COAGULATION
IN
WATER TREATMENT

A DISSERTATION
Presented to the Faculty of Civil Engineering of
the University of Roorkee
for the Degree of Master of Engineering in
Public Health Engineering

By

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PREFACE

In preparing this volume, the attempt has been made by the author to treat the entire subject of coagulation in a systematic manner, as represented by the engineers and the chemists, in the field of water treatment works.

Coagulation in a Water Treatment is a very complicated phenomena comprising a number of variables. The coagulants added are necessary for the coagulation to take place; while the impurities present in water affect the phenomena on too much; and design of flocculation basins improves the efficiency of the process. Uptil now these factors were and are the objects of investigation in this field. Each plays an important role separately in the coagulation process and thus each is dealt with separately in each chapter. The second chapter gives the theoretical aspect of this subject, which is followed by another two chapters which discuss the chemical flocculation in light of properties of water and coagulants added respectively. The fifth chapter is devoted for the design of flocculation basins or flocculators.

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Not fully justified.

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ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

✓

TABLE OF CONTENTS (Contd.)

CHAPTER Page

TABLE OF CONTENTS (Contd.)

LIST OF FIGURES (Contd.)

LIST OF TABLES

CHAPTER I

INTRODUCTION

Minimum basic needs of mankind for its existence are air, water and food. Because of these needs and also the curiosity regarding water, it exhibited much interest what in water qualities and means by which they can be improved ? to satisfy its current needs. Through the ages, needs went ? on increasing with the living standard and so also the introduction of different treatments in this field which gives rise to a separate branch of water purification only, in Public Health Engineering.

Consequently, it is not surprising to note that coagulation of water was practised in ancient times. One of the oldest methods in water treatment is the removal of suspended solids by sedimentation. An Italian Physician who visited Egypt, in as early as sixteenth century, described the then use of almonds as follows :-

> ". . . they smeared the edges of the vessel with five sweet almonds, properly crushed and

> grasping the almonds in the hand, suddenly plunged hand and arm into the water upto the elbow and moved elbow and hand vigorously and violently this way and that through the water, stirring it up until they had made it for more turbid than before. Then they withdrew the arm from the vessel leaving the almonds in the water. They let it clarify and it was properly cleaned in three hours time" (1) *

Similarly it is worthwhile to note the practical use of alum, without knowing the theory behind, from the first decade of the eighteenth century in India also, for cleaning the water on small scale. They rub the alum crystal on the interior surface of the vessel full of water, for three four times, and allow the water to clean itself.

wh ?

In United States coagulation was used in connection with the New Jersey Water Supply in 1885, and studies of aluminium sulphate as a coagulant were undertaken at Rutgers University during the same year. Since 1885, coagulation is, with few exceptions, part and parcel of rapid filtration in America; (1) and it is entering also in big treatment plants on the earth.

With reference to the size of the ultimate particles, the impurities in the water, can be classified broadly as (i), suspended, (ii) colloidal, and (iii) dissolved.

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* The number here in the bracket and throughout the dissertation refer to bibliographical references.

substances so co~~u~~arse that they can be removed by settling, are technically referred to as <u>settleable</u> solids. While the others, which can be removed by ordinary filtration through filter paper or asbestos mat, are said to be in suspension and named as <u>suspended</u> solids. In the dissolved state the divided material or solute is homogeneously dispersed in the solvent to form a true solution. Between the upper limit of true solutions and the lower limit of suspensions lies the colloidal range. The colloidal dispersions cannot be removed from the water by means of ordinary filtration, and they will not settle under the action of gravity because of their "Brownian Motion".

Coagulation process takes care of these colloidal particles. It is a very complex phenomenon, ultimate aim of which is to increase the size of the particles so that the gravitational force will come into play to remove them. Fair and Geyer define coagulation as the destabilization, aggregation and binding together of colloids (2). In water works practice chemical coagulation involves the formation of chemical flocs that adsorb, entrap or otherwise bring together suspended matter more particularly suspended matter that is so finely divided as to be colloidal, with the introduction of some coagulant - a floc forming substance.

Coagulation process consists of (i) addition of coagulating or flocculating agent or agents, (ii) their dispersion throughout the fluid, (iii) agitation to bring

TABLE OF CONTENTS (Contd.)

LIST OF FIGURES

particles in contact with coagulating agent and with each other, (iv) agitation to consolidate the growing particles into agglomerates of suitable size and density. The last two steps are sometimes termed as 'flocculation'. For efficient coagulation not only good chemical flocculation but also mechanical agitation is necessary. They both go hand in hand.

Coagulation process is invariably followed by sedimentation, requirements of which separate it from coagulation. Filtration is the last line of defence against colloidal particles and viruses or bacteria. Thus coagulation is one link in the chain of methods required to produce the high quality of water with minimum cost. The effectiveness of each of these processes affects the efficiency of the others. Coagulation does not end in itself, but is ancillary to other treatment methods. For this reason it is often called as a preparatory process. Coagulation prepares water for sedimentation and/or filtration.

