CHAPTER 4

CHEMICAL COAGULATION AND FLOCCULATION

4.1 General Considerations.

The term " chemical treatment " has been popularly employed in reference to the process " chemical coagulation". As a process for treatment of wastes, coagulation may be defined as the addition of chemicals termed " coagulants," to effect destabilization and aggregation of dispersed materials, followed by separation of the aggregated material from the suspending liquid. The initial operation in the coagulation process is a rapid mix frequently lasting a minute or less in which coagulants and chemicals for pH adjustment are distributed throughout the waste. The mixing operation and chemical addition may consist of several stages. The next operation normally consists of flocculation, a slow mix lasting 10 to 40 minutes employed for the purpose of promoting collisions between destabilized particles resulting in the formation of settleable aggregates. The final operation in the process consists of separation of the destabilized aggregates from the suspending liquid, usually by sedimentation or by floatation. Filtration may be substituted or used in conjunction with sedimentation for separation of aggregated materials.

Chemical coagulation unit employing mixing, flocculation, and sedimentation. (Parsons 1965)

A definition of the difference between coagulation and flocculation is needed because the terms are often used interchangeably. Coagulation involves the reduction of surface charges and the formation of complex hydrous oxides. Coagulation is essentially instantaneous in that the only time required is that necessary for dispersing the chemical coagulants throughout the liquid.

Flocculation involves the bonding together of the coagulated particles to form settleable or filterable solids by agglomeration. This agglomeration is hastened by stirring the water to increase the collision of coagulated particles. Unlike coagulation, flocculation requires definite time intervals to be accomplished. (Culp 1971)

4.2 Purposes of chemical coagulation

Chemical coagulation of waters is performed for several reasons. The major ones are removal of: (1) Turbidity, inorganic and organic; (2) Color, true and apparent; (3) harmful bacteria and other pathogens; (4) algae and other plankton organisms; (5) taste - and odor - producing substances; and (6) phosphates, which serve as nutrients for the growth of algae. Removal of these materials produces a water that is aesthetically acceptable and that can be disinfected properly. In addition,

the clarified water is rendered much more amenable to filtration through sand filters. (Sawyer 1967)

Chemical coagulation is particular useful in situations where industrial wastes toxic to bacteria are present in sewage. In such cases coagulation may serve as the entire treatment or as pretreatment for removal of toxic materials prior to biological treatment. (Parsons 1965)

4.3 Chemical Coagulation

The removal of oxygen - demanding and turbidity - producing colloidal solids from wastewaters is often called intermediate treatment, since colloids are intermediate in size between suspended and dissolved solids. The most common and practical method of removing these solids is by chemical coagulation. This is a process of destabilizing colloids, aggregating them, and binding them together for ease of sedimentation. It involves the formation of chemical flocs that absorb, entrap, or otherwise bring together suspended matter, more particularly suspended matter that is so finely divided as to be colloidal.

The Chemicals most commonly used are : alum, $Al_2(SO_4)_3 \cdot 18H_2O$; Copperas, $FeSO_4 \cdot 7H_2O$; ferric sulfate, $Fe_2(SO_4)_3$; ferric chloride, $FeCl_3$; and chlorinated copperas, a mixture of ferric sulfate and chloride. Aluminum sulfate appears to be more effective in coagulating carbonaceous wastes, while iron sulfates are more effective when a considerable quantity of proteins is present in the waste.

The process of chemical coagulation involves complex equilibria among a number of variables including colloids of

dispersed matter, water or another dispersing medium, and coagulating chemical. Driving forces -- such as the electrical phenomenon, surface effects, and viscous shear -- cause the interaction of these three variables. (Nemerow 1971)

4.4 <u>Coagulation by Neutralization of the Electrical Charges.</u>

This can be accomplished by :

