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Coagulation Chemistry

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Presentation Overview

- Introduction
- Basics of coagulation and the chemistry
- Fundamentals of alkalinity and pH
- Reasons for enhanced coagulation
- Basis for flocculation
- Organic matter chemistry and coagulation
- Summary

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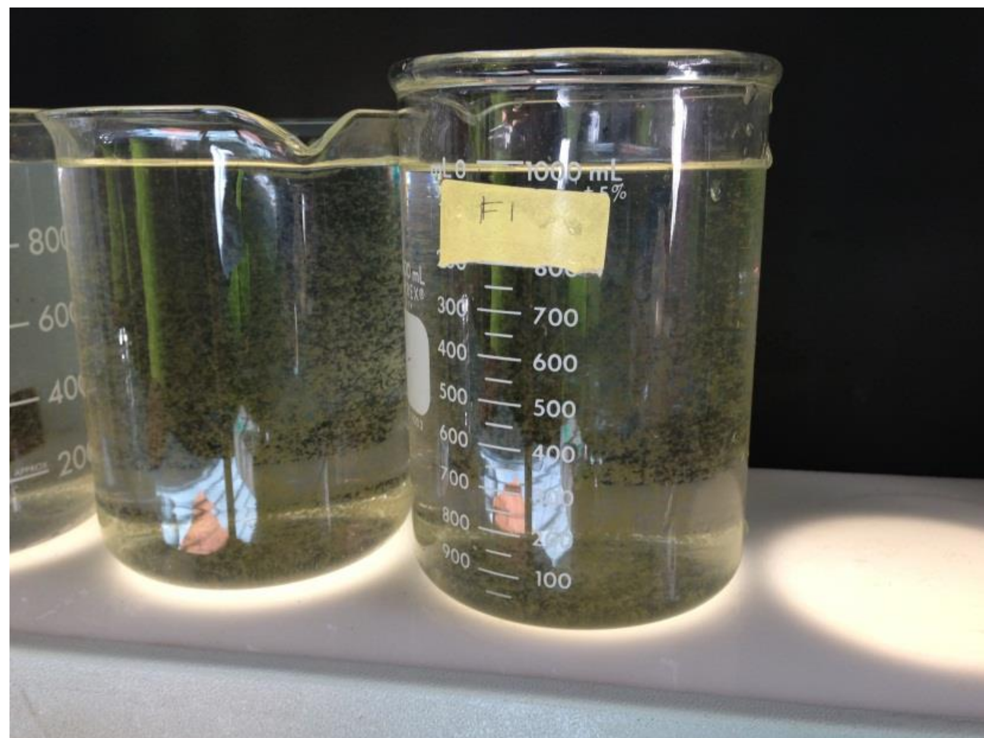
Introduction – Coagulation need?

- The need to clarify water and remove organic matter
- For aesthetics and health
- To form colloids – impart color and turbidity to water – aesthetical acceptability
- Microbes are colloids too



Definitions

Coagulation

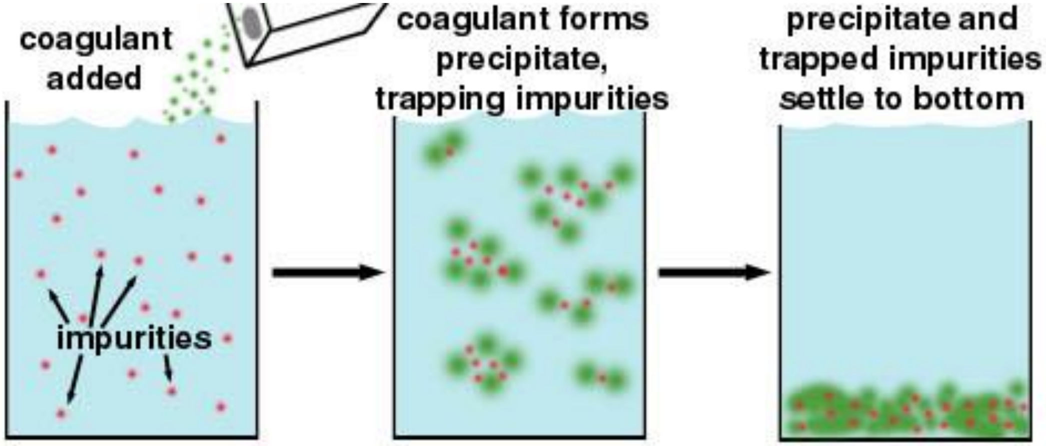
To precipitate dissolved material and change the nature of existing particles to allow settlement to take place

