ENVE 301
Environmental Engineering Unit Operations

CHAPTER: 8
Coagulants

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Coagulants

The most widely used coagulants in water treatment :

- → Aluminum sulfate ($Al_2(SO_4)_3.14H_2O$ or $Al_2(SO_4)_3.18H_2O$)
- → Iron salts

  (e.g. ferrous sulfate, ferric sulfate, ferric chloride)

Aluminum (III) and Fe (III) accomplish destabilisation of colloidal particals by 2 mechanisims :

1. Adsorption and charge neutralization

2. Enmesment in precipitate

If an Aluminum (III) and Fe (III) salt is added to water in concentrations less than the solubility limit of the metal hydroxide:

The hydrolysis products will form and adsorb onto the colloidal particles, causing *destabilization by charge neutralization*.

If the amount of Aluminum (III) and Fe (III) salts added to water is sufficient to exceed the solubility of metal hydroxide;

The hydrolysis products will form as intermediate in the formation of metal hydroxide precipitate

→ Adsorption and charge neutralization by intermediate hydrolysis products

→ Enmeshment of colloids in precipitate ($Al(OH)_3$ or $Fe(OH)_3$) formed

Aluminium Sulfate (Alum)

$Al_2(SO_4)_3.14H_2O$ → Commercial grade

(MW=594.4 Density=600-1100 kg/m^3)

$Al_2(SO_4)_3.18H_2O$ → Reagent grade

→ Tan to gray green in color

→ Available in dry or liquid form

(liquid form requires special shipping containers because of its corrosiveness)

dry form is most common

- granular (most widely used)
- powdered
- lump form

→ The dry chemical may be shipped in;

- bags
- barrels

Feeding of Alum in Water Treatment Plants:

→Alum is dissolved in water at concentration of 3-7%

(5% most common)

Then fed to the raw water by chemical feeders (e.g, dosage pumps)

<u>Reason of diluting coagulant before injection into raw water :</u>

large volumes are easier and quicker to disperse into a large body of raw water than smaller volumes

→ The optimum pH range = 6-8

(aluminum hydroxide is relatively insoluble within this range)

<u>If pH is high;</u> $Al(OH)_3 + OH^- \rightarrow \underbrace{Al(OH)_4}_{\text{soluble}}$

<u>If pH is low;</u> $Al(OH)_3 + H^+ \rightarrow \underbrace{Al(OH)_2}_{\text{soluble}} + H_2O$

In practice, most water treatment plants utilizing alum operate;

Between a pH of 6-7.5 and
with alum dosages of 5-50 mg/L } in the range of insolubility of $Al(OH)_3$

When $Al_2(SO_4)_3.14H_2O$ ($18H_2O$) is added to water

→ It is hydrated to form $Al(H_2O)_6^{+3}$

→ This complex is then pass through a series of hydrolytic reactions in which H_2O molecules in the hydration shell are placed by OH^- ions.

→ Formation of a variety of soluble species

e.g.

$$\left.\begin{array}{l} AlOH^{+2} \\ Al(OH)_2^{+} \\ [Al_2(OH)_2]^{+4} \\ [Al_3(OH)_4]^{+5} \\ [Al_{13}O_4(OH)_{24}]^{+7} \end{array}\right\}$$

Intermediates in the formation of $Al(OH)_3$ precipitate

These species may adsorb very strongly onto the surface of most negative colloids

Coagulation with adsorption and charge neutralization mechanism occurs.

(charge reversal due to overdosing is possible)

If solubility limit of $Al(OH)_3$ is exceeded (typical in water treatment)

- Adsorption and charge neutralization by intermediate soluble species formed
- Enmeshment in $Al(OH)_3$

Both contribute to coagulation

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

Liberated H^+ ions

Depression of pH below the range in which the alum is effective

Optimum pH for $Al(OH)_3$ precipitate formation $\rightarrow$ 6-8

Natural alkalinity of water (which is in the form of bicarbonate ion for the ph range involved) will react with liberated H^+ ions and reduces the variation in pH.

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

If the natural alkalinity of water is insufficient, alkalinity in the form of

- $Ca(OH)_2 \rightarrow$ hydrated lime (calcium hydroxide)
- $CaO \rightarrow$ quick lime (calcium oxide)
- $Na_2CO_3 \rightarrow$ sodium carbonate (soda ash)

must be added to increase buffer capacity

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

$$Al_2(SO_4)_3 14H_2O + 3Na_2CO_3 + 3H_2O \rightarrow 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2 + 14H_2O$$

Example: (Benefield, p.221)

A raw water supply is treated with an alum dosage of 25 mg/L. Calculate the followings:

1. The amount of alum required to treat a flow of 1 MGD (million gallon /day)

2. The amount of natural alkalinity required to react with the alum added in terms of $CaCO_3$

3. The volume of sludge produced per MGD if it is collected at 2% solids. Assume that the sludge has a specific gravity of 1.011 (at 4°C)

Calculation of Sludge Amount

To evaluate the daily sludge production the following equation can be used:

$$M = Q \times (0.44A + SS + others) \times 10^{-3}$$

where

M = dry sludge produced (kg / day)
Q = plant flow (L / day)
A = alum dose (mg / L)
SS = suspended solids in raw water (mg / L)
others → miscellaneous chemical additions such as polymers, pH neutralizing chemical etc. (mg / L)

The insoluble aluminum hydroxide complex $Al(H_2O)_3(OH)_3$ is thought to predominate in most water treatment plant sludges when alum is used. According to the chemical equilibrium, when one mole of alum is used, 2 moles of $Al(H_2O)_3(OH)_3$ precipitate. This species results in the production of 0.44 kg of chemical sludge for each kg of alum added. "0.44" comes from this data.