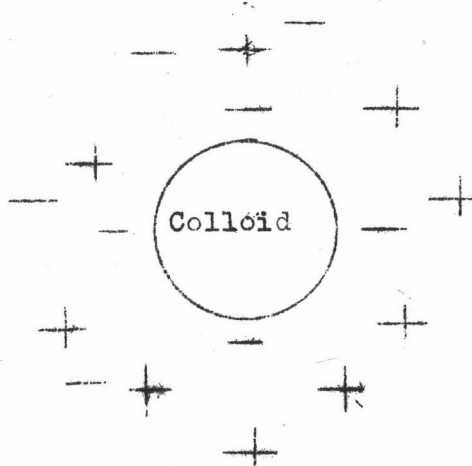(1) Lowering the zeta potential of the colloids. (Fig. 1)

<u>FIG. 1 STABLE COLLOID</u>

Zeta potential is the difference in electrical charge existing between the stable colloid and the dispersing medium.

(2) Neutralizing the colloidal charge by flooding the medium with an excess of oppositely charged ions, usually hydrous oxide colloids formed by reaction of the coagulant with

ions in the water. The coagulant colloids also become destabilized by the reaction with foreign, oppositely charged, colloids and produce hydrous oxide, which is a floc-- forming material.
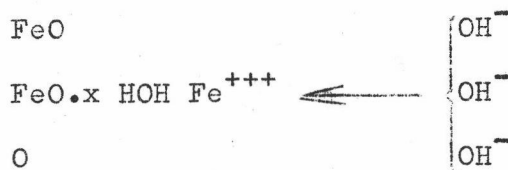
From the standpoint of electrical charges, there are two predominant types of colloid in wastewaters :

(1) Colloids naturally present, including several proteins, starches, hemicelluloses, polypeptides, and other substances, all possess negative charges (mostly lyophilic in nature).

(2) Colloids artificially produced by coagulants, usually the hydroxides of iron and aluminium (mostly lyophobic in nature), are mainly positively charged ions.

In most scientific circles, it is believed that the charge on colloidal particles is due mainly to the preferential adsorption of ions (H^+ or OH^-), from the dispersing medium. The charge may also be due, in part, to the direct ionization of a portion of its structural groups, such as NH_2^+ and COO^-

Hydrous aluminum and iron oxides, as well as other metal sols, can acquire both positive and negative charges. Excess Fe^{+++} makes colloids positively charged. The following expression depicts a resultant positively charged colloid :

$$\begin{array}{l} FeO \\ FeO \cdot x\ HOH\ Fe^{+++} \end{array} \Longleftarrow \left\{ \begin{array}{l} OH^- \\ OH^- \\ OH^- \end{array} \right.$$

Excess OH^- makes colloids negatively charged. The Following expression depicts a resultant negatively charged colloid :

$$\begin{array}{l} FeO \\ FeO \cdot x\ H_2O\ OH^- \\ O \end{array} \Longleftarrow H^+$$
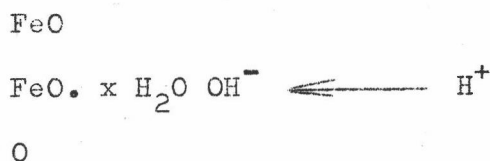
However, a colloid can acquire a charge by means other than adsorption. A protein dissolved in solution can be schematically illustrated as follows :

$$COO^- ---- \left[\text{protein base molecule} \right] ---- NH_2^+$$
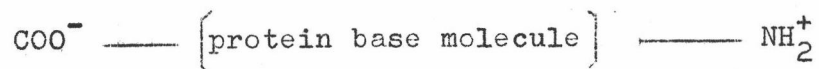
It may become necessary to add up all the positive NH_2^+ groups and the negative COO^- groups to ascertain the final ionic charge of the solution, because of the inherent charge brought about by direct ionization of the particle. The sol is thereby stabilized by inherent ionization of groups within the molecule itself. (Nemerow 1971)

Optimum coagulation will occur when the zeta potential is zero; this is defined as the isoelectric point. Effective coagulation will usually occur over a zeta potential range of ± 0.5 mv. (Eckenfelder 1966)

4.5 Coagulants

The most widely used coagulants for chemical coagulation of wastewater are salts of iron and aluminum. Iron salts are available in either the ferric or ferrous form. Ferric ion, being trivalent, is generally superior for coagulation purposes to divalent ferrous ion.