Chlorination?

Rather a [illegible] [illegible]

Today's Public demand is sparkling clear water and as such coagulation plays an important role and has a number of missions. It has to aid in removing coarse suspended material, microscopic organisms and the even smaller bacteria and viruses. In addition, with the power of adsorption, the flocculent precipitate helps in removing some dissolved materials from water which produce tastes has chlorine demand

and odours or in reducing Chlorine. Coagulation creates the flocs consisting of sufficiently large and/or dense particles, to settle rapidly in order to relieve the filters of as much load as possible. At the same time the floc must be sturdy enough to resist any agitation, so that it will not be broken up prior to sedimentation and also during its removal in filter media. It must be large, tough and dense. ✓

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CHAPTER II

THEORY OF COAGULATION

2.1 Colloids and Colloid Solutions ✓

After the investigation of diffusion in aqueous solutions, in the year 1861, Thomas Graham was the first to distinguish between two groups of substances (3). The substances like glue, proteins, silicic acid, and others, separated from their solutions in the form of amorphous jellies or flakes after evaporation. He called the substances 'Colloids', glue like form, from ἡ κολλα- glue. The substances of the second group such as salts, sugars etc., diffused quickly through the membranes and separated from solutions in crystalline form; he called them as 'Crystalloids'.✓

The solutions of the colloidal substances, known as colloidal solutions or sols had already been the object of investigation, even before the Graham's time. But Graham was the first to characterise and name this set of phenomenon. After this a prominent change was brought about in the last

2.3 Adsorption Phenomenon

The phenomena of adsorption such as accumulation of gases or vapours, or of solute or ions from liquids, or minute particles by solid substances are quite common in disperse structures. Thus it has its own weightage in colloid science. 'Sorption' is the general term used for the adsorption or absorption phenomena, when the nature of the phenomenon is not clear. Then the body that causes accumulation is called 'sorbent' and the substance accumulated is 'sorbate'. But if further experiments show that the foreign substance accumulated diffuses into the body, the process is called absorption. But if it is certain that the substance is accumulated on the surface of the solid without any diffusion into inside, the process is called adsorption; the body that adsorbs is 'adsorbent', and the substance adsorbed is 'adsorbate'. While whole of the system is called 'adsorbant' and the medium containing the substance adsorbed 'medium of adsorption'.

2.3.1 Types of Adsorption

The observations of this phenomenon with the adsorption of gases show that there are atleast two types of adsorptions (7). The adsorption is mainly affected by temperature and heat plays an important role. The first type, known as 'Physical Adsorption' is exhibited by all substances, particularly at low and moderately low temperatures. It is distinguished chiefly by relatively low heats of adsorption, namely 5 to 10 kcal. per mole. These heat exchanges are of the same order as heats of vapourization, it appears therefore that the forces by which the adsorbed molecules are held to the surface of the solid are similar to the forces of cohesion of molecules in the liquid state. In other words the molecules are adsorbed by 'van der Waals forces', (which are also more prominent in liquid state). So the physical adsorption is sometimes referred to as 'van der Waals Adsorption'. The second type of adsorption is called as 'Activated Adsorption' or 'Chemisorption'. The heats of adsorption are much higher than for physical adsorption, namely from 10 to 100 kcal. per mole. Chemisorption occurs in very limited cases and that to also at moderately high temperatures. As the name implies the forces involved in chemisorption are chemical in nature.

Physical Adsorption is generally a quick process so that condition of equillibrium between adsorbed and dissolved adsorbates is quickly reached after the contact of adsorbent with the solution. The quantity of the substance adsorbed depends on the nature of the substance, its concentration, and also the temperature. Higher the temperature or lower the concentration of adsorbate in the medium promotes the separation of adsorbate from adsorbent.

Many attempts have been made to discover the rules expressing the variation in the quantity of material adsorbed with concentration. Two mathematical formulae are in common use. Freundlich equation is strictly empirical but applicable for wide variety of data, particularly for adsorption from liquid solutions. It has a form,

$$y/_m = k\ c^{1/n},$$

in which '$y/_m$' is the amount of material adsorbed per unit weight of adsorbent, 'c' is the concentration of material in solution at equillibrium and 'k' and 'n' are empirical constants.

Second equation, the Langmuir Isotherm, has some theoretical basis. It has a form,

$$y/_m = k\ c/(1+k_1 c),$$

in which constants 'k' and 'k_1' have theoretical significance, but their values are usually obtained empirically from observed data. This equation is somewhat limited in its application.