MW of $Al(H_2O)_3(OH)_3$ = 131.98 g
MW of $Al(SO_4)_3.14H_2O$ = 594.4 g

(2 x 131.98) / 594.4 = 0.44

Source:
- http://www.patentstorm.us/patents/5543056-description.html

Iron Salts

Ferric sulfate ($Fe_2(SO_4)_3$)

Ferric chloride ($FeCl_3$)

Ferrous sulfate ($FeSO_4$)

Less expensive than alum but can cause color problem if the precipitate is not removed completely

Ferric sulfate

Ferric chloride

Ferrous sulfate (copperas)

Ferric Sulfate

$Fe_2(SO_4)_3.yH_2O$ y= 3, 7, 9 MW=399,9 g/mol

⇒ Available in dry form, as granules (most common) or as powder

⇒ **Optimum pH range =** 3.5 – 7 and above 9 (up to 12)

(ferric hydroxide is relatively insoluble within this range)

Typical dosage for $Fe_2(SO_4)_3.9H_2O$ $\rightarrow$ 10-250 mg/L

Reaction of ferric sulfate with natural bicarbonate alkalinity:

$$Fe_2(SO_4)_3.yH_2O + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 \Downarrow + 3CaSO_4 + 6CO_2 + yH_2O$$

The reaction produces a dense, rapid settling floc.

If the natural alkalinity is insufficient for the reaction:

$$Fe_2(SO_4)_3.yH_2O + \underbrace{3Ca(OH)_2}_{\text{Hydrated lime}} \rightarrow 2Fe(OH)_3 \Downarrow + 3CaSO_4 + yH_2O$$

$$Fe_2(SO_4)_3.yH_2O + 3Na_2CO_3 + 3H_2O \rightarrow 2Fe(OH)_3 \Downarrow + 3Na_2SO_4 + 3CO_2 + yH_2O$$

$\Rightarrow$ The chemical is usually dry fed

Ferric Chloride

$FeCl_3 \rightarrow$ MW=162.2 g/mol

Available in dry (powder or lump,lump is most common) or liquid form

($FeCl_3$)	anhydrous form	$\rightarrow$ green-black powder
($FeCl_3.6H_2O$)	heptahydrate form	$\rightarrow$ yellow-brown lump
	Liquid form	$\rightarrow$ dark brown solution

→ Typical dosage = 5-150 mg/L as $FeCl_3.6H_2O$

→ Working pH range = 3.5-6.5 (or above 8.5)

Simplified reaction with natural alkalinity:

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4 + 6CO_2$$

If the natural alkalinity is insufficient;

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

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

Ferrous Sulfate (Copperas)

$FeSO_4.7H_2O$ = 287 g/mol

$FeSO_4.5H_2O$ = 242 g/mol

$\Rightarrow$ Effective pH range = 8.5 or above

Slaked (or hydrated) lime is usually added to raise the pH to a level where the ferrous ions are precipitated as ferric hydroxide.

$$FeSO_4.7H_2O + 2Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4 + 7H_2O$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$\Rightarrow$ is available in dry (granule or lump) or liquid form. Dry form is most common

Chlorinated Copperas

$$3FeSO_4.7H_2O + 1.5Cl_2 \rightarrow \underbrace{Fe_2(SO_4)_3 + FeCl_3}_{\text{Effective coagulants}} + 21H_2O$$

This reaction occurs at a pH as low as about 4

effective pH range = 3.5-6.5 or above 8.5

Polyelectrolytes (Polymeric Coagulants)

Polymer → Long chain, high molecular weight molecules

Comprises of many subunits (MONOMERS)

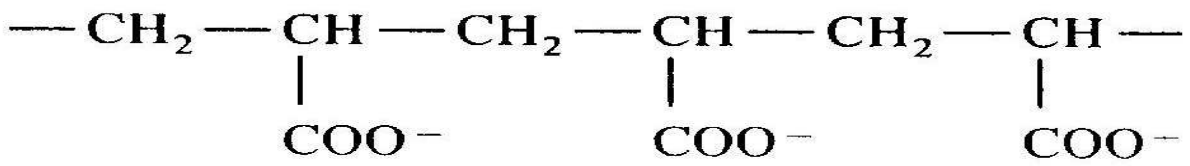
may be classified according to their ionic characteristics as:

- Anionic (negatively charged)
- Cationic (positively charged)
- Ampholytic (contains both positive and negative groups)