The common commercial form of aluminum coagulant is aluminum sulfate, or alum.

Lime, usually high calcium, has to a lesser extent been employed for coagulation of sewage and industrial wastes.

Some characteristics of aluminum sulfate, common ferric, and lime coagulants are given in Table 1.
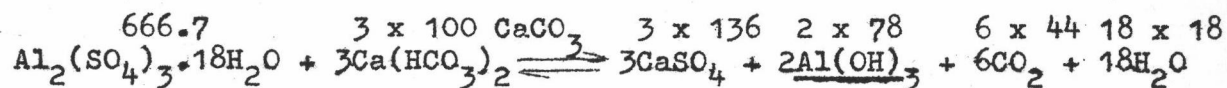
TABLE 1. CHARACTERISTICS OF COAGULANTS

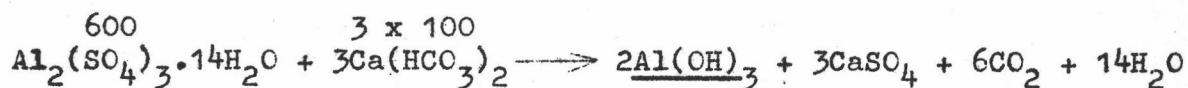| Coagulant | | | Theoretical Precipitate | |
Name	Usual Commercial Formula	Composition	Solubility Product 18° C *	Usual pH Level of Application
Alum	$Al_2(SO_4)_3 \cdot 14H_2O$	$Al(OH)_3$	1.3×10^{-33}	4.5 – 7.0
Copperas	$FeSO_4 \cdot 7H_2O$	$Fe(OH)_2$	1.64×10^{-14}	8.5 – 10.5
Chlorinated Copperas	$Fe_2(SO_4)_3 \cdot FeCl.$	$Fe(OH)_3$	1.1×10^{-36}	4-6 & 8-10
Ferric Chloride	$FeCl_3$	$Fe(OH)_3$	1.1×10^{-36}	4-6 & 8-10
Ferric Sulfate	$Fe_2(SO_4)_3 \cdot 2H_2O$	$Fe(OH)_3$	1.1×10^{-36}	4-6 & 8-10
Lime	$Ca(OH)_2$	$CaCO_3$	9.5×10^{-9}	9-11.5
		$Ca_3(PO_4)_2$	3.8×10^{-29}	10 – 11
		$CaSO_4 \cdot 2H_2O$	2.1×10^{-4}	4 – 10

* Adapted from Handbook of Chemistry and Physics (140)

and other sources. (Parsons 1965)

Aluminum Coagulation

When alum is added to sewage containing calcium and magnesium bicarbonate alkalinity, the reaction that occurs may be illustrated as follows :

$$\overset{666.7}{Al_2(SO_4)_3 \cdot 18H_2O} + \overset{3 \times 100 \; CaCO_3}{3Ca(HCO_3)_2} \rightleftharpoons \overset{3 \times 136}{3CaSO_4} + \overset{2 \times 78}{\underline{2Al(OH)_3}} + \overset{6 \times 44}{6CO_2} + \overset{18 \times 18}{18H_2O}$$

or

$$\overset{600}{Al_2(SO_4)_3 \cdot 14H_2O} + \overset{3 \times 100}{3Ca(HCO_3)_2} \longrightarrow \underline{2Al(OH)_3} + 3CaSO_4 + 6CO_2 + 14H_2O$$
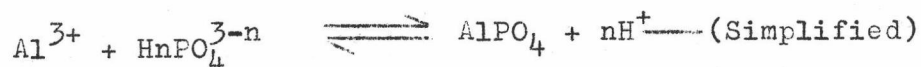
The insoluble aluminum hydroxide is a gelatinous floc that settles slowly through the sewage, sweeping out suspended matter as well as producing other changes. The reaction is exactly analogous when magnesium bicarbonate is substituted for the calcium salt. The numbers above the chemical formulas are the combining molecular weights of the different substances and therefore donote what quantity of each is involved. Because alkalinity is reported in terms of calcium carbonate ($CaCO_3$), the molecular weight of which is 100, the quantity of alkalinity required to react with 10 mg/liter of alum is

$$10.0 \times \frac{3 \times 100}{666.7} = 4.5 \; mg/liter$$

If less than this amount of alkalinity is available, it must be added. Lime is commonly used for this purpose when necessary, but it is seldom required in sewage treatment.