Flocculation

To increase the size and density of particles to aid solid / liquid separation

Clarification

To separate treated water from solid waste



What Is Coagulation?

- Coagulation is the destabilisation of colloids by addition of chemicals that neutralise the negative charges

- The chemicals are known as coagulants, usually higher valence:

  Cationic salts (Al^{3+}, Fe^{3+} etc.)

- Coagulation is essentially a chemical process

Relative coagulating power

$Na^{+} = 1$;	$Mg^{2+} = 30$
$Al^{3+} > 1000$;	$Fe^{3+} > 1000$

Common Coagulants

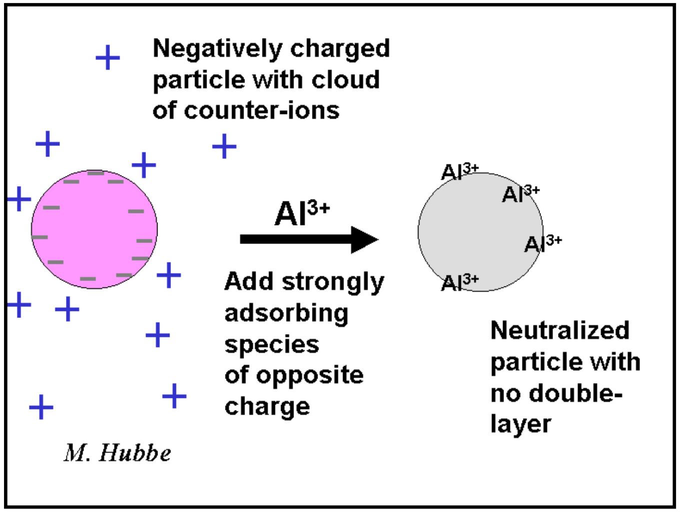
<u>Hydrolysing Metal Coagulants (inorganic)</u>

- Ferric Sulphate, Aluminium Sulphate (Alum) and Polyaluminium Chloride (PACl) used in Ireland

<u>Key Factors that Influence Coagulant Effectiveness</u>

- Temperature
- pH
- Alkalinity
- Dosage
- Mixing energy
- Order of addition

Coagulation Mechanisms



- Charge neutralisation
- Complexation and precipitation (NOM)
- Adsorption (NOM)
- Enmeshment (sweep coagulation)

Hydrolysis

- The Aluminum cation (Al^{3+}) combines with hydroxide anions (OH^{-}) to form these hydrolysis products:

$$Al^{3+} + OH^{-} = Al(OH)^{2+}$$

$$Al(OH)^{2+} + OH^{-} = Al(OH)_2^{1+}$$

$$Al(OH)_2^{1+} + OH^{-} = Al(OH)_3$$

$$Al(OH)_3 + OH^{-} = Al(OH)_4^{1-}$$

Aluminum Chemistry

With alum addition, what happens to water pH?

$$Al_2(SO4)_3.14\ H_2O \Leftrightarrow 2Al(OH)_3\downarrow + 8H_2O + 3H_2SO_4^{-2}$$

1 mole of alum consumes 6 moles of bicarbonate (HCO_3^-)

$$Al_2(SO4)_3.14\ H_2O + 6HCO_3^- \Leftrightarrow 2Al(OH)_3\downarrow + 6CO_2 + 14H_2O + 3SO_4^{-2}$$

If alkalinity is not enough, pH will reduce greatly

Lime or sodium carbonate may be needed to neutralise the acid.