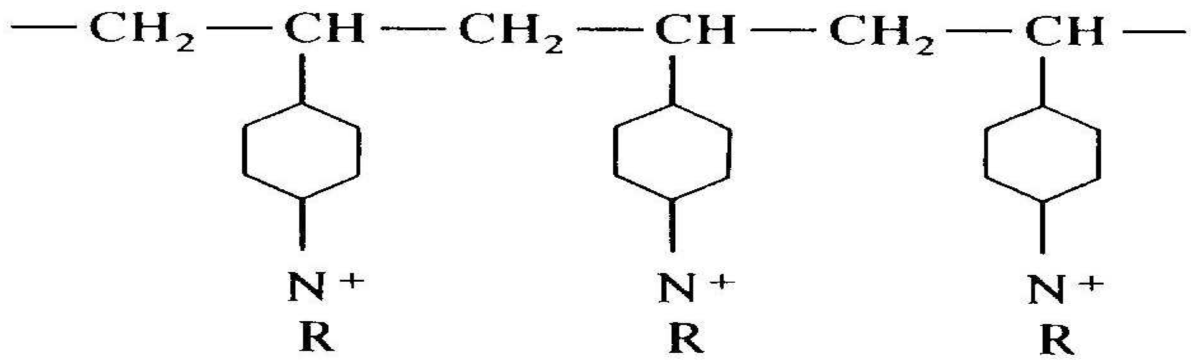
may be of ***<u>natural origin</u>*** **(**e.g. starch, polysaccharide gums**)** OR ***<u>synthetic in origin</u>***

Polymeric coagulants or *polyelectrolytes* are long-chain, high-molec weight molecules which bear a large number of charged groups. The net ch on the molecule may be positive, negative, or neutral. Representative lecular structures are

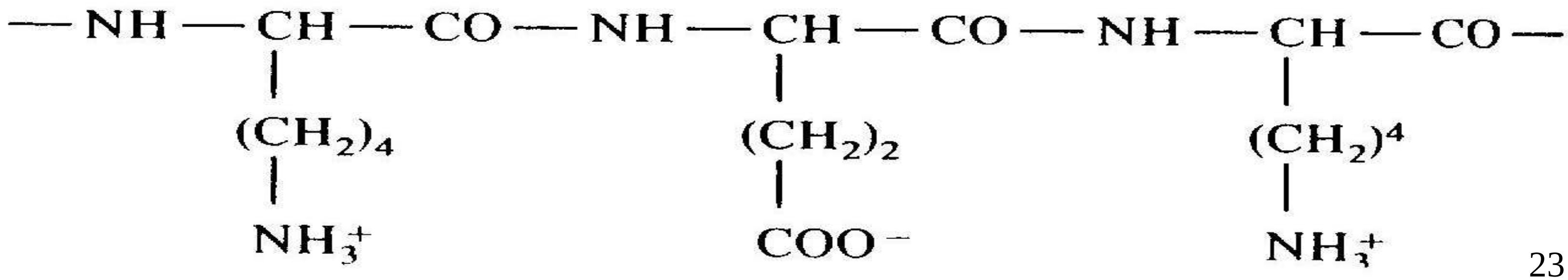
Anionic:



Cationic:



Ampholytic:



May be used as coagulant → not cost effective

Commonly used as coagulant aid in conjuction with coagulants

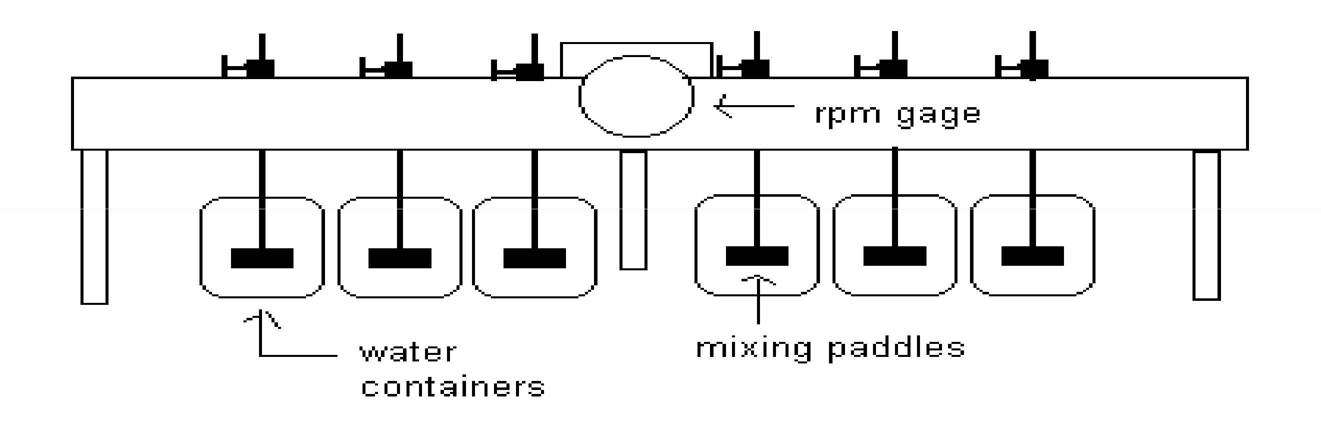
When they are added to water,

- Chemical bridging between reactive groups on the polyelectrolyte and floc occurs
- Polyelectrolyte binds small flocs together by bridging to make larger masses for settling