(Eddy 1972)

In the presence of phosphates, the following reaction also occurs :

$$Al_2(SO_4)_3 + 2\ PO_4 \longrightarrow 2\ AlPO_4 + 3\ SO_4$$

$$Al^{3+} + HnPO_4^{3-n} \rightleftharpoons AlPO_4 + nH^+ \text{---(Simplified)}$$

Alum is available in either dry or liquid form. It is available in dry form as either ground, powder, or lump form in bags, barrels, or cailoads. (Culp 1971)

If the formation of a floc composed of the theoretical precipitate is to be achieved, the pH level must be maintained within a range of low solubility. (Parsons 1965)

The alum floc is least soluble at a pH of approximately 7.0 . The floc charge is positive below pH 7.6 and negative above pH 8.2. Between these limits the floc charge is mixed. (Eckenfelder 1966)

General speaking, the best precipitates are formed at points of low solubility of the hydrous oxides of iron and aluminum. Furthermore, the time required for floc formation is least at these points. (Imhoff 1956)
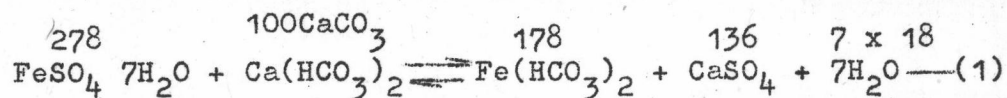
Iron Coagulation

If iron salts are used for wastewater coagulation, a small amount of base, usually sodium hydroxide or lime,
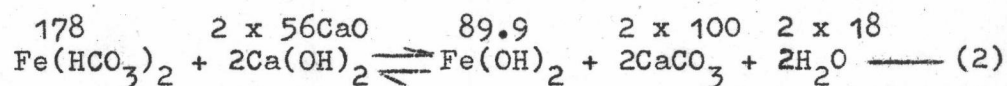
is required to neutralize the acidity of these strong acids
salts in soft water. (Culp 1971)
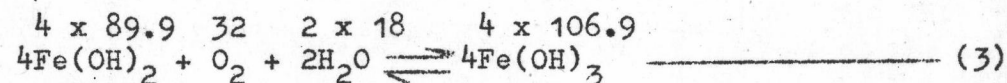
Ferrous Sulfate and Lime

In most cases, ferrous sulfate cannot be used alone
as a precipitant since lime must be added at the same time, to
form a precipitate. The reaction with ferrous sulfate alone
is illustrated in Eq. 1

$$\overset{278}{FeSO_4} \ 7H_2O + \overset{100CaCO_3}{Ca(HCO_3)_2} \Longrightarrow \overset{178}{Fe(HCO_3)_2} + \overset{136}{CaSO_4} + \overset{7 \times 18}{7H_2O} \quad (1)$$

If lime in the form $Ca(OH)_2$ is now added, the
reaction that takes place is

$$\overset{178}{Fe(HCO_3)_2} + \overset{2 \times 56CaO}{2Ca(OH)_2} \Longrightarrow \overset{89.9}{Fe(OH)_2} + \overset{2 \times 100}{2CaCO_3} + \overset{2 \times 18}{2H_2O} \quad (2)$$

The ferrous hydroxide is next oxidized to ferric
hydroxide, the final form desired, by the oxygen dissolved in
the sewage :

$$\overset{4 \times 89.9}{4Fe(OH)_2} + \overset{32}{O_2} + \overset{2 \times 18}{2H_2O} \Longrightarrow \overset{4 \times 106.9}{4Fe(OH)_3} \quad (3)$$