(Optimum pH: 6 – 6.2 for alum)

Alkalinity

- Alkalinity is a quantitative measurement of a waters acid neutralising capabilities
- While pH measures the concentration of the H^+ ions
- In the water, alkalinity measures the capacity of the water to neutralise the H^+ ion
- The capacity to neutralise the H^+ ion is related to the concentrations of carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), and hydroxides (OH^-) present in the water.

Alkalinity Calculation

If 100 mg/L of alum to be added to achieve complete coagulation. How much alkalinity is consumed in mg/L as $CaCO_3$?

$Al_2(SO_4)_3.14\ H_2O + 6HCO_3^- \Leftrightarrow 2Al(OH)_3\downarrow + 6CO_2 + 14H_2O + 3SO_4^{-2}$

594 mg **366 mg**

594 mg alum consumes 366 mg HCO_3^-

100 mg alum will consume (366/594) x 100 mg HCO_3^- = 61.6 mg HCO_3^-

Alkalinity in mg/L as $CaCO_3$ = 61.6 x (50/61) = **50.5 mg/L as $CaCO_3$**

Alkalinity Consumption

1 mg/l of coagulant as metal ion	mg/l alkalinity as $CaCO_3$
Sulphuric Acid 96%	**0.98 mg/l as $CaCO_3$**
1 mg/l as Aluminium Sulphate solution (as 8% w/w Al_2O_3)	**0.24 mg/l as $CaCO_3$**
1 mg/l as PACl solution (as 10% w/w Al_2O_3 and 40% basicity)	**0.17 mg/l as $CaCO_3$**
1 mg/l as Ferric Sulphate solution (as as 12.5% w/w as Fe^{3+})	**0.32 mg/l as $CaCO_3$**

Alkalinity for pH Adjustment and Correction

- Alkalinity can be added in the form of lime, caustic soda or soda ash
- The following table allows for estimation of alkali dose required to match alkalinity consumption upon addition of a coagulant

1 mg/l of product	mg/l of Alkalinity as $CaCO_3$
Calcium Oxide as CaO	**1.79 mg/l as $CaCO_3$**
Lime as $Ca(OH)_2$	**1.35 mg/l as $CaCO_3$**
Soda Ash as Na_2CO_3	**0.94 mg/l as $CaCO_3$**
Sodium Hydroxide as NaOH	**1.25 mg/l as $CaCO_3$**
25%w/w NaOH solution	**0.312 mg/l as $CaCO_3$**
30%w/w NaOH solution	**0.375 mg/l as $CaCO_3$**

