ENVE 301
Environmental Engineering Unit Operations

Lecture 9
Coagulants

SPRING 2014

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Coagulants

Principle use of coagulants is to;

- destablize particle suspensions
- increase the rate of floc formation

Ref;
http://www.oasisenviro.co.uk/coagulant_chemical_treatment.htm

Characteristics of Coagulants

Inorganic coagulants used in water treatment should exhibit following characteristics;

- They are non-toxic at the dosage they are supplied
- They have high charge density
- They are insoluble at neutral pH

Coagulants

Most commonly used coagulants are

- Aluminum sulfate (Alum) – $Al_2(SO_4)_3.xH_2O$
- Iron salts

Hydrolyzing metal salts
(HMS) Coagulants

TABLE 6-1
Frequently used inorganic coagulants

Coagulant	Chemical formula	Molecular weight, g/mole	Remarks
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 14H_2O$	594	Hg contamination may be of concern
Sodium aluminate	$Na_2Al_2O_4$	164	Provides alkalinity and pH control
Aluminum chloride	$AlCl_3$	133.5	Used in blends with polymers
Polyaluminum chloride	$Al_w(OH)_x(Cl)_y(SO_4)_z$	Variable	"PACl" used when Hg contamination is a concern
Polyaluminum sulfate	$Al_w(OH)_x(Cl)_y(SO_4)_z$	Variable	"PAS" used when Hg contamination is a concern
Polyiron chloride	$Fe_w(OH)_x(Cl)_y(SO_4)_z$	Variable	
Ferric chloride	$FeCl_3$	162.5	
Ferric sulfate	$Fe_2(SO_4)_3$	400	

Ref: Davis M.L. *Water and Wastewater Treatment: Design Principles and Practice*. 2010. McGrawHill

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Hydrolyzing Metal Salt (HMS) Coagulants

- Al^{3+} and Fe^{3+} are small, highly positive ions
- These ions form strong bonds with oxygen atoms of six surrounding water molecules
- Oxygen-hydrogen association in the water molecules is weakened and the hydrogen atoms are released to water.
- This process is known as **hydrolysis**.

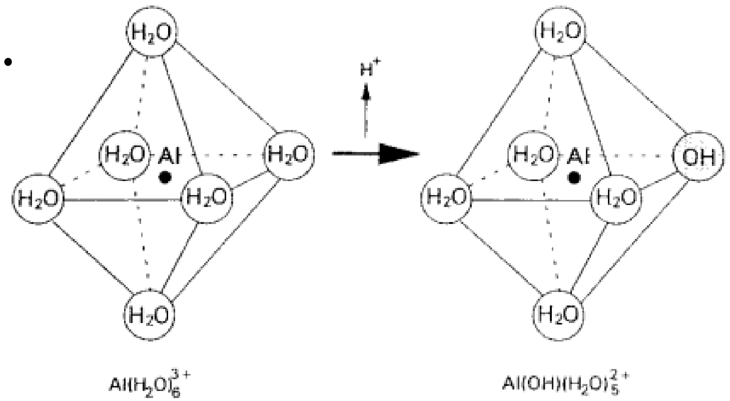

FIGURE 6.7 Deprotonation of the aquo aluminum ion, initial step in aluminum hydrolysis (from Letterman, 1991).

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Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999

Hydrolyzing Metal Salt (HMS) Coagulants

- Hydrolysis is a complex process
- If there is sufficient metal ions, metal precipitates can form.
- Hydrolysis products tend to react with NOM

