

# Chemical coagulants and flocculants

## SEDIMENT CONTROL TECHNIQUE

Type 1 System	✓	Sheet Flow	✓	Sandy Soils	[1]
Type 2 System		Concentrated Flow	✓	Clayey Soils	✓
Type 3 System		Instream Works		Dispersive Soils	✓

[1] Chemical treatment of 'sandy soils' may be required if the dispersive clay fraction contained within the soil is sufficient to cause undesirable turbidity within discharged waters.

## 1. Introduction

Coagulants and Flocculants perform an important function in the operation of sediment basins. The fact sheet describes why they are needed, the coagulation and flocculation process and also provides guidance and a process for product and dosing system selection for use with sediment basins.

## 2. Clay and colloids

Clay is the predominant particle type found in suspension within runoff captured by sediment basins. Clay particles are extremely small (less than 0.002 mm in size) and will not settle readily, if at all, even in still water. The small size of these particles means that they have an extremely high surface area relative to the volume of the particle. Soil colloids are made up of the smallest particles of humus and clay in the soil. Only particles less than 0.001 mm are officially defined as colloids. Humus particles are tiny pieces of organic matter and are known as 'organic colloids'. The clay particles are known as 'inorganic colloids'.

When negatively charged clay particles and other colloids are suspended in water, they tend to repulse each other, much the same way similar poles of two magnets repel each other. The cumulative effect of the repulsion of a vast number of small particles prevents their aggregation into larger, heavier particles that would settle more readily.

Colloids (which includes clay particles) remain suspended in water because:

- Colloids have a very large surface area relative to their mass.
- Colloids typically have a static electric charge. Most colloidal particles in water have a negative charge.
- Static charge is a surface effect. The greater the surface area relative to the particle mass, the greater the effect of the charge.
- The mass of the particles is small enough that even Brownian motion is sufficient to 'stir' the clay particles in suspension.
- The colloids cannot agglomerate into larger particles and settle because they repel one another.

**Table 1 – Particle Size versus Settling Rate**

Particle Diameter - mm	Example	Total Surface Area	Time to Settle 1m
1	Coarse Sand	31.4 cm <sup>2</sup>	9.84 seconds
0.1	Fine Sand	314.2 cm <sup>2</sup>	2.08 minutes
0.01	Silt	0.314 m <sup>2</sup>	1.80 hours
0.001	Clay	3.13 m <sup>2</sup>	7.52 days
0.0001	Colloid	31.8 m <sup>2</sup>	2.07 years

[1] Adapted from Water Quality and Treatment, McGraw-Hill, 3rd edition, 1971

[2] Surface Area based on a total mass of 1.386 grams in the system

[3] Values provided are not reflective of expected times in sediment basins

## 2. Coagulants and Coagulation

A coagulant is utilised to neutralise or destabilise the charge on clay or colloidal particles. Most clay particles in water are negatively charged and therefore any positive ion (cation) can be used as a coagulant. Coagulants may be classified as being inorganic or organic coagulants. Inorganic coagulants include sodium, calcium, aluminium and iron cationic coagulants. Organic coagulants (typically man made) operate similarly to inorganic coagulants through charge neutralisation except the positive charge most commonly comes from an amine (NH<sub>4</sub><sup>+</sup>) group attached to the coagulant molecule.

A sodium compound (like sodium hydroxide), contributes a monovalent ion, Na<sup>+</sup>. A calcium compound (like calcium sulfate) contributes a divalent ion, Ca<sup>2+</sup>. Aluminium and iron coagulants (like aluminium chlorohydrate (ACH) and ferric chloride) contribute trivalent aluminium ions, Al<sup>3+</sup> and trivalent iron ions, Fe<sup>3+</sup> respectively. Schultz in 1882 and Hardy in 1900, demonstrated the greater the charge of the cation, the greater the effectiveness of charge neutralisation. The Schultz-Hardy Rule indicates the relative effectiveness for divalent vs. trivalent ions is in the ratio of 100:1000 respectively. Therefore, a trivalent aluminium ion will be 10 times more effective in charge neutralisation than the divalent calcium ion. Thus aluminium compounds are most often used as coagulants. Calcium salts, such as calcium sulphate or calcium chloride, can achieve coagulation but are substantially less effective than aluminium compounds.