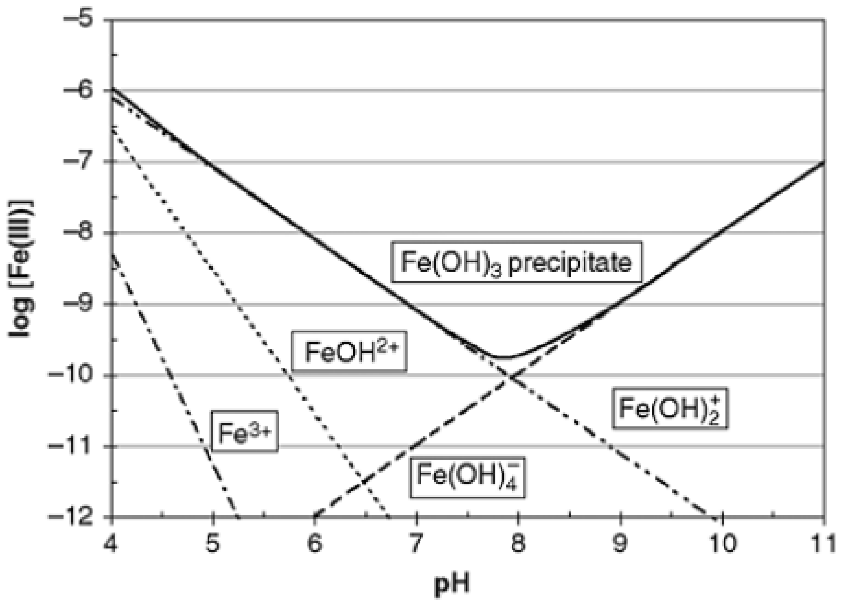
Coagulant - Solubility and Temperature

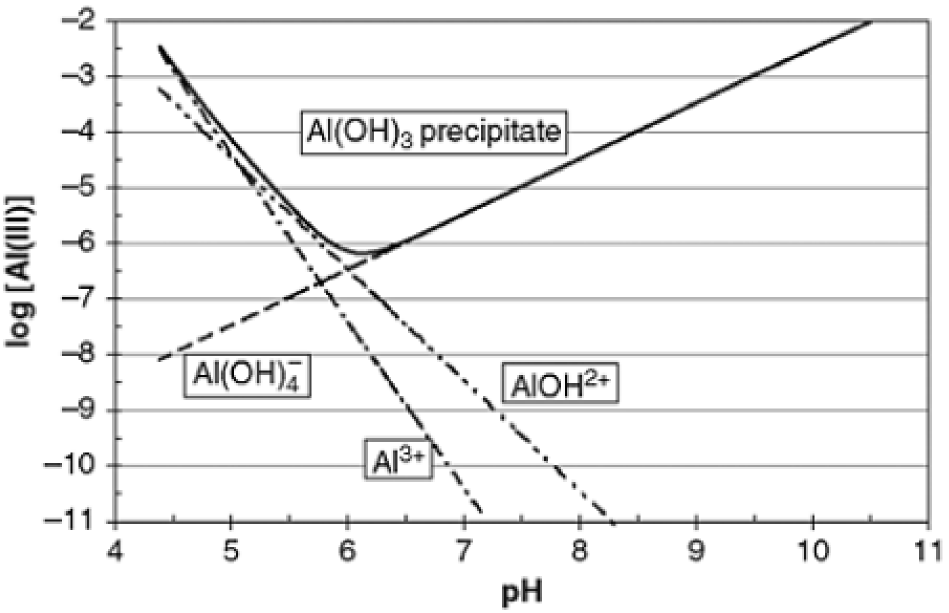
- Recommended optimal pH for aluminium and iron based inorganic coagulants (with respect to minimum solubility):

1. Alum pH 6 – 6.2
2. PACL (low basicity) pH 6.2 – 6.7
3. PACL (high basicity) pH 6.4 – 6.9
4. Ferric sulphate pH 5.5 – 6

- For example Alum - minimum solubility at 5^{o}C occurs around pH 6.2, at 20^{o}C minimum solubility occurs at pH 6.0
- Basicity is a measure of the hydroxyl ions present in the coagulant. Alum has zero basicity, PACl ranges 50 – 85% basicity

Iron and Aluminium Speciation Versus Concentration & pH





Basis of Enhanced Coagulation

- **Coagulation optimised with aim of charge neutralisation and maximum floc insolubility**
- Defined for specific and deliberate targeting of dissolved organic carbon (DOC) for removal (precursor's for THM’s and instead of targeting turbidity)
- Creates conditions required for subsequent agglomeration of larger colloids, turbidity and biological contaminants

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Enhanced Coagulation and pH

- pH of coagulation is most important parameter for proper coagulation performance with respect to charge and solubility
- It affects the surface charge of colloids, charge of NOM functional group, the charge of the dissolved phase solubility
- Careful pH control and chemical dose is fundamental to this mechanism

Enhanced Coagulation (Benefits)

This approach to coagulation focuses on maximising removal of organic matter and therefore reducing the concentration of trihalomethane (THM) precursors prior to disinfection

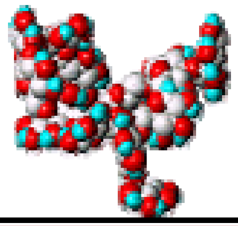
The key benefits are:

- Lower chemical dosing and therefore cost savings
- Lower volume of sludge production
- Optimised charge chemistry for adsorption of organics and destabilisation of contaminants, removal of THM precursors

What is Flocculation?

