



## Chapter II

### LITERATURE SURVEY ON COAGULATION

#### 2.1 History of Coagulation.

A number of **authors** have observed that the use of coagulation to clarify water for drinking purpose, although often regarded as modern, is in fact a very ancient practice. In urban communities it appears to have been unknown or strongly disapproved. D'Arcet at the beginning of the 19th century and Jeunet in 1865 sought to establish the value of the process, but it was not until 1881 that it was first used to treat a public water supply that of Bolton. Its use in Holland and America quickly followed (PACKHAM 1962).

In 1884 the first patent on coagulation was granted to Isaiah Smith Hyatt, who, following a suggestion of Col. L. H. Gardner, Supt. of the New Orleans Water Co., successfully combined the use of perchloride of iron as a coagulant in the treatment of turbid water. In his patent, Hyatt claimed the use not only of perchloride of iron, but of "any other suitable agent which is capable of coagulating the impurities of the liquid and preventing their passage through the filter bed (AWWA 1951).

In the year 1885 that Somerville began its combination coagulation-filtration treatment, professors Austen and Wilber of Rutgers University published the results of the first scientifically conducted studies of alum as a coagulant. Then, in 1893, further careful studies of the coagulation process in conjunction with rapid sand filtration were undertaken by Edmund B. Weston at Providence, R.I. And in the years 1895-97, at Louisville, Ky., George Warren Fuller and his associates conducted a series of important experiments on turbid Ohio River waters, which actually established a thoroughly scientific basis for the use of coagulants with rapid sand filtration (AWWA 1951).

In 1898 William B. Bull at Quincy, Ill., introduced the use of a combination of ferrous sulfate and lime, preparing his ferrous sulfate by burning sulfur and reacting the sulfuric acid with scrap iron in a

procedure devised by William Jewell. It was at Quincy, too, that the first use of commercial ferrous sulfate was recorded in 1902. Ten years later, E.V. Bull reported the first use of chlorinated copperas, and, though this material was not tried again until 1928, it was then found useful by Hodgepeth and Olsen in the coagulation of a highly colored water. This latter application, incidentally, served to focus attention on ferric salts, the use of which is now increasing. In 1937, Olin and Peterson reported successful experiments with bentonite clays, and, in the same year, Baylis described the use of "activated silica" as an aid to coagulation. Also in 1937, Upton and Buswell presented laboratory data on titanium salts as coagulants (AWWA 1951).

Fuller in 1898 publish the results of a similar investigation in which a number of electrolytes had been evaluated for the clarification of a turbid water. He found that the salts of aluminum and ferric ion gave the best results, the sulphates being better than the chlorides. Coagulation was therefore established as a satisfactory water treatment process by 1900. Since then its use gradually become more common, aliminum sulphate being the most widely used coagulant. Like Morison, he found the aluminum sulphate dose was independent of the amount of turbidity. Pirnie, suggested that the coagulant dose was proportional to the amount of colour and turbidity in addition to the alkalinity. He added that when organic pollution was present the aluminum sulphate dose was proportional to the concentration of this, rather than the colour or the turbidity (PACKHAM 1962).

The advantage of pH control was stressed in 1923, by Baylis, who found that a recurring difficulty in treating a river water when the content of organic matter was high, could be overcome by the use of acid to bring the pH within an optimum range. According to Baylis these results suggested that the stabilising effect of the organic matter or the river colloids was at a minimum at acid pH values (PACKHAM 1962).

In 1952 Langelier and his co-workers investigated the effect of particle size on the coagulation of clay suspensions. They found that clay particles smaller than one micron in diameter gave rise to a good floc but that as the particle size increased so the flocs became poorer.

Particles larger than 5 microns had very little effect on coagulation. The dose of coagulant required to bring about coagulation increased slightly as the particle size decreased (PACKHAM 1962).

## 2.2 The Stability of Colloids.

The term "sol" is used for the special case of a colloidal dispersion of a solid in a liquid. In the case of many sols, the addition of a relatively small concentration of a suitable electrolyte brings about aggregation and precipitation of the disperse phase, a process known as coagulation.

**Natural** waters are likely to contain dissolved inorganic and organic substances, and coarse suspended matter as well as substances in a state of colloidal suspension. The colloidal matter may be divided arbitrarily into two main types, that giving rise to turbidity and that giving rise to color. The substances normally producing turbidity or opalescence are clay minerals, with a certain amount of associated organic matter. The size of the particles varies, but the majority are 0.1 to 5.0 microns in diameter.

The substances producing color, as distinct from turbidity, consist either of colloidal metallic hydroxides or of organic compounds having a much lower order of particle size. The color and turbidity forming substances can be removed from water effectively by coagulation under suitable conditions. Aluminium sulphate is the most commonly used coagulant, although sodium aluminate and iron salts are often employed.

A further application of coagulation in water supply occurs in the softening of water by lime addition. The lime reacts with calcium bicarbonate (temporary hardness) in the water to yield calcium carbonate, some of which is often in colloidal form. This can be precipitated by the use of a suitable coagulant (PACKHAM 1962).

## 2.3 The Development of Theories of Colloid Stability.

### 2.3.1 The Nature of a Colloid.

It has already been indicated that particle size is the factor



determining whether or not a dispersion is colloidal. The smallest colloidal particles have dimensions comparable to large molecules, while the largest are just visible with the aid of a powerful optical microscope. It is hardly surprising that within this large range quite marked differences in behaviour are apparent.

Perrin, in 1905, distinguished between the colloids formed by substances such as starch, protein and gums on the one hand and the metals and their oxides on the other. The former substances react with water spontaneously, giving rise to sols which can be dehydrated to the original material and then again redispersed any number of times. In contrast, metallic sols can only be formed by special techniques and suffer irreversible coagulation if dehydrated. Perrin ascribed this behaviour to differences in the affinity of the disperse phase for water, and used the terms hydrophilic and hydrophobic.

Hydrophobic sols generally have a much larger particle size than hydrophilic. There is also a tendency for hydrophobic colloids to be inorganic, and hydrophilic organic.

Freundlich later extended Perrin's conception to cover dispersion media other than water, by using the general terms lyophobic and lyophilic.

The discovery by Reuss, in 1809, that particles of suspended clay under an applied electrical field migrate towards the positive electrode, later achieved great importance in the formulation of early ideas of colloid stability. This phenomenon, which became known as electrophoresis, in conjunction with other observations of a similar nature (Reuss, Quincke, and Dorn) gave rise to the idea that the surface of a colloidal particle had a negative charge. The stability of colloids could be explained by the strong mutual repulsion existing between the particles. This could only be effective below a certain particle size, above which the repulsion could be overcome by the action of the force of gravity, giving rise to sedimentation of the disperse phase.

Of great importance is the ratio of the surface area of a particle to its mass. In a large particle the ratio is low and mass effects (e.g. sedimentation under gravity) predominate. In a very small particle the ratio is high and properties associated with the surface of the



particle (e.g. electric charge) become more important (PACKHAM 1962).

### 2.3.2 The Electrical Double Layer.

Helmholtz in 1879 assumed that at the interface between the colloidal particle and the dispersion medium a separation of charge takes place, giving rise to an electrical double layer. The inner layer of charges is bound to the colloidal particle whereas the outer layer is associated with the dispersion medium. An applied electrical field causes these two layers to be displaced. Using electrostatic theory it was possible to derive a simple formula for the velocity of migration.