2.3.2 Experimental Observations

It follows from the experimental facts that adsorbability - i.e., adsorbate per adsorbent by weight - depends on the condition of the adsorbing surface. Highly polished surface has lesser adsorbing power than rough surface such as those of powders and colloidal particles. The colloid surfaces have large number of 'active centres' - as they are called. Of these, corners and edges are most active, then follow the planes. At these active centres there are free unbalanced residual valencies, because the atoms on the corners and edges are partly saturated by the atoms and ions below. Thus there is plenty of rooms for foreign molecules and during the

As previously stated the colloidal solutions come inbetween the suspensions and true solutions. The lower limit for the size range for suspended solids lies between 0.1 and 1.0 micron. This is about the common size of bacteria and wave length of visible light (0.4 - 0.8 micron), and thus the lower limit of microscopic visibility. While in true solutions, solute is homogeneously and molecularly dispersed. The particle diameter ranges from those of single atom $2X10^{-8}$ to $3X10^{-8}$ cm., upto about 1 milimicron (10^{-7}cm.) i.e., approximately in the limit of the electronic microscope. Thus colloidal particles range from $1\,\mu$ to $1\,\mu\mu$ approximately. (6)

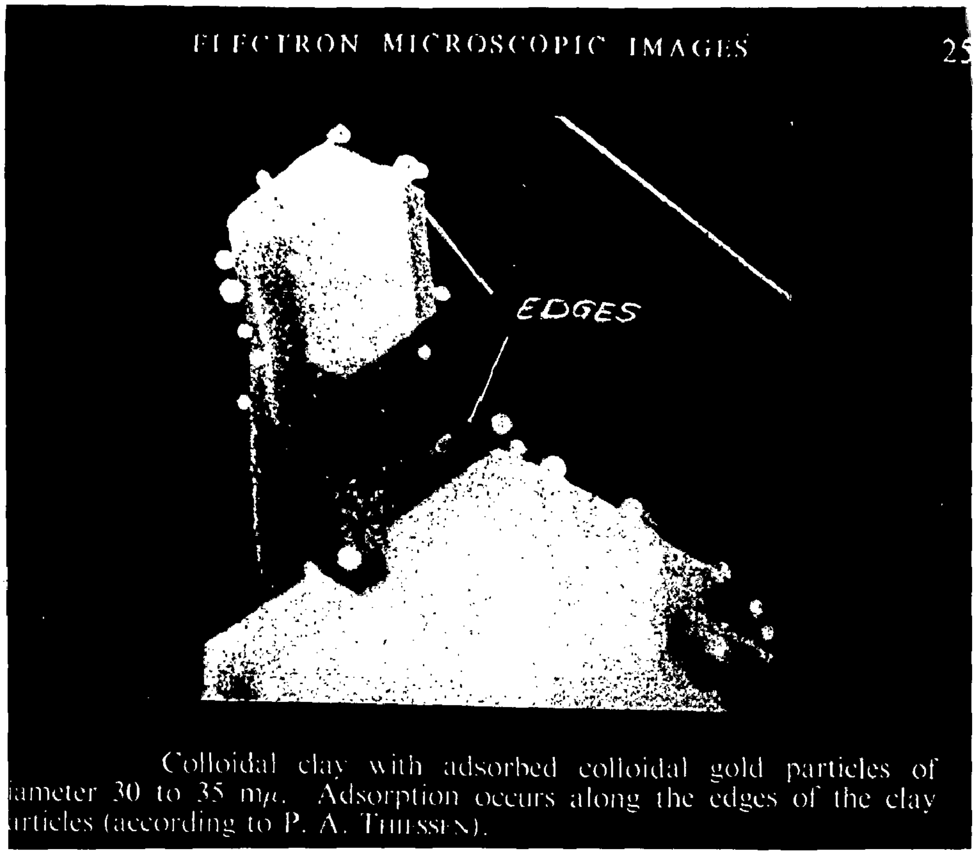
2.2 Properties of Colloids

The main feature of the colloidal material which is mainly responsible for many of their characteristic properties is their large specific surface area. For example 1 cc of colloids consisting of cubical particles 10^{-6} cm. side, has a surface area of 6500 sq. ft.

Two general properties of colloids are of particular interest in coagulation : (1) the tendency of colloidal size material to attract and concentrate the other substances at their surfaces, which leads to the phenomenon known as *adsorption*, and (2) the tendency of their surface to acquire electric charge, which gives rise to *electrokinetic properties.*

years of the nineteenth century, when the theory of solutions was developed. In ordinary solution, the dissolved substance is divided down to its molecules. The question then arose was 'Are the colloidal solutions solutions in true sense, consisting of molecules of colloidal substance or do they contain particles built up of molecules, but too small to be seen by ordinary microscope ?' The question was answered in 1903 by Siedentopf and Zsigmondy. The ultramicroscope invented by them extended the visibility of particles from about 500 $m\mu$ down to 10 $m\mu$ and it then became evident that colloidal solutions contain particles visible ultramicroscopically with diameters in between 500 $m\mu$ and 10 $m\mu$ (1 micron or 1 μ = 10^{-4}cm.) (4). In the case of these sols the division did not extend down to its molecules; each single particle consisted of a large number of molecules. But this does not exclude the existence of colloidal solutions, the particles of which might consist of one very large molecule.