- Flocculation goes in hand with coagulation
- It is the agglomeration of destabilised particles into a large size particles known as flocs which can be effectively removed by sedimentation or flotation

- Gentle mixing or ***flocculation***, then causes the destabilized (reduced charge) colloids to cluster.
- Another method of enhancing agglomeration is to add organic polymers.
- These compounds consist of a long carbon chain with active groups such as amine, nitrogen, or sulfate groups along the chain.



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Flocculation Mechanisms

Occurs after coagulant addition when particles become destabilised

1. Sweep Floc – excess coagulant to form precipitated hydroxide floc (enmeshment, adsorption)
2. Charge Neutralisation **(ENHANCED COAGULATION)** – controlled coagulant dose & pH to target organic matter +*ve* and -*ve* charge chemistry
3. Chemical Bridging – polymer addition to enhance floc density and cohesion

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Chemical Bridging Via Polymer Addition

- Charged (polyelectrolytes) result in the attachment of polymer and colloid (same as charge neutralisation process)
- Poly works best after delayed addition during flocculation stage (5 - 10 minutes after coagulant dose)

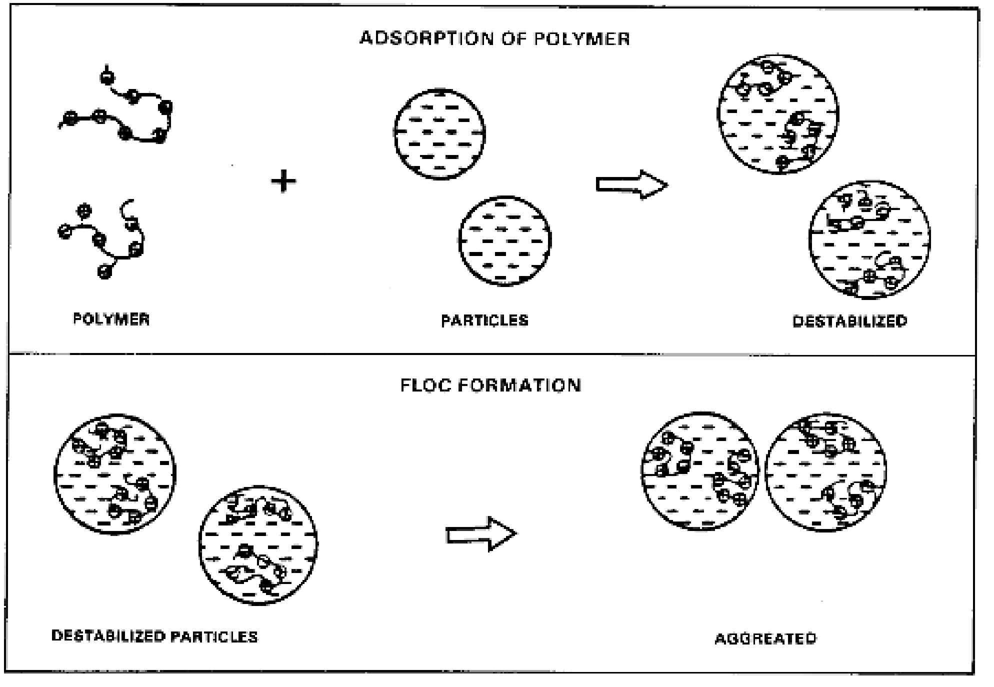
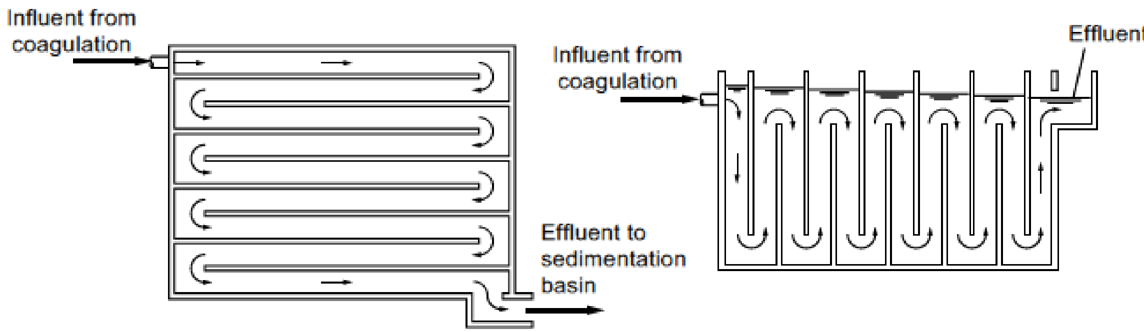