Ten years later Nernst showed how a double layer could be formed at the surface of a metal in contact with a solution of its ions. In such a solution the metal has a tendency to ionise, giving a positive metallic ion and leaving a corresponding negative charge on the surface of the metal. The positive ions formed by this process are attracted to the negative charge on the surface of the metal and a double layer is set up. The double layer tends to prevent the further solution of metallic ions, since these are repelled by the positive charges on the solution side and attracted by the negative charges of the metal. An equilibrium is set up when the forces of the electrical double layer are sufficient to prevent the solution of any more ions.

In 1910 Gouy pointed out the inadequacy of the simple Helmholtz double layer. Any tendency of the ions of the double layer to become concentrated at a definite distance from the surface would be disrupted by thermal agitation. There can be no sudden change in concentration in the vicinity of the double layer, but merely a gradual increase in the concentration of ions of one sign and a decrease of those of the opposite sign.

The Helmholtz and the Gouy concepts are compared in Fig.2.1, in which the potential energy at a point is plotted against the distance from the surface of the colloidal particle. In the Helmholtz diagram the range is limited by the outer layer which is envisaged as fixed; the Gouy theory, presupposing a diffuse layer, gives rise to an asymptotic curve. Chapman calculated the **equilibrium** distribution of ions in such a

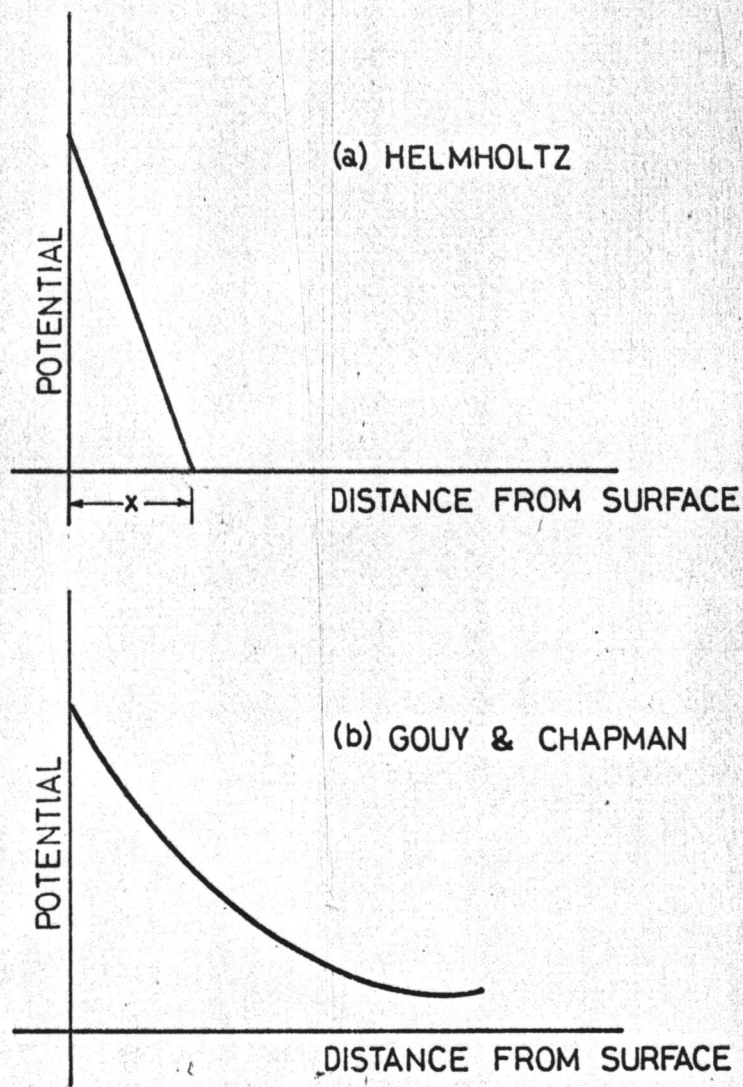


Figure 2.1 Curves of variation of electrical potential with distance from particle surface, illustrative of the double layer concepts of Helmholtz — a fixed single layer of ions — and of Gouy and Chapman — a diffuse cloud of ions.



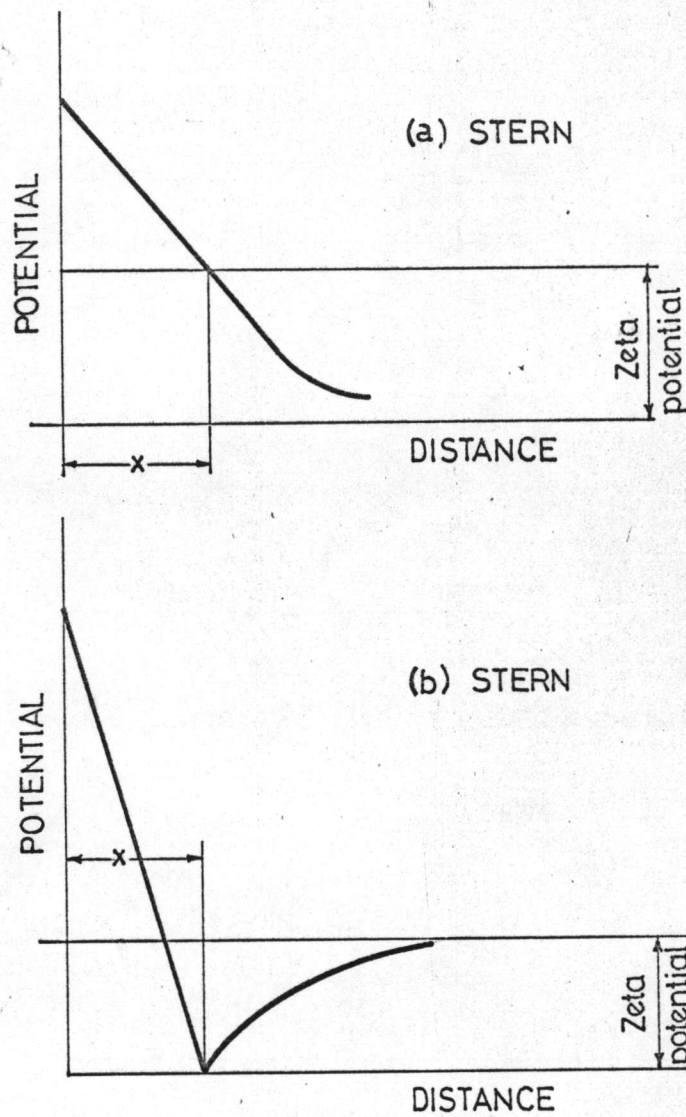


Figure 2.2 Curves of variation of electrical potential with distance from the particle according to the views of stern. (a) When adsorbed ions are insufficient to neutralise the charge on the particle surface. (b) When adsorbed ions more than neutralise the surface charge.





diffuse layer, together with its electrical capacity, but his results were not in agreement with experimental values.

The most comprehensive picture of the double layer was put forward by Stern in 1924. Stern showed that it was necessary to apply a correction to the Gouy-Chapman theory to allow for the possibility of the specific adsorption of ions. The resulting picture is a combination of the simple Helmholtz fixed layer with the Gouy-Chapman diffuse layer.