There is always the possibility of overdosing with coagulants and building up excess positive charge, hence applying within the optimum dosage range is critical. When a cationic coagulant is overdosed the clay and colloidal particles will take on a positive charge and repel each other and limit any settling. The dosage range of a coagulant will vary depending on site water chemistry. Different coagulants also have an optimum pH range over which they are effective and pH buffering may be required depending on the coagulant and water chemistry.

Charge neutralisation in water can occur very rapidly therefore mixing is important for effective treatment of turbid water. The flocs generated by coagulation are generally small and compact. They can also be broken down under high velocity or high shear conditions.

### pH and Alkalinity

Sometimes the term "alkaline" is used instead of "basic" and often "alkaline" is confused with "alkalinity". The pH and alkalinity of a water solution is different. pH is a measure of the concentration of hydrogen ions (H<sup>+</sup>) in water or other liquids. The outcome of a pH-measurement is determined by a consideration between the number of H<sup>+</sup> ions and the number of hydroxide (OH<sup>-</sup>) ions. When the number of H<sup>+</sup> ions equals the number of OH<sup>-</sup> ions, the water is neutral. It will then have a pH of about 7.

Alkalinity is a measure of the water's ability to neutralize acidity. An alkalinity test measures the level of bicarbonates, carbonates, and hydroxides in water and test results are generally expressed as ppm of calcium carbonate (CaCO<sub>3</sub>). With aluminium-based coagulants, the metal ion is hydrolysed to form aluminium hydroxide as well as hydrogen ions. The hydrogen ions will react with the alkalinity of the water and in the process decrease the pH. In situations where there isn't much alkalinity present to start with, the use of alkalinity increasers is required. Common alkalinity increasers include calcium and sodium compounds including calcium hydroxide and sodium hydroxide.

### Basicity

In aluminium coagulants, basicity describes the amount of hydroxide (or OH<sup>-</sup> groups) associated with the aluminium aggregates. It is defined by the equation: Basicity = [OH<sup>-</sup>]/(3 x [Al]). Basicity describes if a coagulant is hydroxylated (pre-hydrolysed). If a coagulant is hydroxylated it will form fewer hydrogen ions in the reaction with water and hence the higher the basicity of a coagulant, the lower the impact it will have on dosed water pH. In simple terms a high basicity coagulant starts with hydroxide (OH<sup>-</sup>) so during the reaction it requires less hydroxide from the water solution, will therefore create fewer hydrogen ions and hence has less impact on pH. During the reaction with water Alum (Aluminium sulfate) will form six hydrogen ions, Poly-aluminium chloride (PAC) three hydrogen ions, and ACH a single hydrogen ion. As such, Alum will tend to cause a more significant decrease in pH (i.e. increase the acidity) than PAC or ACH. This reaction explains the effect these coagulants will have on water pH.

### 3. Flocculation

Flocculation is a process of contact and adhesion whereby dispersed particles form larger-size clusters. Flocculation can occur through the use of a coagulant, flocculant or both. Coagulants achieve flocculation through charge neutralisation whereas flocculants physically bind clay and colloidal particles together.

The use of natural and synthetic polymeric flocculants can be used to generate larger, more stable flocs and may reduce treatment times. This is achieved by bringing dispersed particles together, increasing the effective particle size. Flocculants can be used alone, or in combination with coagulants.

Flocculants may consist of anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) charged functional groups. Charged flocculants are also referred to as polyelectrolytes.

The water chemistry variables that influence polyelectrolyte flocculation are complex, and include, but are not limited to, pH, temperature, ionic strength, dissolved salts concentration and composition, and turbidity.

The nature of the flocculant used can have a significant effect on the effectiveness of flocculation. Charge density, molecular weight and the overall chemical properties relate to the ability of the polymer to participate in hydrophilic (absorbs) or hydrophobic (repels) binding interactions. These interactions play a significant role in flocculant efficacy and subsequent solids separation and management.