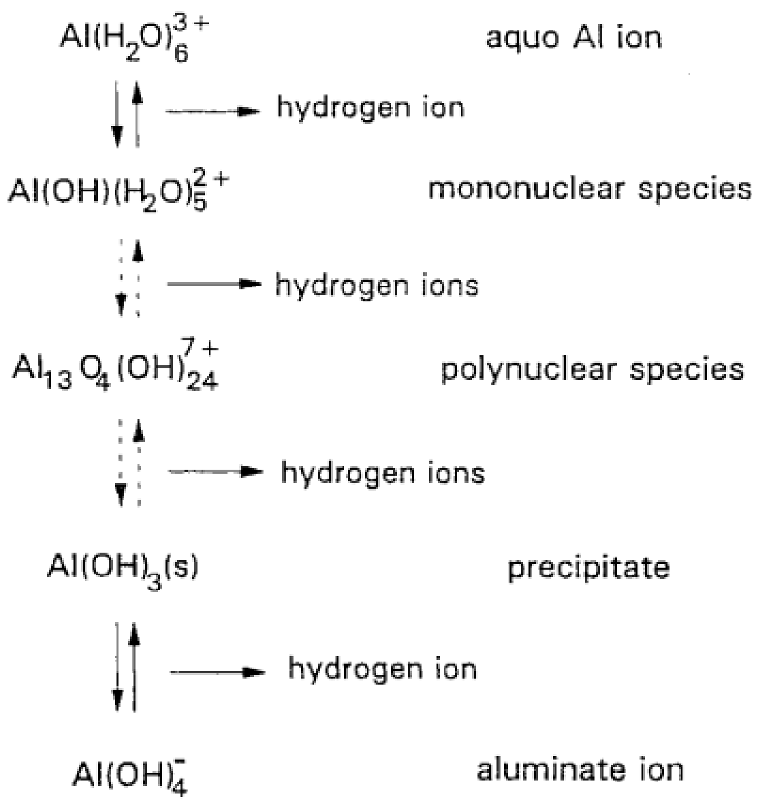

FIGURE 6.8 Aluminum hydrolysis products (from Letterman, 1991).

Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999

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Hydrolyzing Metal Salt (HMS) Coagulants

HMS

Low pH

Positively charged, aquo-metal ions form Fe^{3+} or Al^{3+}

High pH

Negatively charged, Soluble hydrolysis products form $Fe(OH)_4^-$ or $Al(OH)_4^-$

Hydrolyzing Metal Salt (HMS) Coagulants

- Most water treatment plants using alum operate at;
- pH 0f 6-7.5
- Alum dossage of 5-50 mg/L

Hydrolyzing Metal Salt (HMS) Coagulants

- Suspension destabilization mechanisms of HMS's
  - Adsorption and charge neutralization
    - Positively charged coagulants
    - The amount of the added salt is less than the solubility limit
    - Charge reversal due to overdosing is possible
  - Enmeshment in a precipitate
    - Precipitating metal hydroxides
    - The amount of the added salt is higher than the solubility limit

Aluminum Sulfate

- Aluminum sulfate is available in dry or liquid form
- Alum used as coagulant contains 14 waters of crystallization ($Al_2(SO_4)_3 . 14H_2O$)
- Liquid alum is sold approximately 48.8% alum (8.3 % Al_2O_3)alum
- Dry alum is more common and may be in granular, powdered, or lump form.
- Dry alum granules contain 15-22% Al_2O_3

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Aluminum Sulfate

- Sufficient alkalinity must present in water to react with the aluminum sulfate to produce the hydroxide floc.
- If sufficient alkalinity present in water,

$$Al_2(SO_4)_3 \cdot 14H_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 14H_2O + 6CO_2$$

- pH variation due to addition of alum will be prevented

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Aluminum Sulfate

- If the alkalinity is not sufficient in water,

$$Al_2(SO_4)_3 \cdot 14H_2O + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 6H^+ + 3SO_4 + 14H_2$$

- Upon the addition of alum, pH will decrease to levels which alum is no longer effective as a coagulant

Aluminum Sulfate

- If the alkalinity is not sufficient in water, alkalinity in the form of hydroxide ion should be added.
- Calcium hydroxide ($Ca(OH)_2$, calcium oxide (CaO), or calcium carbonate ($CaCO_3$) can be added to increase the buffer capacity.

$$Al_2(SO_4)_3 \cdot 14H_2O + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 14H_2O$$