The adsorbed ions either partially or excessively neutralise the charge on the surface of the particle. The two possible forms of curve are shown in Fig.2.2. The fixed layer (extending a distance  $x$ ), is closely associated with the colloidal particle and will move with it through the dispersion medium. It is generally assumed that the surface of shear is just outside this layer and that it is the potential at this surface that is responsible for electrokinetic phenomena; this potential is known as the electrokinetic or zeta potential. The capacity of the electrical double layer calculated on the basis of Stern's theory was in much closer agreement with experimental results than values derived from previous theories (PACKHAM 1962).

### 2.3.3 The Origin of The Surface Charge.

**Until** recent times there was considerable argument as to the origin of the charge on a colloidal particle. Two main of thought developed, one favouring surface ionisation and the other adsorption as the explanation. It is now realised that both mechanisms play an important part, although one type may predominate in a given system.

It is very likely that, in the case of bentonite clay, the negative charge arises through the ionisation of sodium atoms present on its surface. The fact that many substances which cannot have ionogenic groups (e.g. silica, paraffin wax, cellulose) show a negative charge in pure conductivity water strongly suggests that here the mechanism is the adsorption of hydroxyl ions.

In the case of the classical silver iodide sol, for example, the negative charge could arise from the dissociation of a complex ionogenic group at the surface or the specific adsorption of iodide ions.

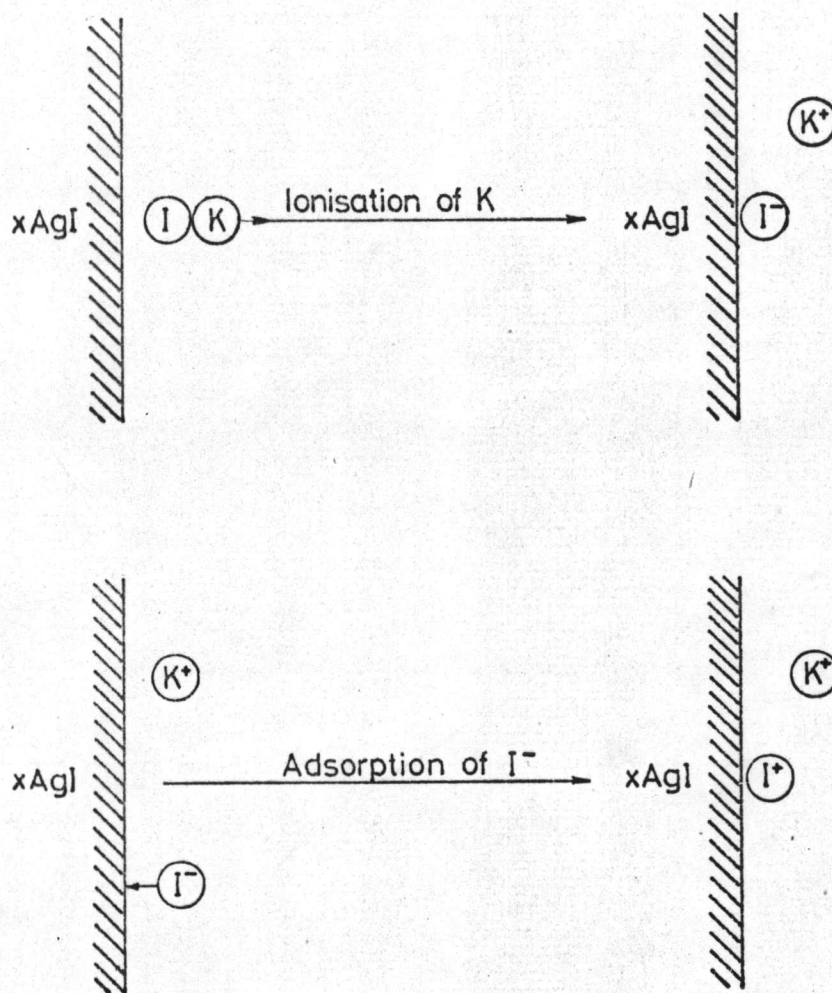


Figure 2.3 The identity of the result when (a) complex formation and subsequent ionisation, and (b) adsorption of ions are postulated to explain the charge of silver iodide sol.

Alexander and Johnson point out that the two theories are not as mutually exclusive as they might at first sight appear to be, since the final state may be the same whichever mechanism is assumed, see Fig.2.3 (PACKHAM 1962).

#### 2.3.4 The Stability of Colloids - Empirical Treatment.

Schultze in 1882 studied the coagulation of arsenious sulphide sols. His work was later put on a more general basis by Hardy in 1900 and the results became known as the Schultze-Hardy rules. The most important points emerging from this work were that coagulation is brought about by the ion having an opposite charge to that of the colloidal particle, and that the coagulating power of an ion is markedly dependent on its valency. Later in 1915 Powis introduced the concept of a critical zeta potential, below which a sol flocculates and above which it is stable (PACKHAM 1962).

#### 2.3.5 The Stability of Colloids - Theoretical Treatment.

##### (a) The Force of Repulsion

The striking effect of increasing valency on the flocculating power of an ion proved to be a major obstacle to the early theories of colloid stability. It was seen found necessary to approach the problem from a different point of view, in particular to consider not the coulomb repulsion between two similarly charged particles, but the much more complicated problem of the interaction between two particles each of which is surrounded by an electrical double layer. Verwey, has established that the effect of double layer interaction is a always to cause repulsion.

##### (b) The Force of Attraction

London in 1930 showed that the spherical symmetry and zero external field of these atoms are purely average effect; on account of nuclear and electronic vibrations such an atom may at any given instant show electrical asymmetry and hence a fluctuating dipole moment. This will induce a temporary dipole moment in surrounding atoms and a force of attraction will result. London derived an expression for the energy of such interaction between two atoms.



It is a fundamental consequence of quantum mechanics that such forces are additive. Hence in an assembly of atoms, each atom attracts every other atom with a force which is to a first approximation independent of the presence of surrounding atoms (PACKHAM 1962).

#### (c) Combination of Repulsive and Attractive Forces

Hamaker in 1936 developed a theory of stability of hydrophobic colloids based on the interplay of double layer repulsion and van der Waals attraction. Hamaker drew curves representing the potential energy as a function of the distance between the surface of two colloidal particles. The force of electrical repulsion can be represented by a curve AB (see Fig.2.4) and the London-van der Waals attractive forces by one BC. The combination of the attractive and repulsive forces can lead to different kinds of resultant curves, according to their variation with distance. Two types are shown in Fig.2.5.

If a sol is to be stable it is necessary that a maximum of sufficient height exists in the potential energy curve. The addition of electrolytes reduces this potential energy barrier until a stage is reached when flocculation takes place (PACKHAM 1962).

#### (d) Double Layer Interaction

In 1948 Verwey and Overbeek applied an extension of Debye and Hückel's theory of strong electrolytes, they calculated the total work associated with the gradual removal of all the ionic charges associated with a double layer. From this they derived the free energy of the system as a function of the distance, and extended their calculations to cover a system of two approaching double layers.

