacturer's recommendations usually do not provide assurance of water quality protection or safety to aquatic organisms. Consideration of water quality protection is necessary in the selection and use of all polymers.

D.1.1 Application Considerations

Application of coagulants at the appropriate concentration or dosage rate for optimum turbidity removal is important for management of chemical cost, for effective performance, and to avoid aquatic toxicity. The optimum dose in a

given application depends on several site-specific features. Turbidity of untreated water can be important with turbidities greater than 5,000 NTU. The surface charge of particles to be removed is also important. Environmental factors that can influence dosage rate are water temperature, pH, and the presence of constituents that consume or otherwise affect polymer effectiveness. Laboratory experiments indicate that mixing previously settled sediment (floc sludge) with the untreated stormwater significantly improves clarification, therefore reducing the effective dosage rate. Preparation of working solutions and thorough dispersal of polymers in water to be treated is also important to establish the appropriate dosage rate.

For a given water sample, there is generally an optimum dosage rate that yields the lowest residual turbidity after settling. When dosage rates below this optimum value (under dosing) are applied, there is an insufficient quantity of coagulant to react with, and therefore destabilize, all of the turbidity present. The result is residual turbidity (after flocculation and settling) that is higher than with the optimum dose. Overdosing, application of dosage rates greater than the optimum value, can also negatively impact performance. Again, the result is higher residual turbidity than that with the optimum dose.

For mixing in coagulation/flocculation, the G-value, or just "G", is often used as a measure of the mixing intensity applied during coagulation and flocculation. The symbol G stands for "velocity gradient", which is related in part to the degree of turbulence generated during mixing. High G-values mean high turbulence, and vice versa. High G-values provide the best conditions for coagulant addition. With high G's, turbulence is high and coagulants are rapidly dispersed to their appropriate concentrations for effective destabilization of particle suspensions.

Low G-values provide the best conditions for flocculation. Here, the goal is to promote formation of dense, compact flocs that will settle readily. Low G's provide low turbulence to promote particle collisions so that flocs can form. Low G's generate sufficient turbulence such that collisions are effective in floc formation, but do not break up flocs that have already formed.

Design engineers wishing to review more detailed presentations on this subject are referred to the following textbooks:

Fair, G., J. Geyer and D. Okun, *Water and Wastewater Engineering*, Wiley and Sons, NY, 1968.

American Water Works Association, *Water Quality and Treatment*, McGraw-Hill, NY, 1990.

Weber, W.J., *Physiochemical Processes for Water Quality Control*, Wiley and Sons, NY, 1972.

D.1.2 Polymer Batch Treatment Process Description

Stormwater is collected at interception point(s) on the site and is diverted by gravity or by pumping to a storage pond or other holding area. The stormwater is stored until treatment occurs. It is important that the holding pond be large enough to provide adequate storage.

The first step in the treatment sequence is to check the pH of the stormwater in the storage pond. The pH is adjusted by the application of acid or base until the stormwater in the storage pond is within the desired pH range. When used, acid is added immediately downstream of the transfer pump. Typically sodium bicarbonate (baking soda) is used as a base, although other bases may be used. When needed, base is added directly to the storage pond. The stormwater is recirculated with the treatment pump to provide mixing in the storage pond. Initial pH adjustments should be based on daily bench tests. Further pH adjustments can be made at any point in the process.

Once the stormwater is within the desired pH range, the stormwater is pumped from the storage pond to a treatment cell as polymer is added. The polymer is added upstream of the pump to facilitate rapid mixing.

After polymer addition, the water is kept in a lined treatment cell for clarification of the sediment-floc. In a batch mode process, clarification typically takes from 30 minutes to several hours. Prior to discharge samples are withdrawn for analysis of pH and turbidity. If both are acceptable, the treated water is discharged.

Several configurations have been developed to withdraw treated water from the treatment cell. The original configuration is a device that withdraws the treated water from just beneath the water surface using a float with adjustable struts that prevent the float from settling on the cell bottom. This reduces the possibility of picking up sediment-floc from the bottom of the pond. The struts are usually set at a minimum clearance of about 12 inches; that is, the float will come within 12 inches of the bottom of the cell. Other systems have used vertical guides or cables which constrain the float, allowing it to drift up and down with the water level. More recent designs have an H-shaped array of pipes, set on the horizontal.

This scheme provides for withdrawal from four points rather than one. This configuration reduces the likelihood of sucking settled solids from the bottom. It also reduces the tendency for a vortex to form. Inlet diffusers, a long floating or fixed pipe with many small holes in it, are also an option.

Safety is a primary concern. Design should consider the hazards associated with operations, such as sampling. Facilities should be designed to reduce slip hazards and drowning. Tanks and ponds should have life rings, ladders, or steps extending from the bottom to the top.

D.2 Adjustment of pH and Alkalinity

The pH must be in the proper range for the polymers to be effective, which is 6.5 to 8.5 for Calgon CatFloc 2953, the most commonly used polymer. As polymers tend to lower the pH, it is important that the stormwater have sufficient buffering capacity. Buffering capacity is a function of alkalinity. Without sufficient alkalinity, the application of the polymer may lower the pH to below 6.5. A pH below 6.5 not only reduces the effectiveness of the polymer, it may create a toxic condition for aquatic organisms. Stormwater may not be discharged without readjustment of the pH to above 6.5. The target pH should be within 0.2 standard units of the receiving water pH.

Experience gained at several projects in the City of Redmond has shown that the alkalinity needs to be at least 50 mg/L to prevent a drop in pH to below 6.5 when the polymer is added. Baking soda has been used to raise both the alkalinity and the pH. Although lime is less expensive than baking soda, if overdosed lime can raise the pH above 8.5 requiring downward adjustment for the polymer to be effective. Baking soda has the advantage of not raising the pH above 8.3 regardless of the amount that is added. Experience indicates that the amount of baking soda sufficient to raise the alkalinity to above 50 mg/L produces a pH near neutral or 7.

Alkalinity cannot be easily measured in the field. Therefore, conductivity, which can be measured directly with a hand-held probe, has been used to ascertain the buffering condition. It has been found through local experience that when the conductivity is above about 100 μ S/cm the alkalinity is above 50 mg/L. This relationship may not be constant and therefore care must be taken to define the relationship for each site.

Experience has shown that the placement of concrete has a significant effect on the pH of construction stormwater. If the area of fresh exposed concrete surface is significant, the pH of the untreated stormwater may be considerably above 8.5. Concrete equipment washwater shall be controlled to prevent contact with stormwater. Acid may be added to lower the pH to the background level pH of the receiving water. The amount of acid needed to adjust the pH to the desired level is not constant but depends upon the polymer dosage, and the pH, turbidity, and alkalinity of the untreated stormwater. The acid commonly used is sulfuric although muriatic and ascorbic acids have been used. Pelletized dry ice has also been used and reduces the safety concerns associated with handling acid.

Note: The Stormwater Management Manual for Western Washington has recently added BMPs for chemical treatment and sand filtration, pH neutralization (carbon dioxide), and pH control.