The insoluble ferric hydroxide is formed as a bulky,
gelatinous floc similar to the alum floc. The alkalinity
required for 10 mg/liter of ferrous sulfate is

$$10.0 \times \frac{100}{278} = 3.6 \quad \text{mg/liter}$$

The lime required is
$$10.0 \times \frac{2 \times 56}{278} = 4.0 \quad \text{mg/liter}$$

The oxygen required is
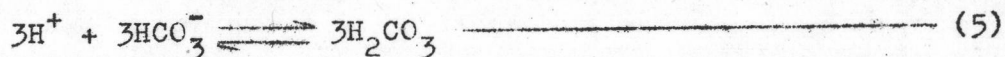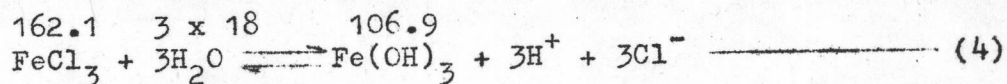$$10.0 \times \frac{32}{4 \times 278} = 0.29 \quad \text{mg/liter}$$

Oxidation is favored by a high pH value, which is established to some extent by the lime.

In sewage treatment, lime is commonly added in excess of the amount required. Experience has shown that the best results are obtained by adding sufficient lime to produce a pink color when phenolphthalein is used as an indicator. Since the formation of ferric hydroxide is dependent on the presence of dissolved oxygen, the reaction is Eq. 3 cannot be completed with septic sewages or industrial waste devoid of oxygen. Ferric sulfate may take the place of ferrous sulfate, and its use often avoids the addition of lime and the requirement of dissolved oxygen. (Eddy 1972)
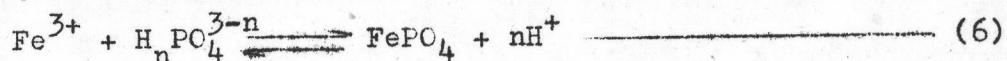
Ferric chloride

Ferric chloride reacts with the natural alkalinity of the water or with the added lime to form ferric hydroxide floc.
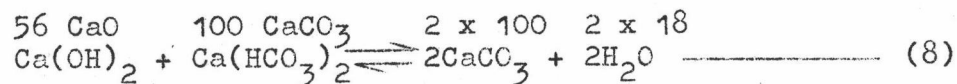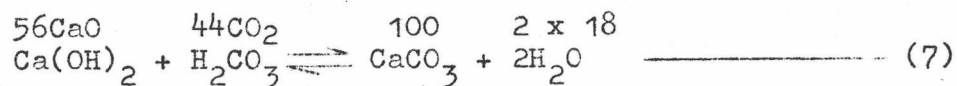
The reactions for ferric chloride are

$$\overset{162.1}{FeCl_3} + \overset{3 \times 18}{3H_2O} \rightleftharpoons \overset{106.9}{Fe(OH)_3} + 3H^+ + 3Cl^- \text{——————} (4)$$

$$3H^+ + 3HCO_3^- \rightleftharpoons 3H_2CO_3 \text{————————————} (5)$$

For Phosphate – Removal Reactions (Simplified)

$$Fe^{3+} + H_nPO_4^{3-n} \rightleftharpoons FePO_4 + nH^+ \text{——————————} (6)$$
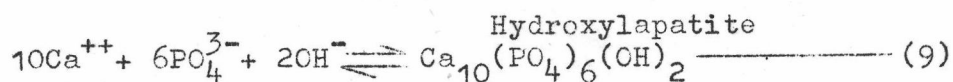
(Eddy 1972)