As the ~~free~~ energy is identical with the amount of work associated with an isothermal and reversible process of building up the double layers, the change of the free energy with the interparticle distance directly equals the change of the potential energy of the two particles with respect to each other. Thus they were able to obtain a potential energy curve showing the change of the repulsive forces of the double layer with distance.

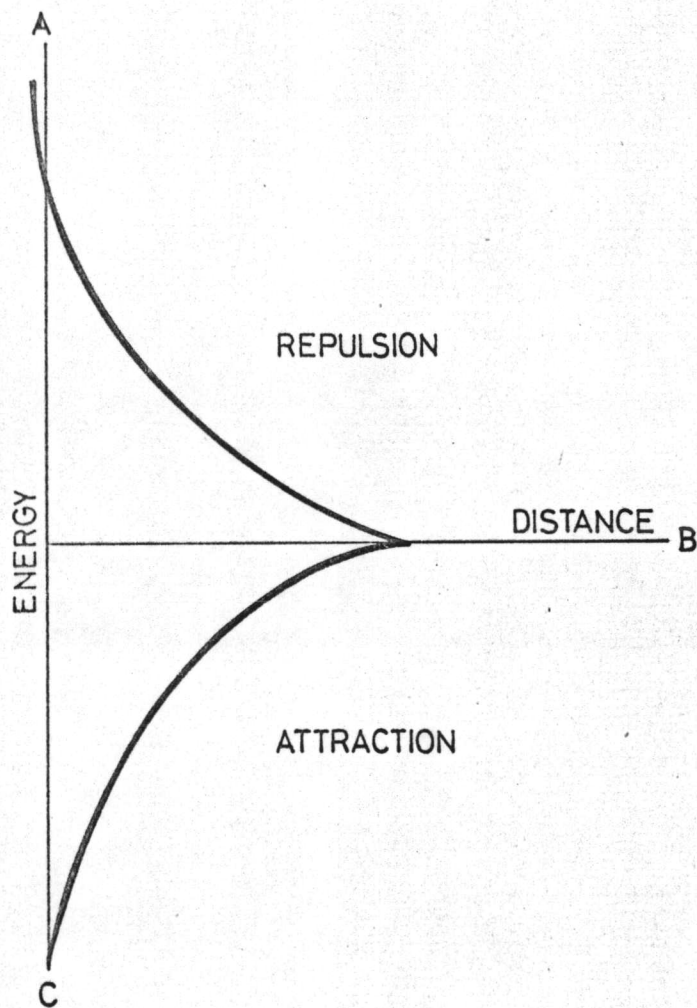


Figure 2.4 Representation of the repulsive force due to double layer (curve AB) and the London-van de waals attractive force (curve BC).

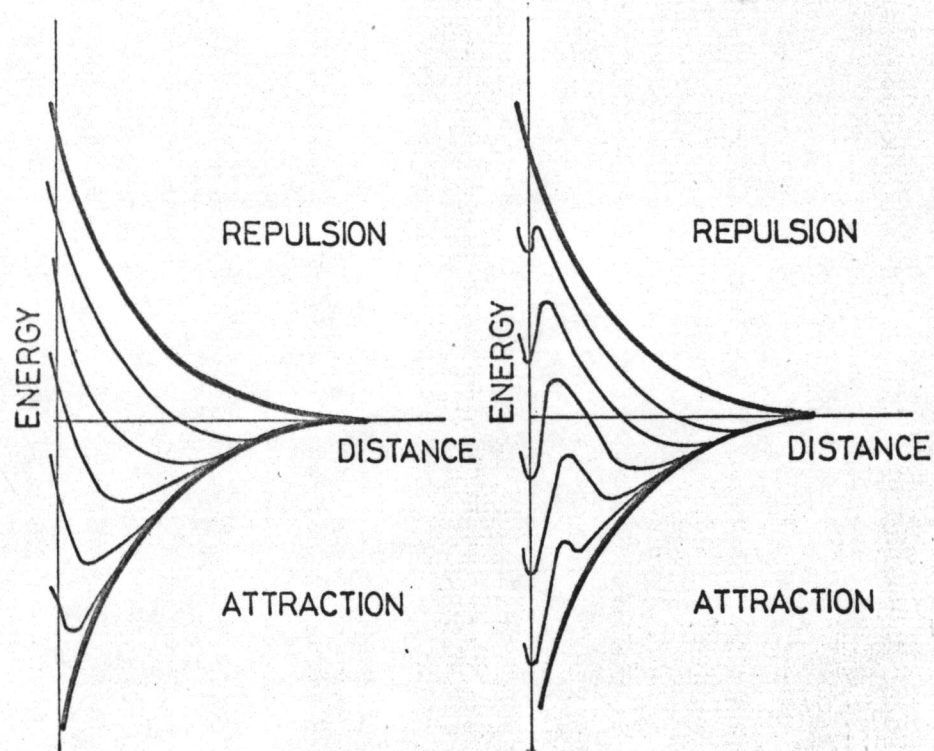


Figure 2.5 Some energy-distance curves — resultants of the attractive and repulsive forces. Increase of electrolytes lowers the curve, reducing the energy barrier to coalescence.



An important point that the zeta potential is no longer considered to be the fundamental factor governing stability. The only potential considered is the total potential of the whole double layer, and this remains constant and independent of the electrolyte concentration. The important variable factor is the distribution of this potential with distance from the colloidal particle - the thickness of the double layer. The effect of electrolytes is to decrease the thickness of the double layer, thus allowing the particles to come closer together (PACKHAM 1962).

### 2.3.6 The Kinetics of Coagulation.

In considering the course of the coagulation process with time, two distinct cases must be recognized.

The first and simplest is when so much electrolyte has been added that attractive forces operate at all distances from the colloidal particle. Every encounter between two particles results in irreversible coalescence.

In the second case enough electrolyte has been added to reduce appreciably the potential energy barrier but not to eliminate it. The height of the maximum in the potential energy curve represents the minimum energy required to bring about a successful collision. Since only a fraction of the particles present have this necessary energy, coagulation is slow.

In 1926 Müller used an extension of the Smoluchowski equation to consider the rapid coagulation of sols having particles of very different sizes (polydisperse). He showed that the probability of collision between particles of different sizes was much greater than that for particles of the same size. He used his theory to explain the previously observed fact that in a polydisperse flocculating system the smaller particles disappeared much more quickly than the larger ones. Müller later considered the rapid coagulation of sols in which the particles were other than spherical. He concluded that the probability of collision is always larger than that between equal or nearly equal spheres.

Overbeek pointed out that the probability of collision is proportional to the product of the constant of mutual diffusion and the

distance of closest approach. Consequently particles which are not spherical **have** a relatively large collision diameter combined with a relatively large diffusion constant and this results in a high probability of collision (PACKHAM 1962).

### 2.3.7 Present Theoretical Position

Colloidal properties are a function of the particle size of the disperse phase and are a result of the high ratio of surface area to mass in particles having a diameter of one micron and below. Because of this, the charge at the colloid particle surface, which may be due to ionisation or adsorption of ions, is of great significance. An electrical double layer is set up at the interface between the particle and the solution, consisting of the charged surface of the particle on the one hand and a cloud of ions tendings to neutralise this charge on the other.

The interaction of the double layers of two adjacent colloidal particles result in a repulsive force. Colloids are stable because this repulsive force, existing between all of the particles in a sol, is sufficient to overcome the force of attraction.