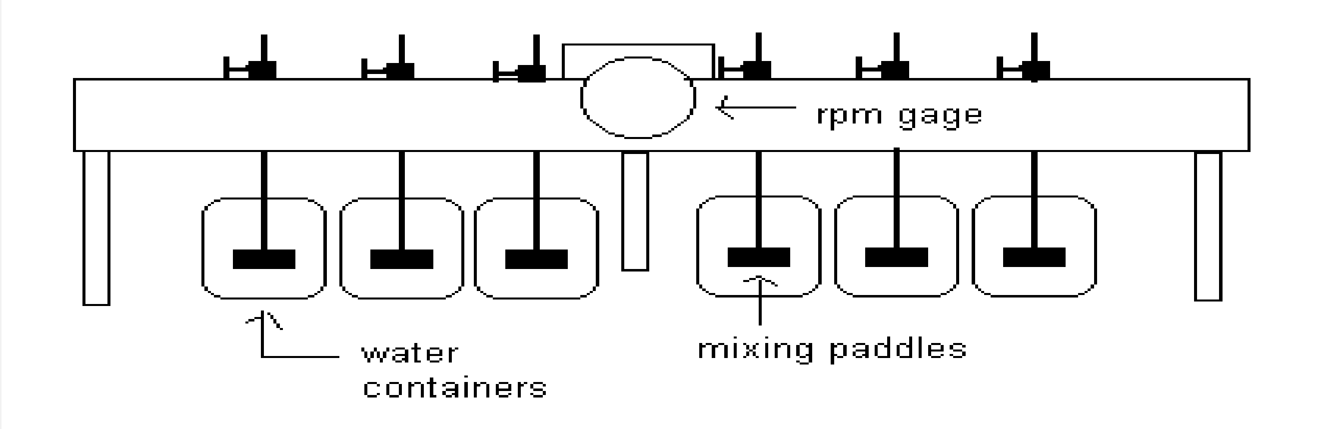
- Usual dosage as coagulant aid = 0.5-1.5 mg/L
- Overdosing → will result in restabilization of colloids
- are not acidic and do not lower the pH of water as alum does

Determination of Coagulant Dosage

JAR TEST



is used to determine the most effective and economical dose of coagulant for a particular mixing intensity and duration



Samples of the water are poured into a series of glass beakers → Various dosages of the coagulant and coagulant aid are added to beakers → Contents are rapidly stirred to simulate RAPID MIXING (coagulation)

→ Then the coagulants are gently stirred to simulate FLOCCULATION → After a given time, the stirring is ceased and the floc formed is allowed to settle