Similarly the concept of colloid had also undergone a change. It no longer characterised a particular substance, as Graham defined, but rather a particular state, as does, for example the concept 'dissolved'. By the colloidal state was understood the extremely intimate mixture of two phases, in which however, the scattered phase is not necessarily divided down to its molecules and only upto particles visible ultramicroscopically and having therefore, their diameters of 500 $m\mu$ and less. (5)



ELECTRON MICROSCOPIC IMAGES 2

Colloidal clay with adsorbed colloidal gold particles of iameter 30 to 35 mμ. Adsorption occurs along the edges of the clay rticles (according to P. A. THIESSEN).

Fig. No. 1.

Colloidal clay with adsorbed colloidal gold particles of diameters 30 to 35 m u along the edges of the clay particles (8).

adsorption process these particles cover first the corners, then the edges and finally the planes. The adsorbed particles may have unsaturated valencies and may bind more molecules. This may give rise to multilayers all over the surface or on limited areas. Now reverse will happen if concentration of the substance to be adsorbed is decreased. The molecules on the outermost of the multilayers will leave first, then those on the planes and finally the molecules on the edges and corners.

It has been found that interatomic or intermolecular forces are of very short ranges, of few Angstroms. (1 Angstrom unit = $1 \mu\mu = 10^{-8}$ cm.). Although the range of action of any particular centre of attraction is limited, attractive forces may be felt over a good distance, giving rise to a comparatively thick adsorption films and surfaces of thousands of Angstroms in thickness. The explanation is simple. One adsorbed layer may attract molecules to form second layer, which in turn may attract molecules to form third layer and so on; exactly similar to the induced magnetism phenomenon. The final thickness of adsorbed film will naturally depend on the efficiency of transferring attractive forces from layer to layer.

2.1.3 Ion Adsorption

Considering the adsorption of ions, experimental facts show that ions of dissociated solutions are also adsorbed like colloidal particles by colloids, but different ions are not adsorbed equally by adsorbent and ion exchangers. Many attempts have been made to discover the rules governing the adsorption of ions. One of the rules is the Fajans-Paneth rule (9, 10), which is useful for giving reasoning for experimental results, as it is only an approximation. It states that "Ion is strongly adsorbed by an ionic lattice if there is possibility of forming a difficulty soluble or weakly ionised compound with the ions of opposite charges on the lattice". It can only be said that ions forming slightly soluble compounds with the adsorbent will generally be adsorbed better than those forming more soluble compound. There is also no exact rule regarding the valency of the ions and adsorbability. Following Bancraft (11), it can be stated that a trivalent ion will be adsorbed more strongly than a bivalent or univalent one. This explains the preferential use of the Alum as coagulant which gives a trivalent Al^{+++} ion. But there are wide variations even in the adsorbabilities of ions of the same valence. why ?

The elimination of excessive tastes, odours from water by activated carbon is most important direct use of adsorption in Water Treatment. Similarly a part of the action of coagulants in removing colour from water may be due to adsorption. Certain processes for removal of silica or fluorides also utilise this phenomenon.

2.4 Electrokinetic Properties

Colloidal particles are normally charged with respect to the surrounding medium. If electrodes of a D.C. source are inserted in the colloidal solution the particles travel towards one or the other of the poles. This phenomenon is known as <u>electrophoresis</u>. Similarly it is found that if the colloidal material is held fixed, D.C. potential causes the liquid to flow in the direction opposite to that of particles. This phenomenon is <u>electroosmosis</u>, and has been used for dewatering of sludge.

From where the colloidal particles acquire the charge is not still known. Scientists give different theories. In 1912, Freundlich and Elissatoff suggested that material of particle itself gives rise to the ions which take part in the formation of double layer (12), and this idea has since been developed in many directions. Preferential adsorption of positive ions or negative ions also helps in acquiring the charge. ✓

Helmholtz (13), was the first to give the structural arrangement of ions in a colloidal particle. According to him the sol or a colloidal solution as a whole is an electrically charged body having collection of statically charged spheres. But there is no external charge on a colloid and no energy can be obtained from it externally, by this means alone. This gives rise to an idea of electrical double layer. The charge resides on the surface of each particle and is compensated by equal and opposite charge on the surface layer of liquid immediately in contact with the particle. Hence the system as a whole appears to be uncharged.