The thickness of the double layer is determined by the ionic composition of the dispersion medium and is particularly affected by the presence of multivalent ions. Such multivalent ions when of charge opposite to the colloidal particle can bring about a contraction of the double layer, allowing the closer **attractive** forces, which are effective over a short distance from the surface. Under these conditions coagulation of the disperse phase takes place (PACKHAM 1962).

## 2.4 Coagulation and Flocculation

The terms coagulation and flocculation are often used interchangeably. In this article, coagulation will be defined as the results of electrical and chemical action brought about in water following the addition of coagulating chemicals. Coagulation involves the reduction of surface charge and the formation of complex hydrous **oxides**. These reactions are nearly instantaneous; the only time required for this completion is that necessary for dispersing these chemicals throughout

the water. Shortly after mixing is achieved, coagulation is complete.

Flocculation, on the other hand, consists of the bonding together of the coagulate particles following the removal of the forces that kept them apart, and the entanglement of the particles by the precipitating hydrous oxides. Growth of the particles required the passage of a definite interval of time. These definitions are arbitrary, but it is necessary that a definition be made so that the meaning of the following sections be clear.

In water treatment practice, the term coagulant means an agent added to water to facilitate the settling out of colloidal or finely divided suspended matter. Coagulation, the treatment process involved, thus refers to the series of chemical and mechanical operations by which coagulants are applied and made effective. And these operations, in turn, are customarily considered to comprise two distinct phases: mixing, wherein the dissolved coagulant is rapidly dispersed throughout the water to be treated, usually by violent agitation; and flocculation, involving agitation of the water at lower velocities for a much longer period, during which the very small particles grow, and agglomerate into well-defined hydrated flocs of sufficient size to settle readily.

The factors governing the successful treatment of water by coagulants are:

1. the physical character of water, especially pH and temperature ;
2. the amount and type of coagulant;
3. the efficiency of mixing;
4. the method and time of flocculation;
5. the type of settling basin and retention time;
6. the efficiency of filtration.

## 2.5 Need for Coagulants.

Coagulants are employed in the treatment of waters of widely varying physical and chemical quality. With unsoftened surface waters, in which the removal of turbidity, organic color and bacteria is the



primary object of treatment, coagulation is all-important; and the overall efficiency of the plant and the quality of the treated water will depend to a very large degree upon its careful control. In many plants, of course, additional treatment, such as prechlorination, the addition of activated carbon for the removal of tastes and odors, stabilization before or after filtration, but coagulation can be an important aid to these as well as serving its own specific function.

Coagulants may or may not be required in the treatment of hard waters softened with lime or with lime and soda ash. When used in combination with water softening, coagulants are intended to produce a well flocculated, settleable sludge, which, in turn, will insure the delivery of a settled water of low turbidity to the filters. In addition, the use of coagulants is often effective in causing the softening reactions to proceed more nearly to completion, thus producing a softened water of lower total alkalinity.

Occasionally, surface or ground waters of objectionable hardness also contain organic color, and iron and hydrogen sulfide. Hardness and color quite frequently occur in areas where wells penetrating porous limestone become recharged with surface waters of high organic color. Sometimes softening by excess-lime treatment will reduce such color to an acceptable value without further treatment. More often, however, it is necessary to soften the water first and then to remove remaining color by secondary coagulation or other suitable treatment. In the treatment of such waters, ferric salts have the added advantage of aiding in the removal of iron and hydrogen sulfide as well as acting as coagulants.

## 2.6 Selection of Coagulant

The importance of the selection of the proper coagulant, that is one that will primarily coagulate the particular water in question the best and in the most economical manner. As the problem of coagulation has been studied, the fact that certain coagulants will not work equally well on all waters has been well established. The cost of coagulants are not so widely divergent, but of recent years the limitations of each

have been discovered through new found knowledge of their performance. Also, it is possible to find the "optimum" pH at which the coagulant will work best in a given water. Time of flocculation may be shortened at the sacrifice of low chemical cost. This is not economical, as additional mixing basin capacity is much cheaper than high consumption of chemicals. A definite relation between chemical dosage and mixing time has not been definitely established, but there are indications that on water requiring low chemical dosage, doubling the dosage will cut the time in half.

Factors to be considered in the choice of chemicals include cost, quantity required, handling, storing, and feeding requirements, and effectiveness in producing desired results. No chemical best fills all requirements under all conditions.

## 2.7 Selection of Doses

Selection of doses for a series of samples is based as a rule on the results of preliminary physical and chemical tests and the experience of the operator with that particular water. Where conditions are new and experience is lacking, it will be necessary to try various doses and combinations of doses until results show the minimum needed for proper floc formation. Characteristics to be observed when making the tests are as follows:

1. Length of time required for first appearance of floc.
2. Appearance of floc at end of specified stirring period.
3. Appearance of supernatant liquid and extent of floc settlement after period of standing equivalent to basin retention.

The lowest dose of chemical giving suitable floc formation is the one to use in the plant. This is the optimum for effective coagulation, and the pH of the sample so treated is the optimum which should be maintained on the water in the mixing chamber.

A permanent record should be kept of jar test results. This should include physical and chemical characteristics of the raw water, doses tried, corresponding floc appearance, and pH of the treated samples.

Information thus maintained is always of value in determining chemical doses, and is especially useful during periods of frequent changes in the raw water.

### 2.8 Determining Dose for Good Floc Production

Numerous advantages of good floc formation have been pointed out but a consideration of this sort would be incomplete without some reference as to how to obtain a good floc.

A chemical analysis of a water is not enough to tell how effectively it can be coagulated and what quantity of chemical is necessary. The physical characteristics of the water, as well as the chemical properties, have a bearing on the coagulant requirements. There is only one real way to determine the dose and that is by means of the simple jar test. A stirring machine for making the floc tests is not absolutely necessary but very desirable, for, depending on the number of water samples that can be stirred in the machine that many different doses can be tried at one time. In the absence of a well-equipped laboratory with a 3-, 4- or 6-place stirrer.

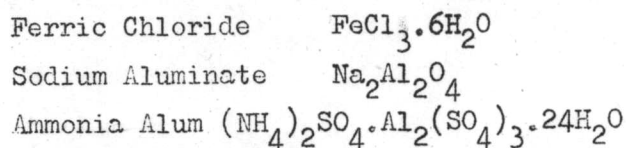
### 2.9 Coagulating Agents.

Of the three groups of coagulants, the most important is the one which includes the direct coagulating agents, consisting principally of aluminum or iron salts of sulfuric or hydrochloric acid. Among these agents, aluminum sulfate is still the most widely used, although ferrous sulfate (copperas) and ferric sulfate are being employed by an increasing number of plants. Ferric chloride, an important chemical in sewage treatment, has, however, found only a limited application in water purification.