Determination of Optimum Coagulant Dose

→ Raw sample pH and turbidity measurement

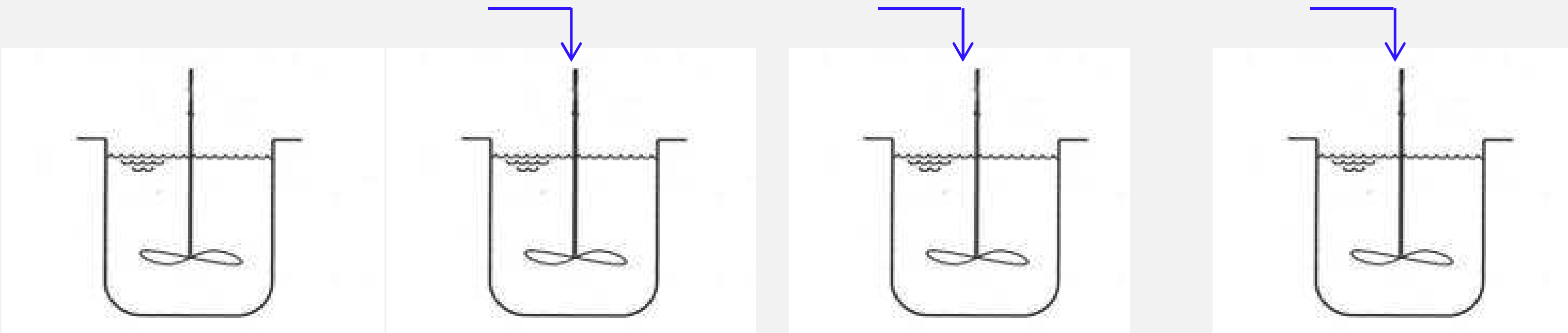
Flash mix (at 80 rpm) 1-3 min

Slow mix (at 10-20 rpm) 30 min

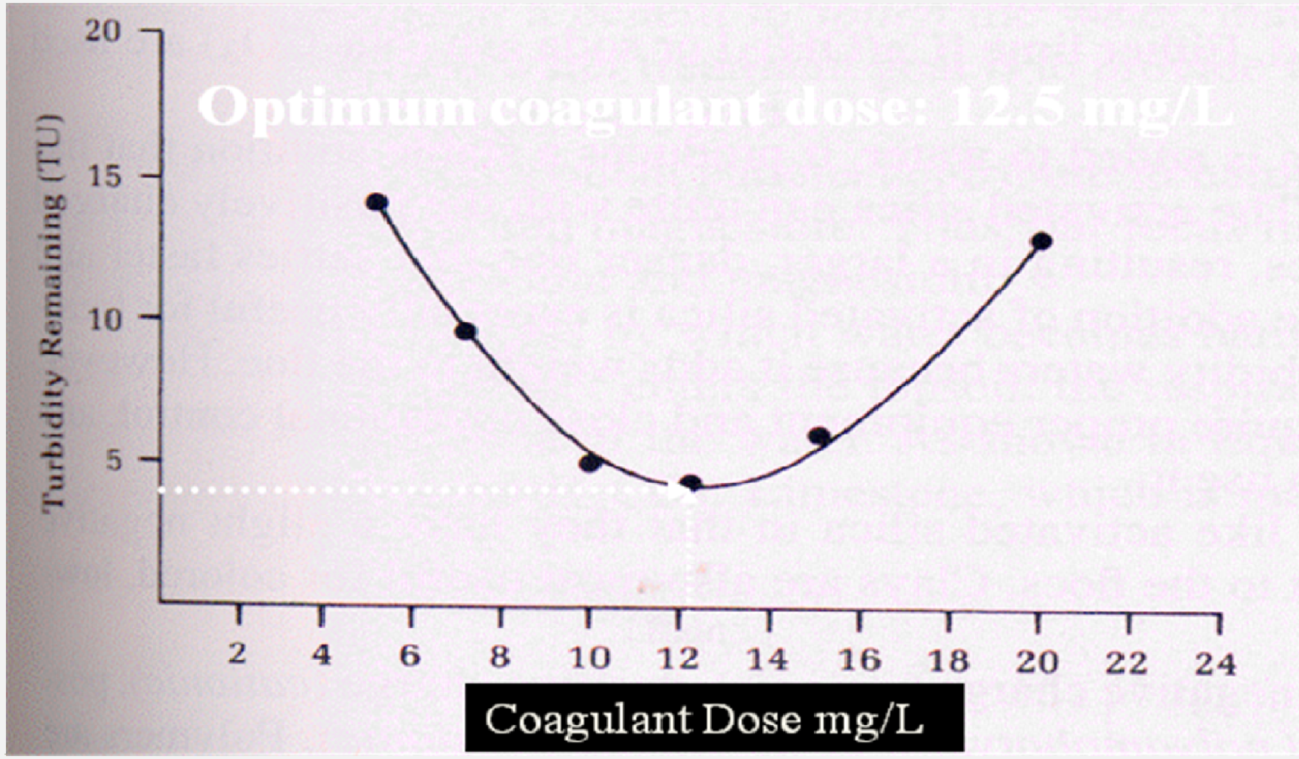
Settle for 20 min

Turbidity of supernatant

10 mg/L alum   20 mg/L alum   50 mg/L alum



No coagulant (blank)


Optimum coagulant dose: 12.5 mg/L
Turbidity Remaining (TU)
20
15
10
5
2
4
6
8
10
12
14
16
18
20
22
24
Coagulant Dose mg/L

Determination of Optimum pH for Optimum Coagulant Dose

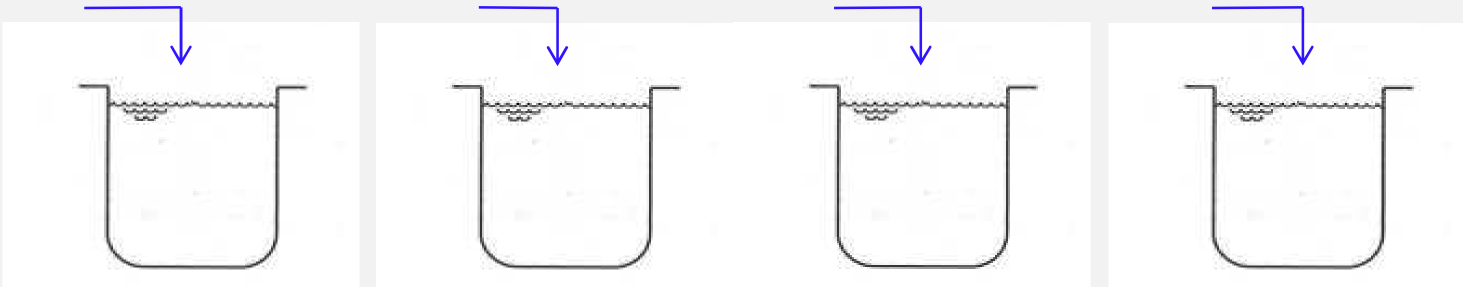
Rapid mix 1-3 min (at 80 rpm)

Slow mix 30 min (at 10-20 rpm)