Cationic flocculants can improve the speed of turbid water treatment through bridging and/or electrostatic patch effects. Requirements of bridging flocculants are that they be strongly adsorbed onto the particles, and that they are capable of spanning the gap between the particles. Natural bio-polymers and synthetic polymers of high molecular weight are long enough for one end to adsorb onto one particle and the other end onto a second particle. Higher molecular weight polymers will adsorb on several particles at once, forming a three-dimensional matrix. With bridging polymers, generally the higher the molecular weight, the better the flocculant.

Natural bio-polymers are derived from plant starches, bacterial gums and chitosan. Synthetic polymers are sourced from polyacrylamide (PAM) and its derivatives.

## 4. Ecotoxicity

The by-products of coagulants and flocculants can, in certain circumstances, become toxic to aquatic life. A high or low water pH is often the trigger for the release of these materials in a toxic form.

### (i) Calcium products

Gypsum (calcium sulphate), the most commonly used coagulant, has a very low solubility (approximately 250 g / 1,000 L of water) and this is one of the reasons why it is relatively slow to act in most situations (i.e. days rather than hours). Because it is relatively cheap, and it is considered non-toxic, over-dosing of basins is common. Whilst only a low quantity would be released from the basin with the treated water (due to its slow solubility), its bi-products are potentially complex, and its toxicity must be considered unknown for all situations.

Calcium chloride is more expensive per unit of calcium than gypsum, but dissolves readily and acts more quickly. Because of these factors, over-dosing is of less concern, and the bi-product (chloride ions), is considered relatively innocuous in most environments however excessive use can result in EC increases.

There is limited published data on the aquatic ecotoxicity of calcium based coagulants such as calcium sulphate and calcium chloride.

### (ii) Aluminium products

It is generally accepted that dissolved aluminium at a concentration between 0.050 and 0.100 mg/L and a pH between 6.5 and 8.0 presents little threat of toxicity. However, at lower pH, the toxicity increases with an effect of possible major concern being the coagulation of mucus on the gills of fish. After the addition of aluminium coagulants to water containing dissolved and/or suspended matter, dissolved aluminium ions are rapidly incorporated into microscopic aluminium hydroxide and aluminium phosphate precipitates. As they form these precipitates, they combine with phosphorus, suspended solids, metals, and other dissolved and suspended matter. The insoluble precipitates that are formed from this process are stable. As the particle size increases, the density also increases, and they tend to sink towards the bottom. The toxic aluminium derived from the coagulant dose is very rapidly reduced by the precipitation and coagulation reactions. Even if a coagulant is added at a dose rate in excess of that required for effective removal of solids and nutrients, the dissolved aluminium is still reduced very rapidly to a low concentration with no serious toxicity implications.

Aluminium compounds can be very effective coagulants, and consequently they are used in many commercial products and operations. An adverse side effect of many of these products is the potential to lower pH. Their associated ecotoxicology is mostly related to the downward shift in pH, and the subsequent dissolving and availability of aluminium from the soil structures, rather than the use of aluminium *per se*. The over-dosing of basins and the subsequent release of the excess aluminium to receiving waters is also problematic where the waters have low turbidity, low buffering capacity, and sediments of silt or sand. In any other situation, the excess aluminium will be neutralised quite quickly.

### (iii) Cationic polymers

Cationic polymers are positively charged, and are recognised as flocculants with greater toxicity implications for fish and other aquatic organisms than anionic or non-ionic polyelectrolytes. This is because the gills of fish are negatively charged, and excess cationic polymer will bind to them and sediment from the water column, resulting in mechanical suffocation. Non-ionic polymers and anionic (i.e. negatively charged) polymers are considered to be the safest to use because of their low toxicity. However their efficacy may not be as effective. The use of both cationic and anionic polymers together can achieve efficient flocculation while reducing the ecotoxicity risk.

#### Technical Note – Ecotoxicity

Ecotoxicity information has been adopted from the Auckland Regional Council TP226 and TP227 documents and other available literature.