The coagulants commonly used are:

Aluminum Sulphate	$Al_2(SO_4)_3 \cdot 18H_2O$
Ferrous Sulphate	$FeSO_4 \cdot 7H_2O$
Chlorinated Copperas	
Ferric Sulphate	$Fe_2(SO_4)_3$



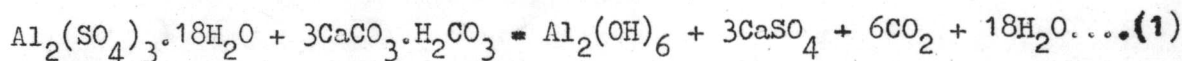


### 2.9.1 Aluminum Sulphate

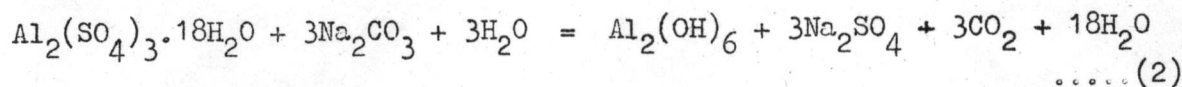
Aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ), commonly called alum, is probably the most widely used chemical for the coagulation of water because of its excellent floc formation, its relative economy, its stability, and its easy in handling. Calcium sulphate is formed when alum reacts with the natural alkalinity of water, thus increasing the sulphate hardness to a slight extent. The increase of free carbon dioxide may be objectionable because of its corrosive nature unless removed by subsequent decarbonation (BABBIT 1955).

In order that aluminum sulphate may react to form a precipitate, it is necessary that the water into which the alum is placed shall contain some alkalinity, usually in the form of calcium carbonate. The hypothetical reactions that occur are

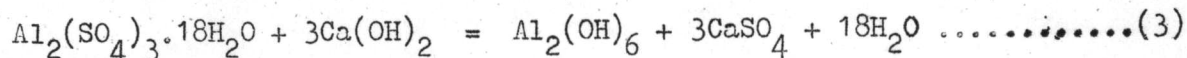
#### 1. Alum and natural alkalinity



#### 2. Alum and soda ash



#### 3. Alum and lime



### 2.9.2 Ferrous Sulphate.

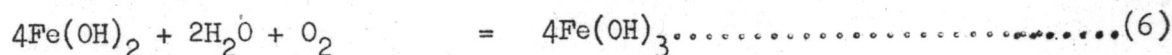
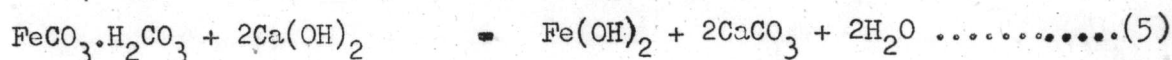
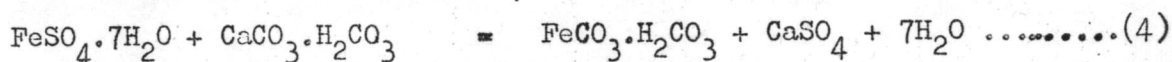
Ferrous sulphate has an advantage over alum in that it may be less expensive and the floc is heavier and sinks more rapidly. An outstanding disadvantage is the need for using lime with it. More complete chemical control is required, and there are greater dangers from after precipitation in the distribution system due to the reaction between surplus lime and bicarbonate alkalinity. Ferrous sulphate is unsuitable for treatment of soft colored waters because they are best

coagulated at a pH below 7.0. The **color** appears to become set by the addition of alkali to colored waters; hence the use of ferrous sulphate is limited to those waters in which alkalinity will not interfere with color removal. It is best suited to use in turbid waters of high natural alkalinity (BABBIT 1955). There is usually insufficient alkalinity in natural waters to react with ferrous sulphate, so that lime must usually be added to produce a floc and in order to avoid soluble compounds of iron remaining in the treated water.

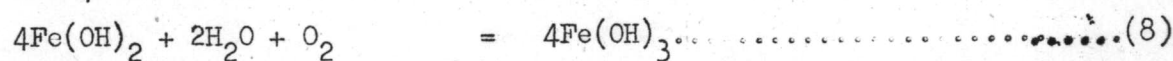
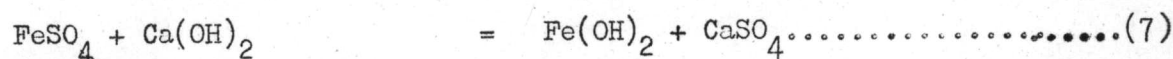
#### Reactions with Ferrous Sulphate.

The chemical reactions that occur when ferrous sulphate and lime are used in coagulation depend, in part, on the order in which the chemicals are added to the water.

When iron is added first, the reactions are :



When lime is added first the reactions are :

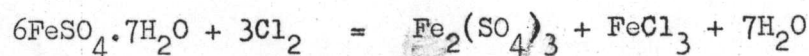


The ferrous hydroxide  $\text{Fe}(\text{OH})_2$  forms a desirable, heavy, gelatinous precipitate. It is, however, oxidized according to Eq. (6) to ferric hydroxide  $\text{Fe}(\text{OH})_3$  likewise a satisfactory gelatinous precipitate.

#### 2.9.3 Chlorinated copperas

When chlorine is added to the copperas in the ratio of 1 part chlorine for each 7.8 parts copperas, its effectiveness is tremendously increased and the disadvantage of necessary high alkalinity entirely eliminated (HEDGEPEETH 1934).

The reaction proceeds as follows:



thus producing a powerful mixture of ferric sulphate and ferric chloride.

In practice copperas may be feed from the usual alum dry feeder, dissolved with water and the resulting copperas solution merged with the discharge solution of a chlorinator.

Chlorinated copperas solutions are very corrosive and should be handle with rubber, glass or ceramic equipment (AWWA 1951).

#### 2.9.4 Ferric Sulphate

The composition of ferric sulphate is usually, not less than 90 per cent  $\text{Fe}_2(\text{SO}_4)_3$  for the anhydrous form and not less than 60 per cent, for the crystalline form (AWWA 1951).

Success in dissolving ferric sulphate requires careful attention and special equipment. Ferric sulphate solutions, although not as aggressive as ferric chloride or chlorinated copperas, are significantly corrosive and should be handled with rubber, glass, ceramic or stainless steel equipment.

Dry ferric sulphate is sufficiently hygroscopic to require tight packages for prolonged storage, particularly under humid conditions. Shipments are made in bulk, in moisture-tight barrels and in multi-wall shipping bags (AWWA 1951).

#### 2.9.5 Ferric Chloride

Ferric chloride is shipped; as 60 per cent  $\text{FeCl}_3$  crystals ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in liquidtight wooden barrels; as 98 per cent  $\text{FeCl}_3$  anhydrous in thin steel, nonreturnable drums; and as 39 to 45 per cent  $\text{FeCl}_3$  liquid in flass carboys, rebber-lined drums and rubber-lined tank cars. The liquid form is very corrosive and may be handled successfully only with rubber, glass or ceramic equipment. Dry crystal or abhydrous ferric chloride may be stored only in tight packages (AWWA 1951).

#### 2.9.6 Sodium aluminate

An alkaline compound of alumina and caustic soda which in its completely pure and 1 : 1 mol. ratio corresponds to the formula  $\text{Na}_2\text{O}$  :



$Al_2O_3$ , often expressed as  $Na_2Al_2O_4$  or  $NaAlO_2$  (HEDGEPEATH). Sodium aluminate is used most effectively on those waters requiring an alkali with the alum. Contrary to the general impression extant in the water purification field its cost per unit of alumina and sodium oxide is not out of line with equivalent weights of these active ingredients in filter alum and soda ash or caustic soda. Sodium aluminate has been found particularly efficacious as a secondary coagulant on those waters having an optimum pH in ranges where residual coagulant is likely to be excessive.