Settle for 20 min

Turbidity of supernatant

Optimum coagulant dosage determined in part A



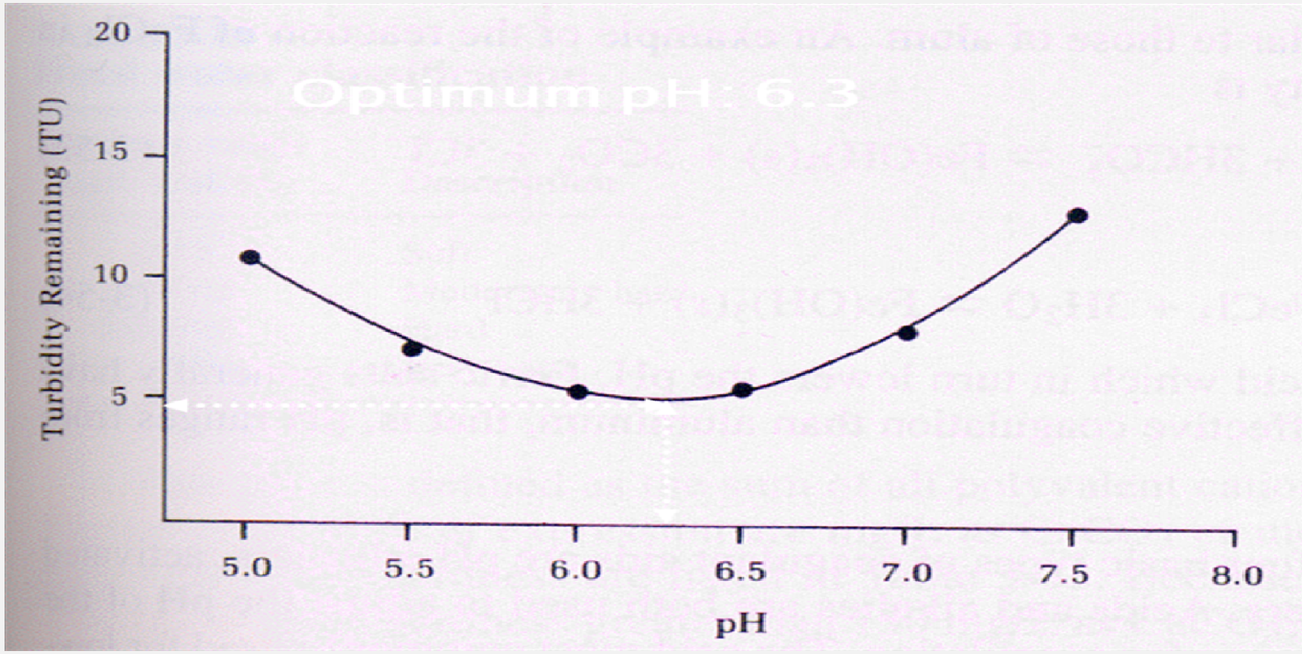
as-is pH

adjust pH 5

adjust pH 6

adjust pH 8

W/ { NaOH, H_2SO_4 }


Optimum pH: 6.3
Turbidity Remaining (TU)
20
15
10
5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
pH

The most important aspects to note during the JAR TEST:

- Time for floc formation
- The floc size
- Floc's settling characteristics
- Turbidity removed
- pH

APPARATUS REQUIRED

1. Jar tester (a stirring machine with 3 to 6 paddles , variable speed adjustment for the paddles from 0 to 100rpm to simulate rapid mix and slow quiescent motion for floc formation)
2. Turbidimeter for turbidity measurement.
3. A titration set up for both alkalinity and hardness
4. A large dial timer to note time of mixing, stirring, and floc formation.
5. pH meter
6. Analytical hot plate for lime dissolution.
7. An analytical balance that will weigh to 0.010 mg accuracy.
8. Four 1L beakers for the jar tester.
9. An assortment of beakers of 250 ml to 1000 ml capacity to aid in making solutions.
10. Several 1000 ml capacity volumetric flasks.
11. Several 1, 5, and 10 ml pipettes graduated in 0.1 ml graduations.

REAGENTS NEEDED

- **Standard Aluminum Sulfate Solution [$Al_2(SO_4)_3.18\ H_2O$] (1 % solution by weight)** ***(1 ml of solution is equivalent to 10 mg Aluminum sulfate)***

  Prepare 1 L of solution by dissolving 18.9 g of $Al_2(SO_4)_2.18H_2O$ in 1000 ml of distilled water in a liter volumetric flask. This solution contains 10 mg as aluminum sulfate for each ml. Store in a screw-capped glass or plastic reagent bottle and make fresh annually.

- **Polymer Solution (0.05 - 0.1% solution by weight)**

  0.05%polymer : 1 ml of solution is equivalent to 0.5 mg polymer.
  0.1% polymer : 1 ml of solution is equivalent to 1 mg polymer.