Hydrolyzing Metal Salt (HMS) Coagulants
Aluminum Sulfate

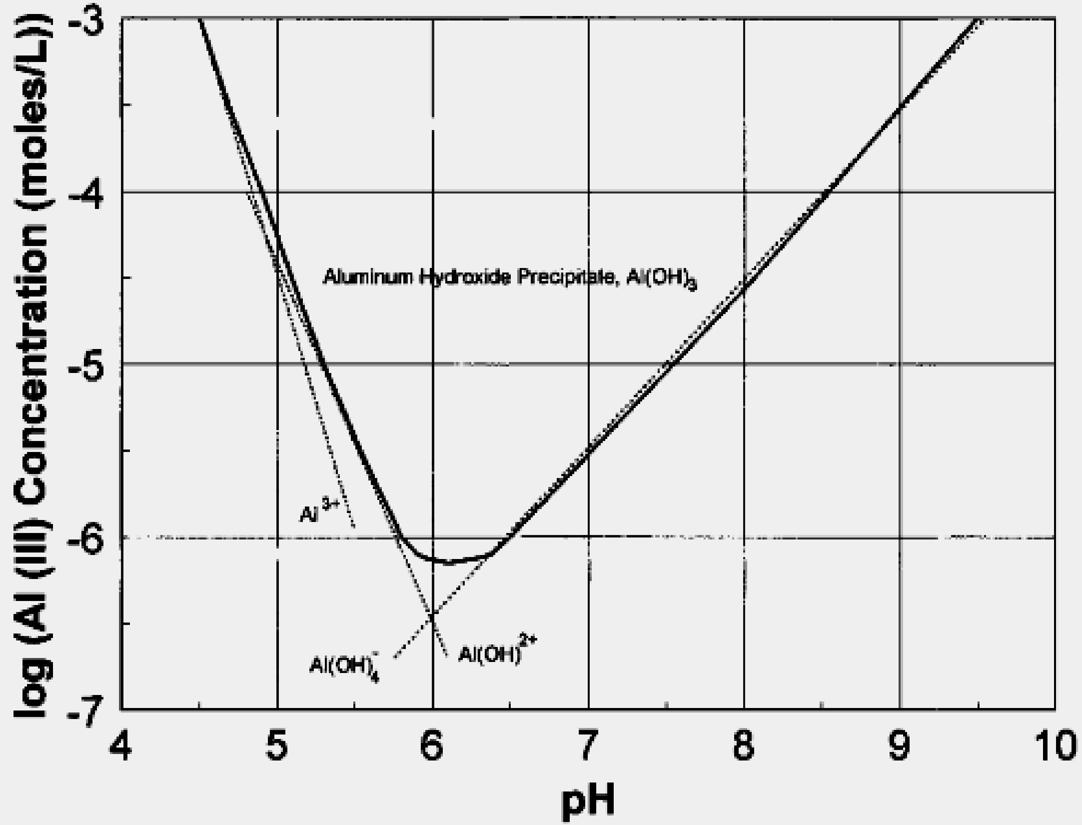

FIGURE 6.9 Solubility diagram for amorphous, freshly precipitated aluminum hydroxide. Water molecules are omitted in species notation.

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Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999

Hydrolyzing Metal Salt (HMS) Coagulants
Aluminum Sulfate

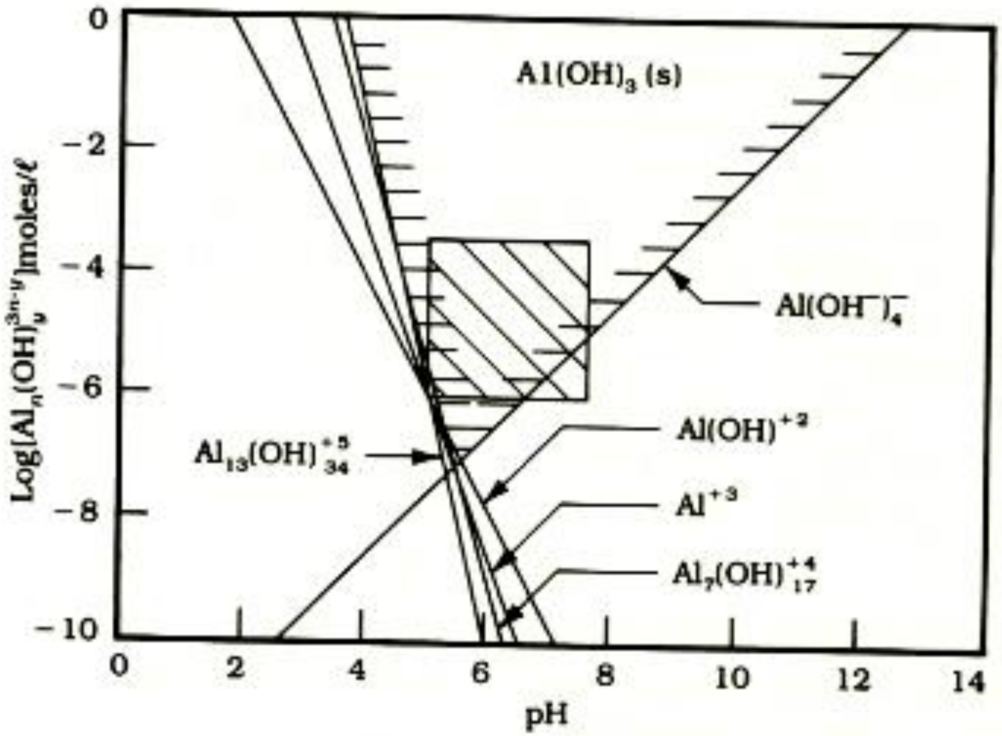

FIGURE 8.5 ***Solubility of Aluminum Hydroxide. (Shaded area is the usual operating region used in water treatment.)***

Adapted from *Journal of American Water Works Association*, 60, no. 5 (May 1968), by permission. Copyright 1968, the American Water Works Association.

Ref: Reynolds, T. D., and P. A. Richards. Unit Operations and Processes in Environmental Engineering. 2nd ed. Boston, MA: PWS Publishing Company, 1996.

Ferrous Sulfate

- Requires alkalinity in the form of the hydroxide ion to produce a rapid reaction.
- Slaked or hydrated lime, $Ca(OH)_2$, is added to raise pH
- At high pH, ferrous ions are precipitated as ferric hydroxide.
- Oxygen must present in water

$$2FeSO_4 \cdot 7H_2O + 2Ca(OH)_2 + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \downarrow + 2CaSO_4 + 13H_2O$$

- pH must be raised to about 9.5 for this reaction to occur.