The methods of manufacture used in producing sodium aluminate are such that the impurities are insignificant. Shipments are made as aqueous solutions in steel drums or as dry powder in thin-walled steel drums or moistureproof multiwall paper and textile shipping bags. Sodium aluminate must be stored in tight containers.

#### 2.9.7 Ammonia Alum

Ammonia alum of the formula  $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  is not important in water purification except in very small installations—e.g., swimming pools, ice plants and laundries—where alum is fed by means of a solution pot connected across a venturithroat. Because of its tendency to plug the solution pot, ordinary filter alum is not suitable for use in such equipment.

There are two recognized advantages of ammonia alum over filter alum :

(a) It is slowly soluble, thus adapting itself admirably to those plants or swimming pools equipped with solution pots connected across venturi tubes.

(b) Its ammonium radicle content is available for chlorine stabilization. Compared on the basis of aluminum oxide contained therein its cost is three times that of filter alum.

## 2.10 Selection of Aluminum or Iron Coagulants.

Both filter alum and ferric sulfate have certain specific advantages. Alum, for instance, does not cause the unsightly red-brown staining of floors, walls and equipment which may result when iron salts are used, nor is its solution as corrosive as the ferric forms of iron salts. The trivalent aluminum ion is not reduced to a more soluble bivalent ion, as may be the case when iron salts are used with waters high in organic matter. On the other hand, ferric floc is denser than alum floc and is more completely precipitated over a wider pH range. It is known, of course, that the dissolving of ferric sulfate offers difficulties not encountered with alum or copperas and that good flocculation with alum is not possible in some waters. Weighing these various factors, the choice of the coagulant to be used for any particular water should be based upon a series of jar tests, so planned that it will permit an accurate comparison of the materials being studied under identical experimental conditions.

## 2.11 Ferrous Sulphate as a Coagulant

The most common form of iron coagulation, and by that is meant the one most familiar to all of us, is coagulation with ferrous sulphate and lime. This form of coagulation has been called, by many authorities, the most economical means of water coagulation (NICKEL 1946). The author does not entirely agree with this statement, however, since many of the difficulties encountered with the actual coagulation raise the total cost to the point where initial economy is hardly a consideration.

Ferrous sulphate itself, is water soluble and will remain in solution for a long time in any water near pH7. In order to have any coagulating value whatsoever, the ferrous sulphate must be converted to ferric salt. This is normally accomplished by raising the pH with lime and then adding the ferrous sulphate. The reaction result is the formation of ferric hydroxide, the same coagulating material obtained with almost any ferric salt. A certain portion of the ferrous sulphate

however, will be converted to ferric carbonate, which has absolutely no coagulating value. From this it can be readily seen that only a portion of the iron actually available in the ferrous sulphate is utilized in coagulation. Furthermore, if excess lime is added, an unbalanced water may be produced, and the sand grains on the filters may be seen to grow. If an insufficient amount of lime is used, some of the ferrous sulphate will remain in solution and will pass the filters still in solution. This will cause red water difficulties in the distribution system, as well as inefficiency in the actual coagulation process.

Ferrous sulphate in conjunction with lime was first used in Florida as a coagulant in 1898 by Bull at Quincy, Ill.. During the past 30 years, the combination of ferrous sulphate and lime has been extensively used in Florida particularly in the middle west and mainly for the removal of turbidity. The treatment has not, as a rule, proved satisfactory for color removal, since the color is "fixed" or "set" at the high alkalinity necessary for the oxidation of the ferrous iron. Furthermore, incomplete oxidation may result in high values for residual iron in the treated water (BLACK 1934).

Ferrous sulphate is the end product of the reaction between iron and sulfuric acid. The salt is soluble in water and, when crystallized and dried, has a greenish color. It is a green crystalline salt readily soluble in water and contains about 100 per cent  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . (GETTRUST 1952).

Ferrous sulphate is a waste product of the steel industry and as such it may contain undesirable impurities, but a supply of suitable quality was obtained from a local agent. It was stipulated that it was required for purifying a public water supply, but no specification was issued. Analyses gave the following result :

Ferrous iron (Fe)	...	19.0 - 19.5 %
Total iron (Fe)	...	19.5 - 20.0 %
Manganese (Mn)	...	0.17- 0.22 %
Sulphate ( $\text{SO}_4$ )	...	34.4 - 34.9 %
Insoluble matter	...	about 0.1 %



Ferrous sulphate content calculated as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  varied from 94.3 to 96.8 per cent (JOSEPH 1963).

A ferrous sulphate of iron of definite crystalline composition of the formula  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The most suitable grade for water works use is "Sugar Sulphate," consisting almost entirely of uniform small crystals of the size and dryness of ordinary granulated sugar. It contains very little if any free acid and is a relatively high concentrated material, having 28.8 percent water soluble  $\text{Fe}_2\text{O}_3$  as compared with the 17.2 percent  $\text{Al}_2\text{O}_3$  of filter alum (HEDGEPEETH 1934).

Before iron is fashioned into final manufactured products, the stock must be cleaned. It is common practice to clean the stock of scale and rust by dipping it in hot sulfuric acid. In time, the acid becomes exhausted and the resulting ferrous iron solution is discarded. This expended pickling liquor is the basis of commercial ferrous sulphate.

There are two methods by which ferrous sulphate can be used as a water coagulant. The first is the old lime and iron process that has been in use many years but is gradually losing ground to other coagulants, mostly because of its inability to coagulate colored waters. In this method the ferrous sulphate is changed to ferrous hydroxide by the addition of lime and then the ferrous hydroxide is oxidized to ferric hydroxide by the natural oxygen in the water.

The second method utilizes chlorine to oxidize ferrous sulphate to ferric sulphate. Ferric chloride is formed in the reaction. The resulting ferric compounds, called chlorinated copperas, are then added to the water to be coagulated. These iron compounds react with the natural bicarbonates to form the hydrates. This reaction is similar to that of aluminum sulphate.

#### 2.11.1 Handle and Storage

The physical form almost always used in water treatment is fine "sugar of copperas" crystals. Kramer and Graf (AWWA 1951) have indicated that these crystals store better, without hardening, when slightly dehydrated.

The equipment used to handle them should be made of rubber, lead,

glass, ceramic material or stainless steel.

The container used to storage them should be made of concrete, steel or wood. Granular iron salts should be stored in a dry place, If stored in a warm humid atmosphere, caking is apt to result. Kramer and Graf found that if they specified and obtained for use at the St. Louis plants a copperas containing not less than 105 per cent (of theoretical)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , it would store without caking (KERSLAKE 1964).

Shipment of this material are made in bulk or in packages. Slack wooden barrels are preferred for shipments of less than carloadlot size, and multiwall paper bags, for carloads of packaged copperas.

The difficulties alone are sufficient to rule against the use of ferrous sulphate and lime in most water works plants, Ferrous sulphate, moreover, has a tendency to cake and normally cannot be used in all types of dry feeders because of this tendency. If stored in large bulk hoppers it will often cake in the hoppers and may even require the use of air hammers to be broken losses. The most common method of storing ferrous sulphate is, of course, in water-proof bags, and most plants do use the material in that form.