Chemical specific ecotoxicity information should be sought from chemical suppliers in accordance with the regulating authority's requirements.

## 5. Jar testing

The purpose of jar testing is to select appropriate coagulants and/or flocculants along with determining their optimum dose rates. The recommended testing procedure is described below.

Where possible jar tests are conducted on a four or six-place gang stirrer. Jars (beakers) with different treatment programs or the same product at different dosages are run side-by-side, and the results compared to an untreated beaker. Where access to a laboratory is not practicable jar tests can be undertaken in the field following a similar process to that described in the procedure with stirring and settling timeframes. Testing should be undertaken by a suitably qualified person in the use of coagulants and flocculants.

Preference is given to the use of raw water collected on site which is representative of runoff (including water temperature, which affect settlement characteristics) during the life cycle of the sediment basin. Where raw water is not available representative soil from the site is to be mixed with water to create indicative runoff water chemistry. To create a water sample from soil, a recommended procedure is provided below:

### **Soil / water solution procedure:**

- Step 1. Obtain a soil sample from representative soils to be exposed during the life cycle of the sediment basin. Where multiple soil types are likely to be encountered within the life cycle of the basin, jar tests should be undertaken for the range of soil types.
- Step 2. Crush the soil (if dry) and shake through a 1 mm sieve to remove any coarse material.
- Step 3. Place approximately 100 grams of soil into 10 litres of water. Ensure the water has the same temperature as the expected water temperature within the *Sediment Basin* during the settling phase.
- Step 4. Stir rapidly until soil particles are suspended.
- Step 5. Leave solution for 10 minutes.
- Step 6. Stir rapidly to resuspend any settled material.
- Step 7. Decant into beakers for jar testing.

### **Jar testing procedure:**

- Step 1. Fill the appropriate number of (matched) 1000 mL transparent beakers with well-mixed test water, using a 1000 mL graduate. Record starting pH, temperature and turbidity.
- Step 2. Place the filled beakers on the gang stirrer, with the paddles positioned identically in each beaker.
- Step 3. Mix the beakers at 40–50 rpm (i.e. slow stir) for 30 seconds. Discontinue mixing while coagulant or flocculant is being added.
- Step 4. Leave the first beaker as a control, and add increasing dosages of the first coagulant/flocculant to subsequent beakers. Inject coagulant/ flocculant solutions as quickly as possible, below the liquid level and about halfway between the stirrer shaft and beaker wall.
- Step 5. Increase the mixing speed to 100–125 rpm for 15–30 seconds (rapid stir).
- Step 6. Reduce the mixing to 40 rpm (slow stir) and continue for up to 5 minutes.
- Step 7. Cease mixing allow settling to occur.
- Step 8. After settling for a period of time, note clarity and record on *Floc Performance Report*. Record pH and turbidity.
- Step 9. Remove the beakers from the gang stirrer, empty the contents and thoroughly clean all equipment.
- Step 10. Repeat the procedure as required for different chemicals, dose rates or soil/water mixtures.

Sometimes both a coagulant and flocculant are required to achieve the desired treatment efficiencies. In these situations, the coagulant should be tested first followed by the flocculant.

For all sediment basins, including Type A, B and D, a *Floc Performance Report* should be prepared to determine a suitable chemical and dose rate for the sediment basin. A report template is provided in this section. When a variety of soils with different properties are likely to enter a basin during its life cycle (e.g. natural subsoil and imported fill), testing should be completed for all soil types. A single floc report for multiple sediment basins on a site should only be undertaken when soil properties are uniform for all basins.