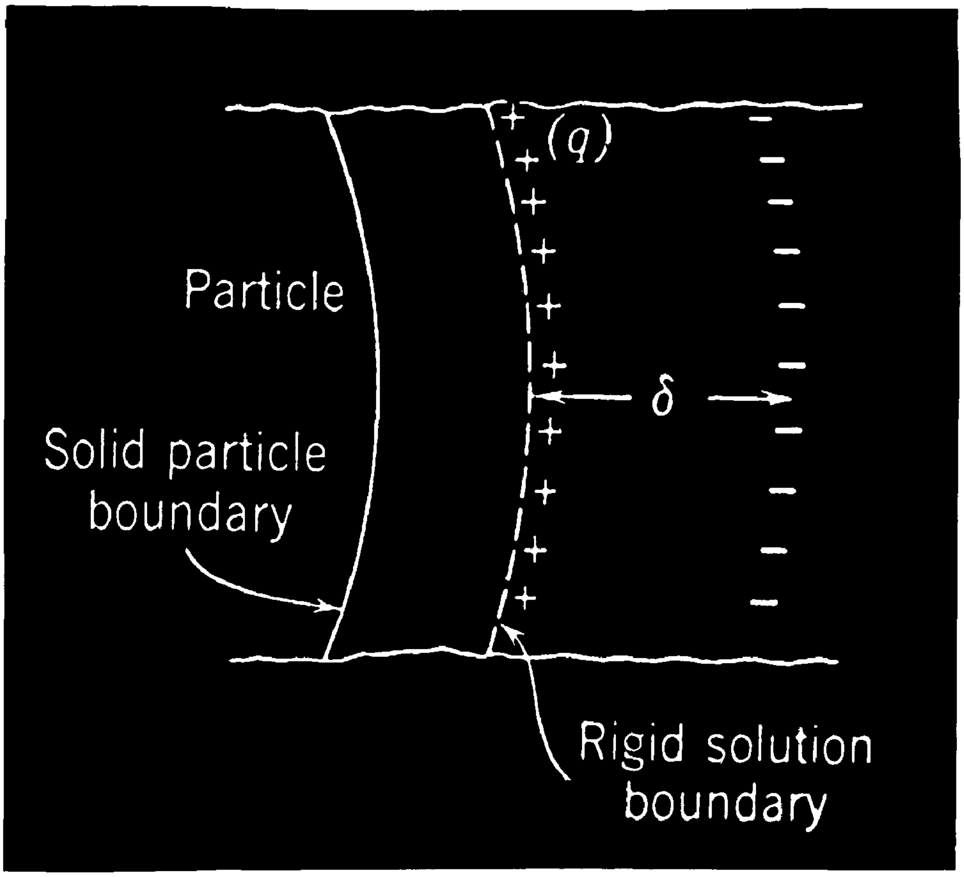
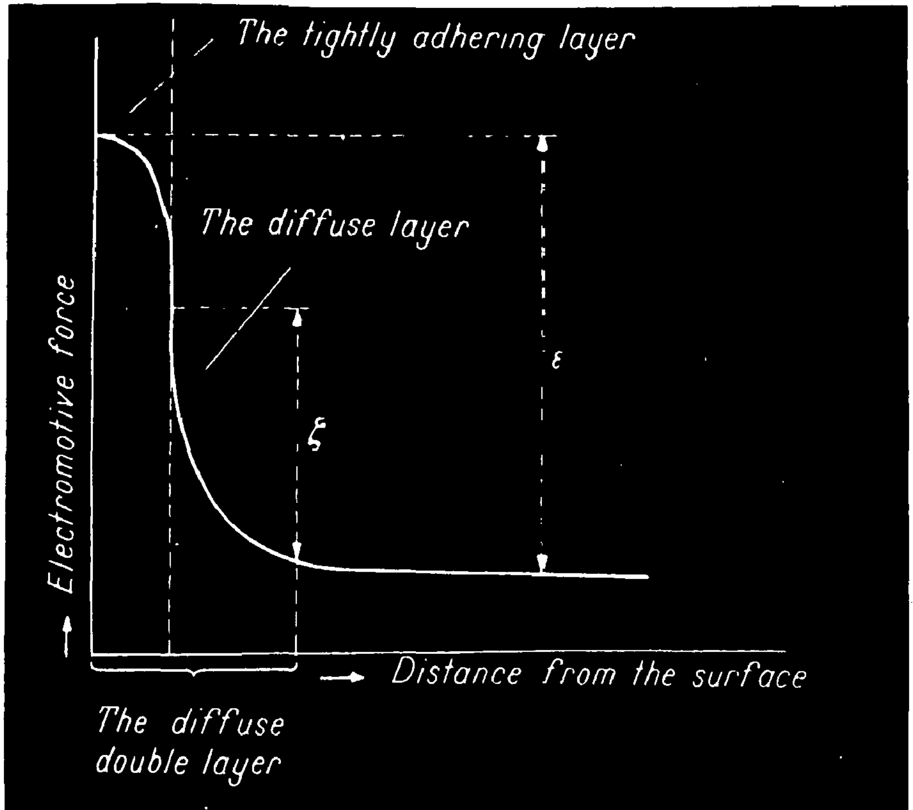


Fig. No. 2.