- **Standard Lime Solution [CaO, unslaked lime] (1 % solution by weight)** ***(1 ml of solution is equivalent to 10 mg lime)***

  Prepare 1L of solution by dissolving 13 g of lime (CaO) in 800 ml of distilled water in a liter beaker. Heat the suspension to almost boiling and stir continuously to dissolve as much suspension as possible. *[Caution: If the distilled water used contains carbon dioxide, the lime will react with the carbondioxide and form calcium carbonate which will not dissolve under the present conditions. Cool to room temperature and transfer to a liter volumetric flask. Wash the beaker one or three times with CO_2 -free distilled water (do not overshoot the liter mark on volumetric flask)]* Once the dissolution takes place dilute to exactly 1L of final solution. Store in a screw-capped plastic bottle and make fresh annually.
  Caution: *Lime slurries should be mixed by shaking every time they are used.*

- **Sodium Hydroxide [NaOH] (0.1 N)**

  Dissolve 4 g of reagent grade NaOH in 1000 ml of distilled water in a liter volumetric flask. Store in a plastic reagent bottle and prepare fresh once every six months.
  Caution: *An exothermic reaction occurs during the dissolution of NaOH in water.*

- **Sulfuric Acid solution (H_2SO_4) (0.02 N)**

  Dilute exactly 200 ml of a stock 0.1N H_2SO_4 to exactly one liter using a liter volumetric flask with distilled or deionized water. Store in a glass or plastic reagent bottle and prepare fresh once every six months.
  Caution: *An exothermic reaction occurs during the dilution of acids. Acids are always added onto water.*

PROCEDURE

A- Determination of optimum coagulant dose

1. Initialy, the raw sample prior to testing mus be measured for the following:
   pH
   Turbidity

2. Fill each of the 500 ml beakers on the stirring machine with sample to be tested. Then add the following volumes of 1% standard alum solution to each of 4 beakers.

Beaker	Coagulant (alum) to be added
# 1	no coagulant
# 2	4 ml alum -> 40 mg alum / 500 ml sample = 80 mg / L alum
# 3	8 ml alum -> 80 mg alum / 500 ml sample = 160 mg / Lalum
# 4	12 ml alum->120 mg alum / 500 ml sample= 240 mg / L alum

3. Flash mix (at 80 rpm) each beaker, 1 to 3 minutes.

4. Set timer for 30 minutes, and slow paddles down to 10 to 20 rpms and slowly mix and watch floc formation. Note how long it takes before a floc begins to form in each of the beaker.
   Measure and record pH of each sample 10 minutes before the end of the 30-minute solution mixing period.
   Note the floc type observed as follows :

Floc Size Observed	Floc Type
extremely fine floc	PIN POINT
3 - 4 mm in diameter	FINE
7 - 8 mm in diameter	SMALL
8 - 12 mm in diameter	FAIR
12 - 23 mm in diameter	GOOD
60 mm or larger in diameter	LARGE STRAGGLER

5. After the stirring period is over, stop the stirrer, **allow the mixture to settle for 20 minutes.**
Note how long it takes for the floc to settle to the bottom of the beaker.
Note the comments on settling as follows:

Minutes to settle	Comment
Less than 2	Excellent
2 to 4	Good
4 to 7	Fair
More than 10	Poor

6. After allowing the floc to settle , determine the turbidity of the supernatant(the liquid above the settled floc).

7. Plot coagulant(alum) dose (mg /L) vs. turbidity (NTU) graph and determine the optimum coagulant dose for maximum removal of turbidity.

B- Determination of optimum pH for optimum coagulant dose

1. Fill each of the four beakers with a new 500 ml of original sample.
2. Add the optimum coagulant dosage determined from A to each of four beakers.
3. Adjust the pH of each beaker as follows:

Beaker	What to do to each beaker
# 1	no adjustment but measure the "as is" pH
# 2	adjust the pH to 5.0
# 3	adjust the pH to 6.0
# 4	adjust the pH to 8.0

(Beakers # 2 – # 4:) use 0.1 N NaOH and 0.02 N H_2SO_4 for pH adjustment.

4. Rapid mix (80 rpm) for 1 to 3 minutes.

5. Set timer for 30 minutes, and slow paddles down to 10 to 20 rpms and slowly mix and watch floc formation.
Note how long it takes before a floc begins to form in each of the beaker.
Measure and record pH of each sample 10 minutes before the end of the 30-minute solution mixing period.
Note the floc type observed as follows :

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6. After the stirring period is over, stop the stirrer, allow the mixture to settle for 20 minutes.
Note how long it takes for the floc to settle to the bottom of the beaker.
Note the comments on settling as follows:

Minutes to settle	Comment
Less than 2	Excellent
2 to 4	Good
4 to 7	Fair
More than 10	Poor

8. After allowing the floc to settle , determine the turbidity of the supernatant(the liquid above the settled floc).

9. Plot pH vs. turbidity (NTU) graph and determine the optimum pH dose for maximum removal of turbidity.

C- Determination of necessary lime amount

1. Once the optimum coagulant dose and pH are determined, then fill a new beaker with 500 ml of raw sample.

2. Add the optimum coagulant and rapid mix (80 rpm) for 3 minutes.

3. Then insert a pH electrode and set speed of paddle at 20 rpm. slowly add the lime until the optimum pH is achieved, recording the amount of lime solution consumed.

D- Determination of coagulant aid (Polyelectrolyte) dose:

1. To determine if polyelectrolytes can help the coagulation - flocculation process, fill each of the four beakers with a 500 ml raw water.
Add the optimum coagulant dosage determined from A to each of four beakers.