# Floc Performance Report

**BASIN IDENTIFICATION CODE/NUMBER:** .....

**SITE / PROJECT:** .....

**PREPARED BY:** ..... **DATE:** .....

Chemical name:	Soil description:					
<b>Dose rate:</b>	0.00 Control					
<b>Starting pH</b>						
<b>Starting turbidity</b>						
<b>Clarity<sup>[1]</sup> after 5 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 15 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 30 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 60 mins (mm)</b>						
<b>Final pH</b>						
<b>Final turbidity</b>						

Chemical name:	Soil description:					
<b>Dose rate:</b>	0.00 Control					
<b>Starting pH</b>						
<b>Starting turbidity</b>						
<b>Clarity<sup>[1]</sup> after 5 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 15 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 30 mins (mm)</b>						
<b>Clarity<sup>[1]</sup> after 60 mins (mm)</b>						
<b>Final pH</b>						
<b>Final turbidity</b>						

**Note:**

- [1] For the purposes of a floc report, 'clarity' is defined as a level of turbidity that is likely to meet discharge requirements at a depth from the water level surface in the beaker. Clarity can be estimated visually or with the use of a turbidity meter.

## **6. Chemical Selection for Type A and B basins**

Type A and B basins require a fast acting coagulant or flocculant to perform based on the design procedure in Step 5. To ensure a suitable coagulant or flocculant is specified for the automated dosing system, the jar test assessment is critical for selection. A coagulant or flocculant should therefore only be selected if the jar test demonstrates the product will achieve a clarity of at least 100 mm within 15 minutes to allow a factor of safety. A factor of safety is required as actual settling times in the basin are likely to be longer than that in the jar testing procedure due to many factors including dosing, mixing, flow velocity and wind action.

## **7. Application of coagulants and flocculants**

Mixing of coagulants and flocculants is critical to the successful treatment of turbid water. The use of passive and active treatment systems where the coagulants and/or flocculants are added to turbid water as it enters the sediment basin is recommended to speed up sediment settling rates and reduce the risk of over-dosing.

## **8. Manual batch treatment**

A broad range of application techniques can be utilised for batch treatment including broad casting or spraying and single point injection with circulation. The optimum treatment method will vary depending on basin size, basin characteristics and the chemical used. Guidance from chemical suppliers or a suitably qualified sediment basin operator should be sought for appropriate application methods including safety precautions.

## **9. Passive systems**

Passive systems include:

- The application of dry products such as calcium sulphate (gypsum) to the entire disturbed contributing catchment area.
- The application of dry products such as calcium sulphate (gypsum), PAMs and biopolymers to the basin inlet drains.
- The placement of PAM or PAC block products in the basin inlet basins.
- The placement of biopolymer gel socks in the basin inlet drains.

While passive systems can be cost effective in some situations it is difficult to control the dosing rate. It relies on the ability of the flowing water to dissolve and mix the chemical. Passive systems require regular maintenance during flow events to replenish the used products or replace blocks/socks that have been washed into the basin. They are generally ineffective in high intensity or long duration rainfall events.

Where passive systems are the preferred application system for a Type A or B basin, the performance of the strategy will need to be significantly monitored during a wide range of storm durations and intensities to determine the appropriateness of the approach. Where monitoring indicates the strategy is not performing to the required standard, adopting an active system should be undertaken.

## **10. Active systems**

Active systems involve either rain or flow activated liquid dosing systems that inject the chemical(s) into the turbid water flowing into a sediment basin. Such systems maximise mixing and minimise chemical usage compared with batch or passive dosing.

Flow activated systems in their simplest form apply a static dose rate determined from jar testing however the more sophisticated units utilise real time turbidity, as well as pH, EC and flow monitoring to adjust the dose rate as flow and water quality conditions change.

Flow activated systems are preferred to rain activated systems as chemicals are dosed into the inflow as soon as it occurs with no assumptions around rainfall losses. Flow activated systems also have the benefit of being able to accurately dose pumped water entering basins from other holding zones after a rainfall event has occurred. The systems typically require little maintenance as large chemical holding tanks can be utilised.