#### 2.11.2 Solution Feed

Initially dry feeding was tried but it proved an **absolute** failure the copperas was **not** free-flowing. The copperas had therefore to be made into a solution of definite strength for dosing purposes. A saturated solution of copperas is roughly 30 to 34 per cent weight per volume, so it was considered that a 15 per cent solution could be readily made up without prolonged stirring, which proved to be the case (JOSEPH 1963).

The solution was delivered to the dosing equipment by alkathene pipes. Vacuum solution feed was used for a while and it proved reasonably successful but was later changed to the more positive pump feed, which worked very well (JOSEPH 1963).

## 2.12 Lime

Lime is used in water treatment less for coagulation than for other reasons such as increasing pH and adding alkalinity in coagulation; reducing carbonate hardness in water softening; reducing dissolved carbon dioxide, as a disinfectant; and increasing the length of filter runs in the presence of algae.

Unslaked lime or calcium oxide ( $\text{CaO}$ ) is a dry white amorphous powder. It has a dangerous affinity for water, which it can remove from the air or combine with in the liquid state with the generation of heat. The action is called slaking, and it results in the formation of the relatively inert slaked lime  $\text{Ca}(\text{OH})_2$ . Slaked lime is an amorphous white powder, relatively insoluble in water.

## 2.13 Sulphuric Acid

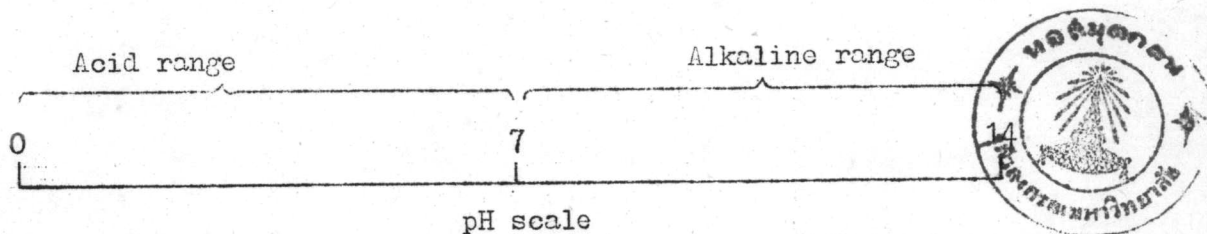
Sulphuric acid,  $\text{H}_2\text{SO}_4$ , is a strongly corrosive, dense, oily liquid, colored clear or dark brown, depending on purity. It is available in a number of grades, containing from 60 to 94 %  $\text{H}_2\text{SO}_4$ . In the 93 % grade it is noncorrosive to steel drums, or tanks. Once diluted, it is highly corrosive and should be contained in rubber, glass, or plastic-lined equipment to the point of application. Complete protective equipment is necessary in handling sulphuric acid. It may be fed with any corrosion-resistant (rubber-covered) liquid-chemical feeding device. (AWWA 1971).

## 2.14 Hydrogen-Ion Concentration (pH)

pH is a term used rather universally to express the intensity of the acid or alkaline condition of a solution. It is a way of expressing the hydrogen-ion concentration, or more precisely, the hydrogen-ion activity. In the field of water supplies, it is a factor that must be considered in chemical coagulation, disinfection, water softening, and corrosion control. For these reasons and because of the fundamental relationships that exist between pH, acidity, and alkalinity, it is very important to understand the theoretical as well as the practical aspects of pH.



The pH scale is usually represented as ranging from 0 to 14, with pH 7 representing absolute neutrality.



Acid conditions increase as pH values decrease, and alkaline conditions increase as the pH values increase. pH 7 has little significance as a reference point in water chemistry and therefore is of little importance in sanitary engineering practice.

### 2.15 Turbidity

The term turbid is applied to waters containing suspended matter that interferes with the passage of light through the water or in which visual depth is restricted. The turbidity may be caused by a wide variety of suspended materials, which range in size from colloidal to coarse dispersions, depending upon the degree of turbulence. In lake or other waters existing under relatively quiescent conditions, most of the turbidity will be due to colloidal and extremely fine dispersions. In rivers under flood conditions, most of the turbidity will be due to relatively coarse dispersions. As the rivers progress toward the ocean, they pass through urban areas where domestic and industrial wastewaters, treated or untreated, may be added. The domestic waste may add great quantities of organic and some inorganic materials that contribute turbidity. Certain industrial wastes may add large amounts of organic substance and others inorganic substances that produce turbidity. Street washings contribute much inorganic and some organic turbidity. Organic materials reaching rivers serve as food for bacteria, and the resulting bacterial growth and other microorganisms that feed upon the bacteria produce additional turbidity.

In turbid waters, most of the harmful organisms are exposed to the

action of the disinfectant. However, in cases in which turbidity is caused by sewage solids, many of the pathogenic organisms may be encased in the particles and protected from the disinfectant. For this and aesthetic reasons the U.S. Public Health Service has placed a limit of 5 units of turbidity as the maximum amount allowable in public water supplies.

Because of the wide variety of materials that cause turbidity in natural waters, it has been necessary to use an arbitrary standard. The standard chosen was

$$1 \text{ mg SiO}_2/\text{l} = 1 \text{ unit of turbidity}$$

and the silica used must meet certain specifications as to particle size.

## 2.16 Alkalinity

The alkalinity of a water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due primarily to the salts of weak acids, although weak or strong bases may also contribute. Bicarbonates represent the major form of alkalinity.

There are three kinds of alkalinity :

- a) Hydroxide (OH)
- b) Normal carbonate ( $\text{CO}_3$ )
- c) Bi-carbonate ( $\text{HCO}_3$ )

There are five conditions of alkalinity possible in a sample :

- a) Hydroxide alone,
- b) Hydroxide and normal carbonate.
- c) Normal carbonate alone,
- d) Normal carbonate and bicarbonate,
- e) Bicarbonate alone.

## 2.17 Hardness

Hard waters are generally considered to be those waters that require considerable amounts of soap to produce a foam and that also

produce scale in hot-water pipes, heaters, boilers, and other units in which the temperature of water is increased materially. To the engineer, the scaling problem is the most challenging.

Waters are commonly classified in terms of the degree of hardness, as follow :

0-75 mg/l	Soft
75-150 mg/l	Moderately hard
150-300 mg/l	Hard
300 up mg/l	Very hard

Hardness is caused by divalent metallic cations. Such ions are capable of reacting with soap to form precipitates and with certain anions present in the water to form scale. The principal hardness-causing cations are calcium, magnesium, strontium, ferrous iron, and manganese ions. Aluminum and ferric ions are sometimes considered as contributing to the hardness of water. However their solubility is so limited at the pH values of natural waters that ionic concentrations are negligible

Hardness may exist in two forms, namely,

- 1) Carbonate hardness, and
- 2) Non-carbonate hardness.

Carbonate hardness is sometimes called temporary hardness because part of it is removable by boiling; and non-carbonate hardness is also called permanent hardness because it is not affected by boiling. Carbonate hardness is due to calcium and magnesium carbonate and bicarbonates,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{MgCO}_3$ , and  $\text{Mg}(\text{HCO}_3)_2$ . Non-carbonate hardness is generally due to calcium and magnesium sulfates and chlorides,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{MgCl}_2$ . Sodium and potassium salts also add to the alkalinity but do not affect the hardness.