2. Then add the following volumes of 0.05% polymer solution to each of 4 beakers.

Beaker	Polymer to be added
# 1	no polymer
# 2	0.5 ml polymer-> 0.25 mg polymer / 500 ml sample = 0.5 mg / L polymer
# 3	0.8 ml polymer-> 0.40 mg polymer / 500 ml sample = 0.8 mg / L polymer
# 4	1.0 ml polymer-> 0.50 mg polymer / 500 ml sample= 1.0 mg / L polymer

3. Add the lime dosage determined from C to each beaker to adjust optimum pH value.

RECORDING SHEETS FOR JAR TESTING

DATE : ....

<u>RAW WATER ANALYSIS</u>

Turbidity : .... **NTU**

pH : ....

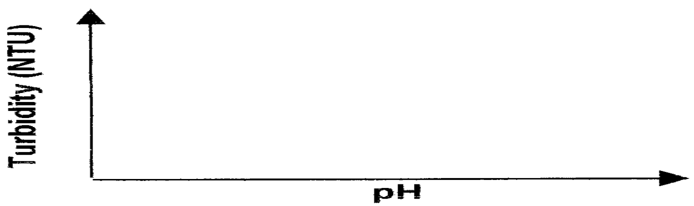
A - DETERMINATION OF OPTIMUM COAGULANT DOSE

JAR	ALUM (mg / L)	Floc Form (min)	pH (20 min)	FLOC TYPE	Settling Rate (min)	Comment on settling	Supernatant Turbidity (NTU)
1							
2							
3							
4							

B - DETERMINATION OF OPTIMUM pH FOR OPTIMUM COAGULANT DOSE

Optimum coagulant dose added to each beaker : .... **mg / L**

JAR	pH	Floc Form (min)	pH (20 min)	FLOC TYPE	Settling Rate (min)	Comment on settling	Supernatant Turbidity (NTU)
1							
2							
3							
4							



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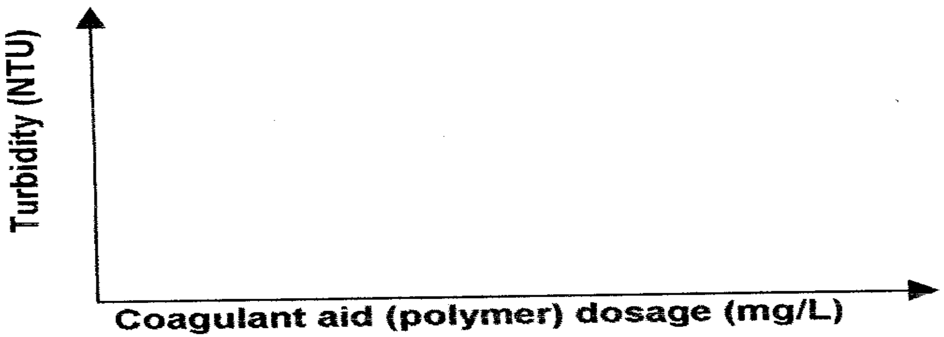
C - DETERMINATION OF NECESSARY LIME AMOUNT

Optimum coagulant dose added to each beaker : .... mg / L
Optimum pH :
Amount of lime solution to be added to achieve optimum pH : .... ml
Lime concentration to be added to achieve optimum pH : .... mg / L

D- DETERMINATION OF COAGULANT AID (POLYELECTROLYTE) DOSAGE

Optimum coagulant dose added to each beaker : .... mg / L
Lime dosage added to each beaker : .... mg / L

JAR	POLYMER (mg / L)	Floc Form (min)	pH (20 min)	FLOC TYPE	Settling Rate (min)	Comment on settling	Supernatant Turbidity (NTU)
1							
2							
3							
4							



Classification of Surface Water with Regard to Coagulation

Low turbidity < 10 JTU

High turbidity > 100 JTU

Low alkalinity < 50 mg/L as $CaCO_3$

High alkalinity >250 mg/L as $CaCO_3$

Group 1 (High turbidity – Low alkalinity)

- → With relatively small dosages of coagulant water of this type should be easily coagulated by "adsorption and charge neutralization"
- → May need to add alkalinity if ph drops during treatment

Group 2 (High turbidity – High alkalinity)

- → Because of the high alkalinity, adsorption and charge neutralization will be less effective mechanism than in waters of low alkalinity
- → Higher coagulant dosage should be used to ensure sweep coagulation
- → The pH will be relatively unaffected by coagulant addition

Group 3 (Low turbidity – High alkalinity)

→ The small number of colloids make coagulation difficult. Addition of some turbidity may decrease the amount of coagulant needed.

→ The principal coagulation mechanism is sweep flocculation with moderate coagulant dosage

Group 4 (Low turbidity – Low alkalinity)

→ The small number of colloids make coagulation difficult and low alkalinity prevents effective $Al(OH)_3$ formation

→ Additional turbidity can be added to convert this water to that of group 1 or additional alkalinity can be added to convert it to group 3

→ It may be adventegous to add both turbidity and alkalinity