Simple Helmholtz Double Layer of colloid particle showing net charge and double layer distance .



The electrothermodynamic potential ϵ, and the electrokinetic potenti

Fig. No. 3.

Electrostatic Potential ϵ, and Electrokinetic Potential.ζ

The Helmholtz idea has been replaced by the concept of 'diffused double layer' mainly due to Gouy. According to him the potential gradient is not sudden but is diffused over a short distance.✓ The double layer is supposed to be built up of two diffused layer ions, concentration of say the positive ions decreasing and that of negative ions increasing with the distance from the centre. He also calculated the thickness of double layer, and for ordinary sols it is of few Angstroms.✓ The same idea is supported strongly by Freundlich and Rona (14). The diffused double layer again consists of a rigid solution layer just around the particle and a moving solution layer, the two separated by a rigid solution boundary.✓ They studied carefully the potential across the rigid particle boundary and the farthest layer of diffused double layer - it is termed as 'electrostatic potential', ϵ - and the potential across the rigid solution boundary and the farthest layer of diffused double layer - it is termed as 'electrokinetic' or 'zeta' potential - ζ. Freundlich and Rona pointed out that the electrokinetic potential ζ, measured by cataphoretic and electro-osmotic methods is less than the static boundary potential ϵ. Another difference is that electrostatic potential is affected very little by the presence of ions while the electrokinetic potential varies very greatly with the kind and quantity of ions present. The valency of ions also have no influence on electrostatic potential, but is almost important in determining electrokinetic potential.

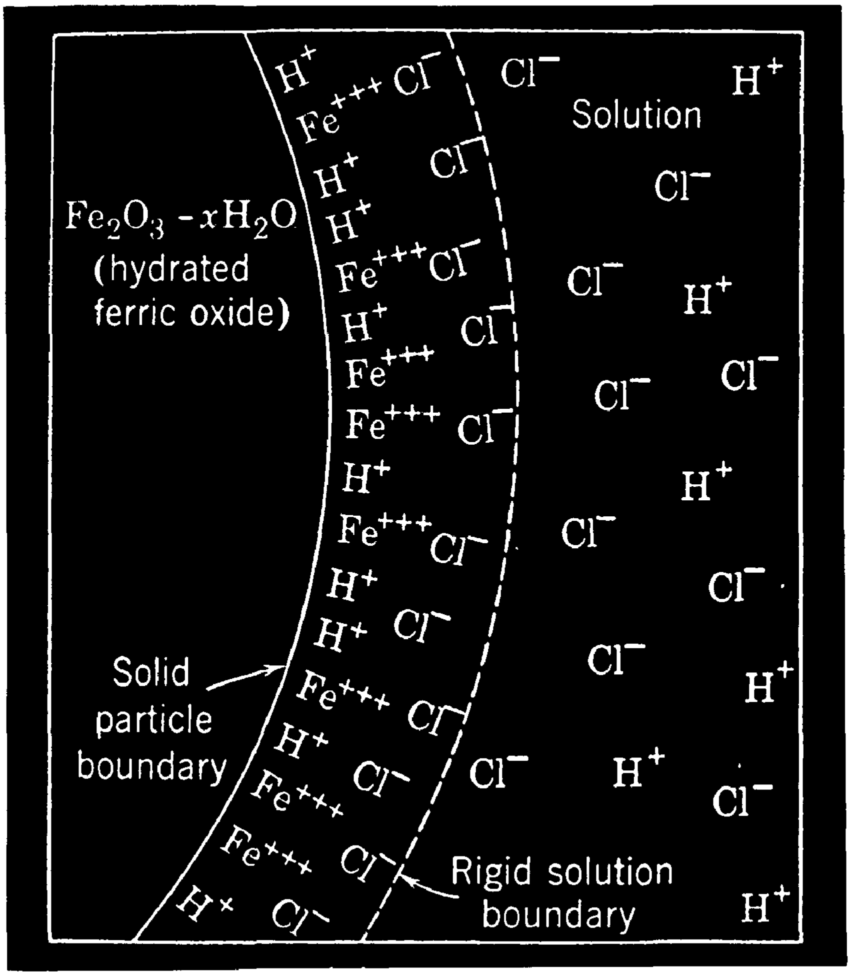


Fig. No. 4.

Charge distribution in the neighbourhood of surface of ferric hydroxide colloid particle formed by dispersing $FeCl_3$ in water.

Electrokinetic potential is the measure of potential difference between the moving and the stationary part of the liquid, while electrostatic potential measures 'total' difference of potential between the solid wall and the liquid.