Ferrous Sulfate

- Ferrous sulfate is more expensive than alum
- In general, the precipitate is a dense quick settling floc
- Ferrous sulfate is available in dry (granules or lumps) or liquid form
- Dry granules contain 55% $FeSO_4$
- Ferrous sulfate can be treated with chlorine (Chlorinated copper treatment)—reaction occurs at a pH as low as 4

$$2FeSO_4 \cdot 7H_2O + 1.5Cl_2 \rightarrow Fe_2(SO_4)_3 + FeCl_3 + 21H_2O$$

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Ferric Sulfate

- If alkalinity present in water (x=3, 7, 9);

$$Fe_2(SO_4)_3 \cdot xH_2O + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaSO_4 + 6CO_2 + xH_2O$$

- If natural alkalinity is insufficient, slaked lime can be used.

$$Fe_2(SO_4)_3 \cdot xH_2O + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaSO_4 + xH_2O$$

$$Fe_2(SO_4)_3 \cdot xH_2O + 3Na_2CO_3 + 3H_2O \rightarrow 2Fe(OH)_3 \downarrow + 3Na_2SO_4 + 3CO_2 + xH_2O$$

- The optimum pH range =4-12
- Typical dosage = 10-250 mg/L as $Fe_2(SO_4)_3.9H_2O$

Hydrolyzing Metal Salt (HMS) Coagulants
Ferrous Sulfate

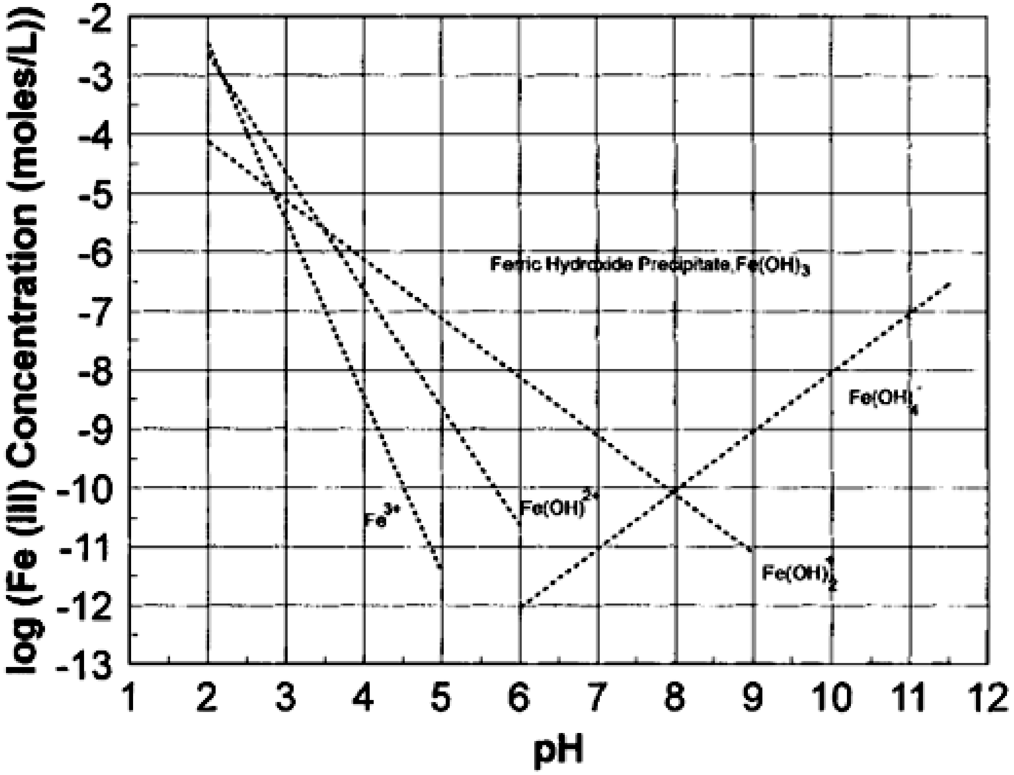

FIGURE 6.10 Solubility diagram for amorphous, freshly precipitated ferric hydroxide. Water molecules are omitted in species notation.

Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999

Hydrolyzing Metal Salt (HMS) Coagulants
Ferrous Sulfate

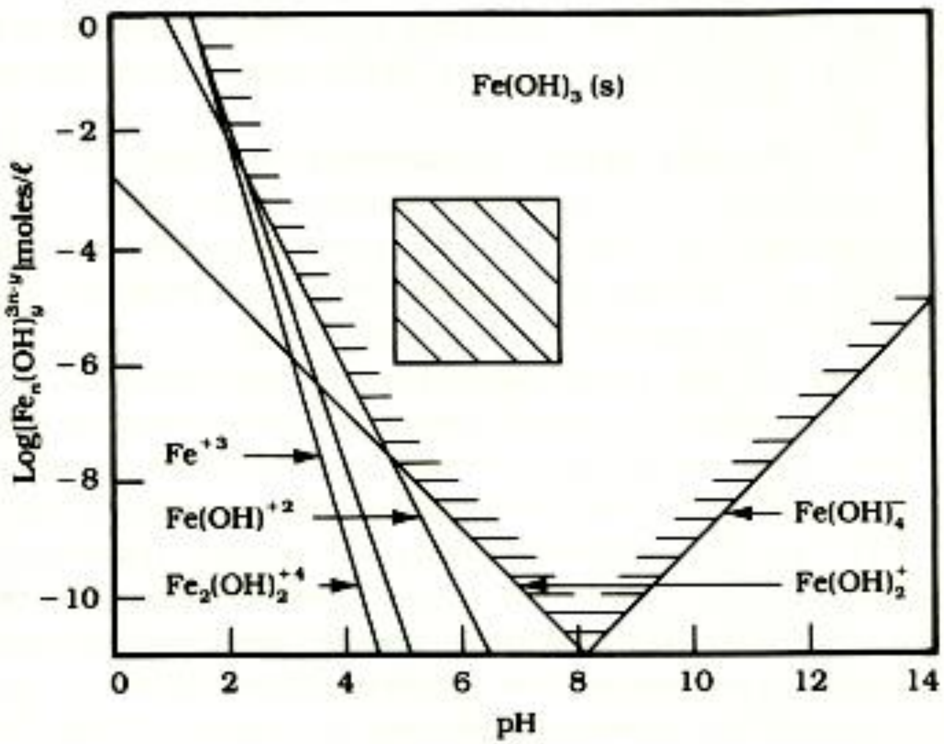

FIGURE 8.6 ***Solubility of Ferric Hydroxide. (Shaded area is the usual operating region used in water treatment.)***

Adapted from *Journal of American Water Works Association* 60, no. 5 (May 1968), by permission. Copyright 1968, the American Water Works Association.

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Ferric Chloride

- If alkalinity present in water;

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaCl_2 + 6CO_2$$

- If natural alkalinity is insufficient;

$$2FeCl_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 \downarrow + 3CaCl_2$$

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O \rightarrow 2Fe(OH)_3 \downarrow + 6NaCl + 3CO_2$$

- Optimum pH=4-12
- Typical dosage= 5-150 mg/L as $FeCl_3.6H_2O$

Ferric Chloride

- Available in dry or liquid form
- Dry chemical may be in powder or lump form
- Lumps contain 59-61% $FeCl_3$ contain six waters of crystallization
- Powdered or anhydrous form is 98% $FeCl_3$ and contains no water of crystallization