Rainfall activated systems generally come in two forms:

- Displacement systems
- Electronic systems

Displacement systems utilise a catchment tray sized on the contributing catchment. A displacement tank utilises captured rainfall from the catchment tray to displace and inject the chemical through a hose. The systems have been widely used and accepted in New Zealand and can be constructed by the basin operator or purchased from proprietary suppliers. A typical detail of the commonly used rainfall activated displacement system can be found in Auckland regional Council's *Guideline Document 05 – Erosion and Sediment Control Guide for Land Disturbing Activities in the Auckland Region* available on-line to the public and in Appendix E of *Managing Urban Stormwater: Soils and Construction* (Landcom, 2004). The system requires the holding tank to be emptied of rainwater and the chemical to be replaced frequently depending on the capacity of the system.

Electronic systems typically utilise a tipping bucket rain gauge to control a dose pump connected to a chemical supply. The system typically requires little maintenance as large chemical holding tanks can be utilised.

Dosing systems will need to be maintained and operated in accordance with the supplier's specifications. Dosing systems should be capable of housing and/or deploying chemical for runoff volumes up to the 5 year 24 hour storm event (e.g. 171 mm in Brisbane, 169 mm in Sydney).

## 11. Product selection

Product selection should be based on site characteristics and jar testing of products on site specific turbid water. An indicative guide to product selection and dose rates is provided in Table 1.

The information provided in Table 1 is for guidance only and chemical specific guidance should be sought from suppliers including dose rates, application methods and environmental risks. Guidance has only been provided on polyelectrolytes and calcium and aluminium based products. Other coagulants and flocculants are available including ferric compounds and poly amines (Poly DADMAC) however they are rarely used in sediment basins.

### Notes for Table 1:

- [1] The dosage rates are only indicative and will vary according to the suspended sediment load, and soil and water quality characteristics.
- [2] The most efficient (time and cost) coagulant/flocculant can only be determined through jar tests as they are dependent upon both soil and water chemistry.
- [3] Control of water pH is critical prior to any discharge.

**Table 1 – Characteristics of various flocculating agents**

<b>Agent</b>	<b>Indicative dosage &amp; form</b>	<b>Pros</b>	<b>Cons</b>	<b>Precautions</b>
Gypsum (calcium sulphate)	300–600 kg/ML Powder	Readily available. Can be used in passive system. Little pH change. Potentially Low ecotoxicity	Slow acting. Poor solubility (hard to mix). Large quantities required.	Causes an increase in EC.
Calcium Chloride	250–1000 kg/ML Typically in flakes but can be supplied in liquid.	More soluble than gypsum. Can be used in passive system. Little pH change. Potentially Low ecotoxicity.	Generally slow acting.	Potentially large increase in EC.
Alum (aluminium sulphate)	50–150 kg/ML (powder) 100–250 L/ML (liquid) Liquid and powder form	High solubility, fast acting.	Likely to require pH buffering post treatment. No basicity and requires high levels of alkalinity to perform.	Causes a decrease in pH. Potential ecotoxicity to aquatic organisms due to bioavailability at pH's < 5.
PAC (poly-aluminium chloride)	50–200 L/ML Liquid and powder form	High solubility, fast acting. Low dose rates. Can be used in both active and passive systems. Higher basicity than Alum.	Can cause a decrease in pH. Lower basicity than ACH. Requires medium levels of alkalinity to perform.	Can cause a decrease in pH Potential ecotoxicity to aquatic organisms due to bioavailability at pH's < 5.
ACH (aluminium chloro-hydrate)	20–100 L/ML Liquid form only	High solubility, fast acting. Low dose rates. Higher basicity than PAC and Alum. Little pH change.	Requires low levels of alkalinity to perform.	Potential ecotoxicity to aquatic organisms due to bioavailability at pH's < 5.
Bio-polymers (Chitosan, Xanthum gums, starches)	Product dependent	Fast acting. Large stable flocs. Completely biodegradable. Can be used in both active and passive systems.	May need to be used in conjunction with a coagulant.	An anionic biopolymer may be required following the use of a cationic biopolymer to neutralise any excess so as to minimise potential ecotoxicity.
PAM (poly-acrylamide)	Product dependent	Can be used in both active and passive systems.	Excess dosing with cationic PAMs can result in potential ecotoxicity risk.	High ecotoxicity risk associated with the cationic form (poly DADMAC). Low environmental risk with anionic PAMs