Ferric chloride is available commercially in liquid, crystalline and anhydrous form. Liquid ferric chloride is very corrosive and must be transported in rubber – lined tank cars or in glass carboys. The strength varies from 31% to 45% ferric chloride by weight, depending on the temperature. The crystalline form of ferric chloride contains 60% ferric chloride by weight and is supplied in barrels holding about 198 kg. (435 lb.). Anhydrous ferric chloride is free from water of crystallization and is supplied in steel drums holding about 45 kg. (100 lb.). The material remains non – corrosive to the drums as long as moisture is excluded. (Cox 1964)

Lime   When lime alone is added as a precipitant or is used in excess of the amount required for the precipitation of the iron in the previous reactions, the principles of clarification are explained by the following reactions :

$$56CaO \qquad 44CO_2 \qquad 100 \qquad 2 \times 18$$
$$Ca(OH)_2 + H_2CO_3 \rightleftharpoons CaCO_3 + 2H_2O \makebox[3cm]{\dotfill} (7)$$

$$56\ CaO \qquad 100\ CaCO_3 \qquad 2 \times 100 \quad 2 \times 18$$
$$Ca(OH)_2 + Ca(HCO_3)_2 \rightleftharpoons 2CaCO_3 + 2H_2O \makebox[2cm]{\dotfill} (8)$$

For Phosphate - Removal Reactions (Simplified)

$$\overset{\text{Hydroxylapatite}}{10Ca^{++} + 6PO_4^{3-} + 2OH^- \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2} \makebox[2cm]{\dotfill} (9)$$

A sufficient quantity of lime must therefore be added to combine with all the free carbonic acid and with the carbonic acid of the bicarbonates (half - bound carbonic acid) to produce calcium carbonate, which acts as the coagulant. Much more lime is generally required when it is used alone than when sulfate of iron is also used. Where industrial wastes introduce mineral acids or acid salt into the sewage, these must be neutralized before precipitation can take place.

(Eddy 1971)

The alkalinity ratio of pure calcium oxide (CaO) to pure calcium hydroxide $\left[Ca(OH)_2\right]$ is 1 : 1.32 .

(Cox 1964)

4.6 Coagulant aids

Many waters are difficult to coagulate by the simple addition of aluminum or ferric salts. Activated silica, and

more recently certain materials called polyelectrolytes, are added to stimulate floc formation. Activated silica is a negatively charged sol and acts to aid in flocculation of the positive charged metallic hydroxide sol formed by the metallic salt.

Polyelectrolytes may be devided into two categories ; natural and synthetic.

Polyelectrolytes are water - soluble high - molecular - weight polymers that contain groups capable of undergoing electrolytic dissociation to give large highly charged ions. Polymers that dissociate to form negatively charged polymeric ions, such as those with carboxylic groups, are called anionic polymers. Polymers having amino groups that dissociate to form positively charged ions are called cationic polymers. Some polymers dissociate to yield both large positive ions and large negative ions. These are erroneously referred to as nonionic polymers.

The polyelectrolytes when serving as coagulant aids undoubtedly act to reduce the stability of colloidal systems and to facilitate their coagulation.

The use of polyelectrolytes as coagulant aids has not been reduced to an exact science. This shortcoming may be attributed to the fact that they are of three widely differing

classes. Furthermore they are applied to a wide variety of materials possesing markedly different characteristics. However, their demonstrated effectiveness in certain instances has indicated their significant potential for more effective and economical coagulation. (Sawyer 1967)

4.7 Efficiency and usefulness of chemical precipitation

Colloidal solids and very finely divided suspended matter cannot be removed from wastes by plain sedimentation unless they are rendered settleable by the addition of coagulants or flocculating chemicals. The combination of flocculation and sedimentation is called " chemical precipitation "

As a treatment proccss, chemical precipitation accomplishes removals of solids and BOD about midway between plain sedimentation and complete biological treatment. Removal of about 80 % of the suspended solids and 65 % of the BOD are generally recorded for chemical dosages of about 30 mg/liter of ferric chloride. If the amount of chemical is doubled, removals as high as 90 % of the suspended solids and 80 % of the BOD may be reached.

Within the limits of the process, one of its attractive features is its flexibility. Efficiencies can be varied as needed. (Imhoff 1956)