Coagulant Aids

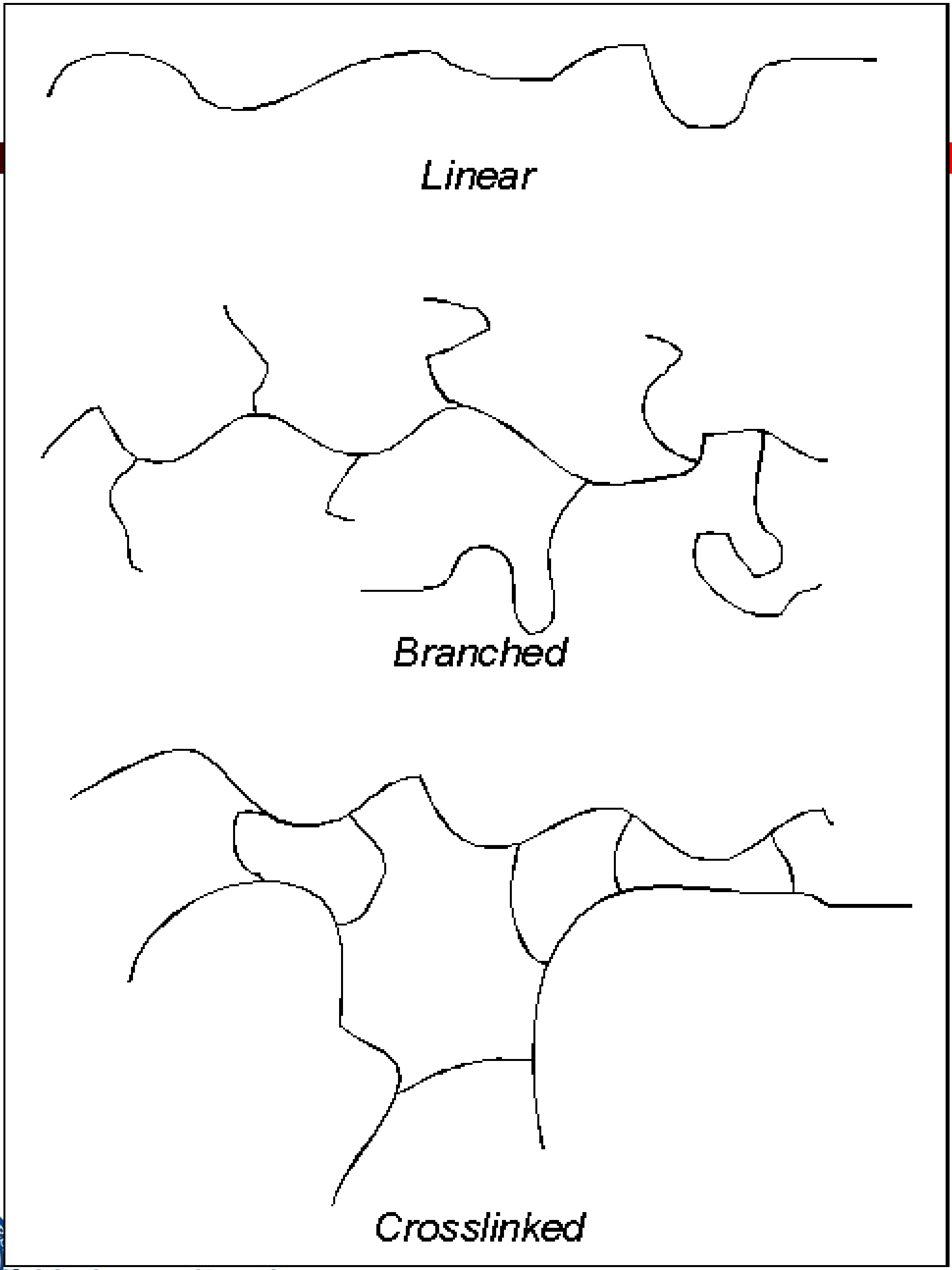
- Coagulant aids are sometimes used to produce quick-forming, dense, rapid-settling flocs.
- Coagulant aids are;
  - Alkalinity addition (already seen)
  - Polyelectrolytes
  - Turbidity addition
  - Adjustment of pH

Coagulant Aids
Alkalinity addition

- Required to aid coagulation if the natural alkalinity is insufficient
- Lime is used (slaked or hydrated lime)
- Soda-ash (Na_2CO_3) is used to lesser extent

Coagulant Aids
Polyelectrolytes

- Polyelectrolytes are high molecular weight polymers
- Polymers have strong tendency to adsorb on the surfaces of most particles in aqueous suspension
- Polyelectrolyte polimers consist of subunits called monomers
- Polymers can be manufactured such that the chains can be linear, brached or cross-linked



Ref:
http://chem.chem.rochester.edu/~chem421/intro1.htm

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Coagulant Aids
Polyelectrolytes

- Monomer units in a polymer may have positively and negatively charged sites.
- Polymers with predominantly negative sites—anionic (Activated silica)
- Polymers with predominantly positive sites—cationic
- Polymers with no charged sites—nonionic
- Polymers with both positive and nigative sites—Ampholyte polymers

Coagulant Aids
Polyelectrolytes

- Polyelectrolytes may be of natural origin
  - Starch or polysaccharides
- Polymers are mostly synthetically produced
- Polymers assist in chemical bridging, interaction between reactive groups
- Ployelectrolytes can be used as a sole coagulant
- Dosage =0.5 – 1.5 mg/L
- Overdosing may gas restabilization of colloids

Coagulant Aids
Turbidity Addition

- Turbidity addition is occasionally required to furnish sufficient particulate concentrations for rapid coagulation
- Usually achieved by recycling some precipitated sludge
- Clays are sometimes used for turbidity addition instead of recycled sludge