It is worth noting that the stability of colloid is dependent on the electrokinetic potential or the zeta potential and not on the electrostatic potential. The difference between the two is represented in the Figure No. 3 (14). The zeta potential is represented by the equation,

$$\zeta = 4\,\pi\delta q/D,$$

in which 'q' is the charge on the particle (or the charge difference between the particle and the body of the solution), 'δ' is the thickness of the layer around particle through which the charge difference is effective, and 'D' is the dielectric constant of the medium. At isoelectric point this zeta potential is zero. The colloids are stable if their zeta potential exceeds a certain critical limit. If it drops down below this, coagulation tends to occur slowly in the immediate neighbourhood of critical zeta potential and much more rapidly as it tends to zero.

2.5 Mechanism of Coagulation

The process of coagulation involves complex equillibria among a number of variables including the colloids or dispersed matter, the water or the dispersion medium, and the coagulating chemical. The main forces include : (i) a lowering down of zeta potential of the colloids present in water, and (ii) a neutralization of charge on the colloids present by oppositely charged hydrous oxide colloids formed by reactions of the coagulant with ions in the water. Most of the laboratory research done uptilnow in connection with water clarification is in the coagulation with aluminium and ferric salts. Various theories have been given to explain the role of alum in coagulation. In 1948, Black (15) attempted to summarise existing theory of coagulation. Colloids initially present in water, like clay and tealike organic colour are negatively charged colloid particles. While the colloids formed by the added coagulants, the hydrous oxides of iron or aluminium for example, are generally positively charged.

According to him, coagulation takes place in three stages :

1. As the coagulant dissolves, trivalent aluminium or ferric ions are formed. They neutralize the negative charge on the particles of colour and/or turbidity. Neutralizing power of bivalent and trivalent ions is greater than that of univalent ions due to their preferential adsorption. As shown in Table No. 1 (16), coagulating power of ions rapidly increases with valence. This is known as Schulze-Hardy Rule. This stage, in the opinion of most of the authorities, is the most important phase of coagulation and it takes place long before the formation of visible floc particles. It is evident that

zeta potential of the colloids present in water, and (ii) a neutralization of charge on the colloids present by oppositely charged hydrous oxide colloids formed by reactions of the coagulant with ions in the water. Most of the laboratory research done uptilnow in connection with water clarification is in the coagulation with aluminium and ferric salts. Various theories have been given to explain the role of alum in coagulation. In 1948, Black (15) attempted to summarise existing theory of coagulation. Colloids initially present in water, like clay and tealike organic colour are negatively charged colloid particles. While the colloids formed by the added coagulants, the hydrous oxides of iron or aluminium for example, are generally positively charged.

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TABLE NO. 1. ✓

Coagulating Effect of Various Ions

(after Glasstone)

Ferric Oxide (Positive) Sol			Arsenious Sulphide (Negative) Sol		
Electrolyte	Anion valence	Minimum concentration*	Electrolyte	Cation valence	Minimum concentration*
KCl	1	103	NaCl	1	51
KBr	1	138	KNO_3	1	50
KNO_3	1	131	K_2SO_4	1	63
K_2CrO_3	2	0.325	$MgSO_4$	2	0.81
K_2SO_4	2	0.219	$BaCl_2$	2	0.69
$K_2Cr_2O_4$	2	0.238	$ZnCl_2$	2	0.68
$K_3Fe(CN)_6$	3	0.096	$AlCl_3$	3	0.09

* - Milimols per litre.