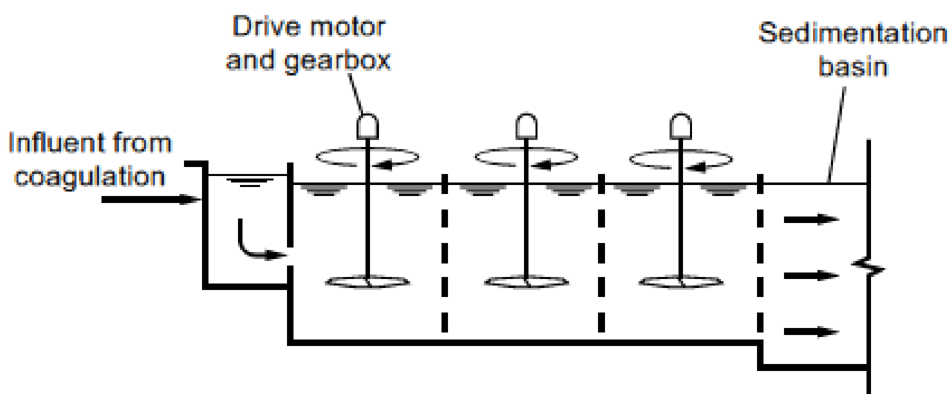
Figure 1-2. Floc formation process

FLOCCULATION TANK ARRANGEMENTS

1. Basic flocculation – either hydraulic or mechanically mixed tank(s)



2. Tapered – 2 or 3 tanks in series, different mixing speeds dedicated to promoting controlled floc growth



Coagulation and Organic Matter in Natural Water

- Is a complex mixture of organic compounds
- It results from the degradation of vegetative matter in the catchment or from surface affected groundwaters
- Consists of compounds resulting from the growth and decomposition of algae and weeds within the surface water source itself
- Molecules are large and contain many organic functional groups that affect their behavior

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Organic Matter and Coagulation

- Historically, the significance of NOM in drinking water was related to its impact on aesthetic quality. Types vary between each water source

- It imparts a yellowish tinge to water that many people find unpalatable

- More recently, concern has focused on ability to react with chlorine and form disinfection by-products (DBP’s) which are often carcinogenic

UV_{254} Absorbance - Relationship with NOM

- Like TOC/DOC, UV_{254} absorbance is a surrogate for the NOM concentration
- Can be used as a simple predictor tool for trihalomethane (THM) precursors
- UV_{254} absorbance relationship is unique for each water source
- Used for setting coagulant dosages for water treatment in which NOM controls coagulation requirements

Coagulation - Treatability & Removal of NOM

- Organic matter is typically removed by coagulation via addition of a metal salt (aluminum or ferric based)
- Coagulation tends to preferentially remove the higher-MW, more hydrophobic fractions of NOM.
- Humic substances are highly negatively charged (50 times greater than charge clay minerals)
- The portion of NOM preferentially removed by enhanced coagulation tends to correspond to the fraction that preferentially forms DBPs
- The hydrophobic fraction of NOM typically forms more DBPs than the hydrophilic fraction

Summary

- Understanding coagulation very important to water utilities to assist in optimising chemical dosing for NOM removal
- Organic matter is complex and is critically linked to THM formation potential
- Understanding the seasonal variation is key to good coagulation control and maximising removal
- Good coagulation is also critical to removal of colloidal matter including protozoa and micro-organisms to maximise the clarification and filtration processes