Coagulant Aids
Adjustment of pH

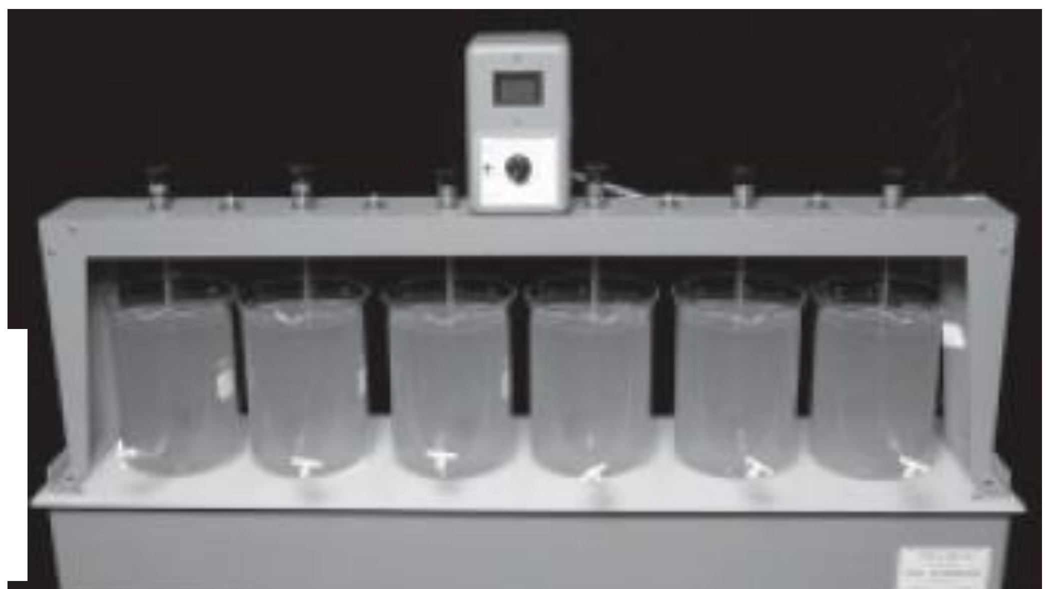
- Required if the pH of the coagulated water does not fall within the pH of minimum solubility of the metallic hydroxide
- pH is increased by the addition of lime
- pH reduction is achieved by the addition of mineral acid (sulfuric acid)

Determination of Coagulant Dosage
Jar Tests

- Jar Tests are used to determine;
  - Proper coagulant and the coagulant aid
  - Chemical dosages required for the coagulation in particular water.

Determination of Coagulant Dosage
Jar Tests

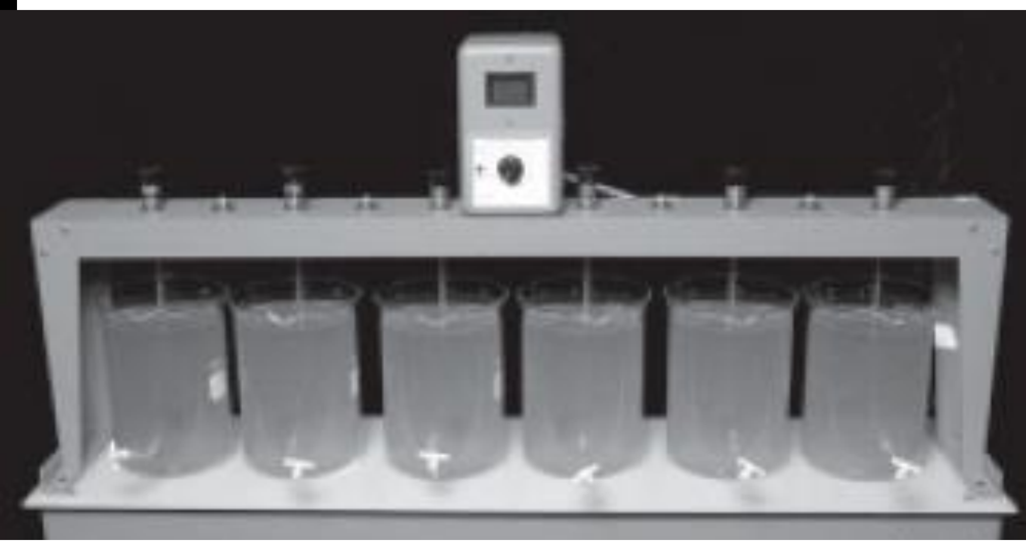
1) Samples of the water are poured into a series of glass beakers
2) Various dosages of coagulant and coagulant aid are added to the beakers
3) The contents are rapidly stirred to simulate rapid mixing
4) Then gently strirred to simulare slow mixing
5) After a given time stirring is ceased and the formed flocs are allowed to settle

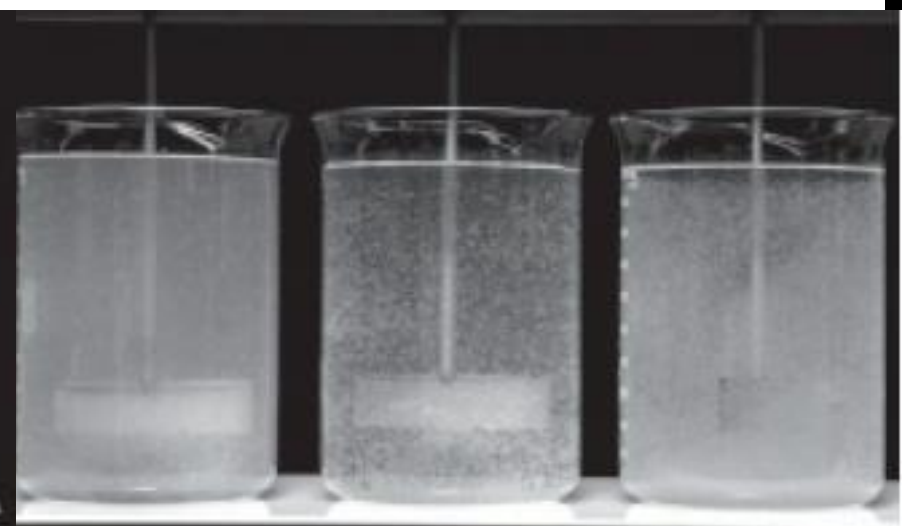


Ref: Davis M.L. *Water and Wastewater Treatment: Design Principles and Practice*. 2010. McGrawHill

Determination of Coagulant Dosage
Jar Tests

1) Time for floc formation
2) The floc size
3) Floc settling characteristics
4) The percent turbidity and color removed
5) The final pH of the coagulated and settled water should be determined





Ref: Davis M.L. *Water and Wastewater Treatment: Design Principles and Practice*. 2010. McGrawHill

Determination of Coagulant Dosage
Jar Tests

- Rapid Mix 1-3 min (80 rpm)
- Slow mix 30 min (10-20 rpm)
- Settle for 20 min

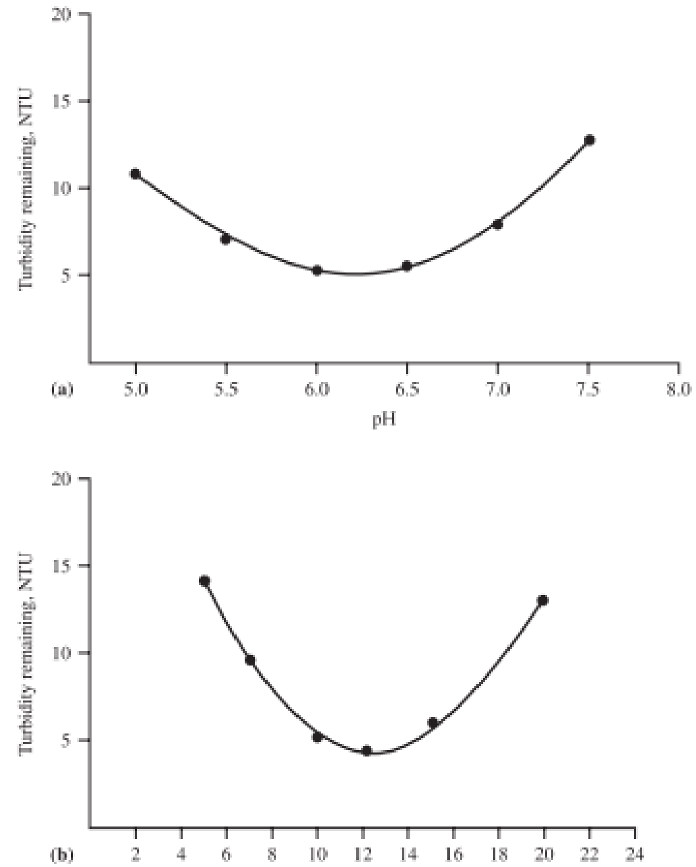
Jar test I

	Jar numbers					
	1	2	3	4	5	6
pH	5.0	5.5	6.0	6.5	7.0	7.5
Alum dose (mg/L)	10	10	10	10	10	10
Turbidity (NTU)	11	7	5.5	5.7	8	13

Jar test II

	Jar numbers					
	1	2	3	4	5	6
pH	6.0	6.0	6.0	6.0	6.0	6.0
Alum dose (mg/L)	5	7	10	12	15	20
Turbidity (NTU)	14	9.5	5	4.5	6	13

FIGURE 6-11
Results of jar test. (*a*) Constant alum dose, (*b*) constant pH.



Ref: Davis M.L. *Water and Wastewater Treatment: Design Principles and Practice*. 2010. McGrawHill

Classification of Surface Water with regard to Coagulation

- Low turbidity < 10 JTU — Low alkalinity < 50 mg/L as$CaCO_3$
- High turbidity >100 JTU — High alkalinity < 50 mg/L as$CaCO_3$

<u>Group 1: High turbidity, low alkalinity</u>

- Small dosages of coagulant will be sufficient to achieve charge neutralization
- Alkalinity addition may be required

<u>Group 1: High turbidity, high alkalinity</u>

- Adsorption and charge neutralization will be less effective due to alkalinity
- High coagulant dosage may be required to achieve sweep coagulation
- pH will be stable

Classification of Surface Water with regard to Coagulation

<u>Group 3: Low turbidity, high alkalinity</u>

- Turbidity addition may be required
- Sweep coagulation with moderate coagulant addition can be achieved

<u>Group 4: Low turbidity, low alkalinity</u>

- Additional turbidity can be added to get group 1
- Additional alkalinity can be added to get group 3