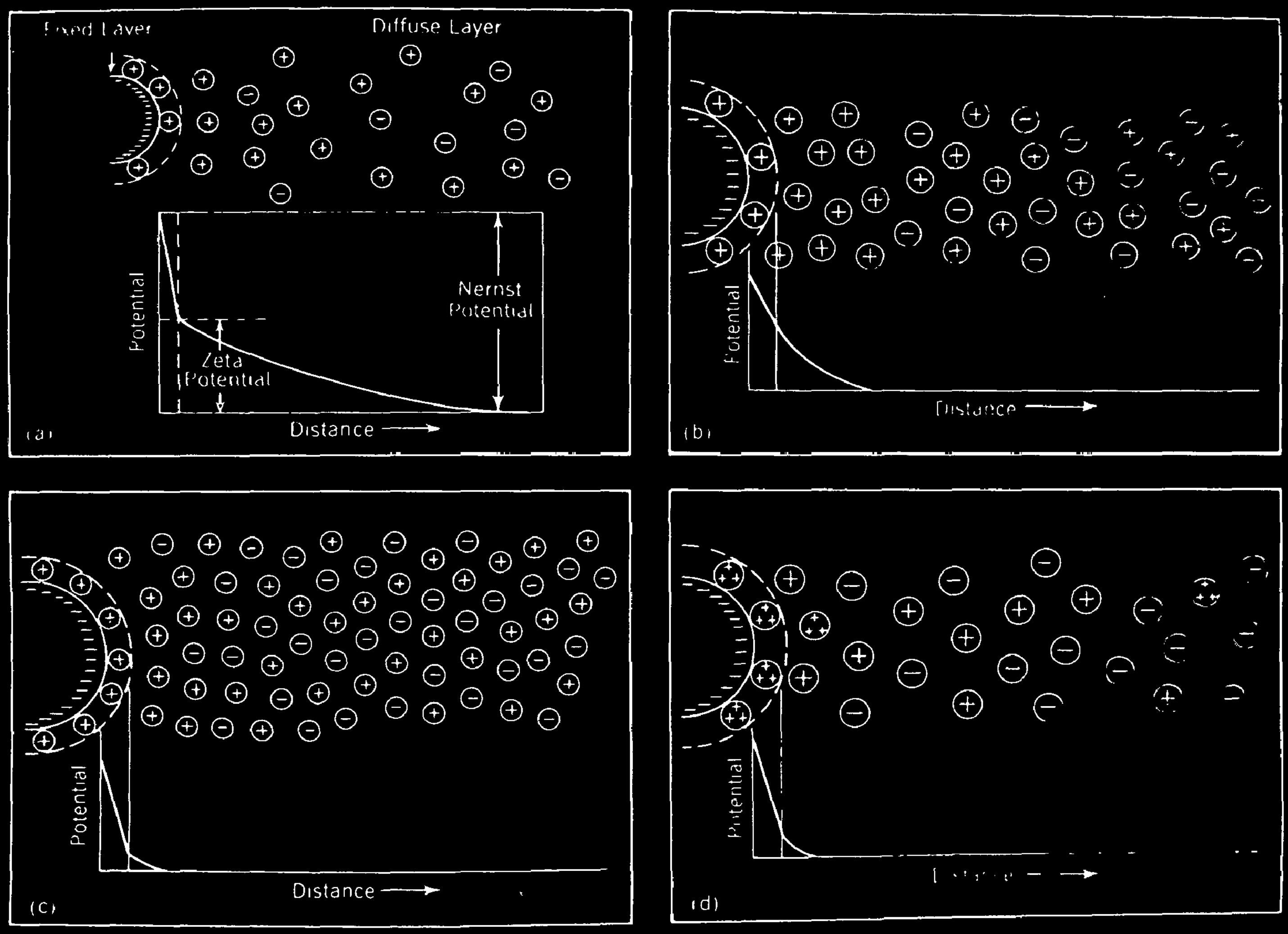

Fig. 1. Source of Zeta Potential and Effect of Ions of Opposite Charge

Fig. No. 5.

Source of Zeta Potential and Effect of Univalent, and Polyvalent Ions of Opposite Charge this action will be more effective if the coagulant can be brought into intimate contact with the turbid particles, before the secondary reaction takes place. Thus this necessitates the <u>rapid mixing</u> of coagulant in the first step of coagulation.

2. When the positively charged alum or ferric ions have neutralised a considerable portion of the negatively charged colloid particles of colour and/or turbidity, the resulting flocs may be called 'microflocs', as they are still beyond the limits of visibility and are too small to settle under the gravitational force. Furthermore it has been shown that in the acid range of coagulation, they still retain positive charge, possibly due to adsorption of positively charged hydrogen ions from the solution. These positively charged microflocs continue to remove negatively charged particles of colour and turbidity and this forms the second phase of coagulation. Fig. No. 5 gives the idea of zeta potential and also the effect of addition of univalent and polyvalent ions to the solution (17). Generally in practice, aluminium or iron salts are used for this purpose. Aluminium or iron ions added first, replace all the exchangeable cations present in colloidal system; when this is achieved zeta potential drops down to critical value. But this is not sufficient and small 'extra' amount of alum or iron is necessary, which after hydrolysis binds the microflocs together for

rapid settling in third stage (See Chapter No. 3).

3. During both of the above stages no visible floc particles are formed. The <u>mechanical treatment</u> of water from this point onwards consists of slow stirring, termed by some authors '<u>conditioning</u>'. During slow stirring operation microflocs cluster together and agglomerate with the formation of floc particles which steadily grow in size, until they are in a proper condition for sedimentation. During this phase of floc growth the third action, that of surface adsorption takes place. Impurities in the water and also viruses, bacteria etc. may be adsorbed by these growing flocs.

It is worth noting that the formation of a large and well formed floc, even though important from the stand-point of sedimentation, is not necessary for successful coagulation, since most important function of the coagulation takes place before the floc ever attains visible size as shown above.

Coagulation process is too sensitive to the change in the initial properties of water and also to the type of coagulant used.

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CHAPTER III

FLOCCULATION PHENOMENON

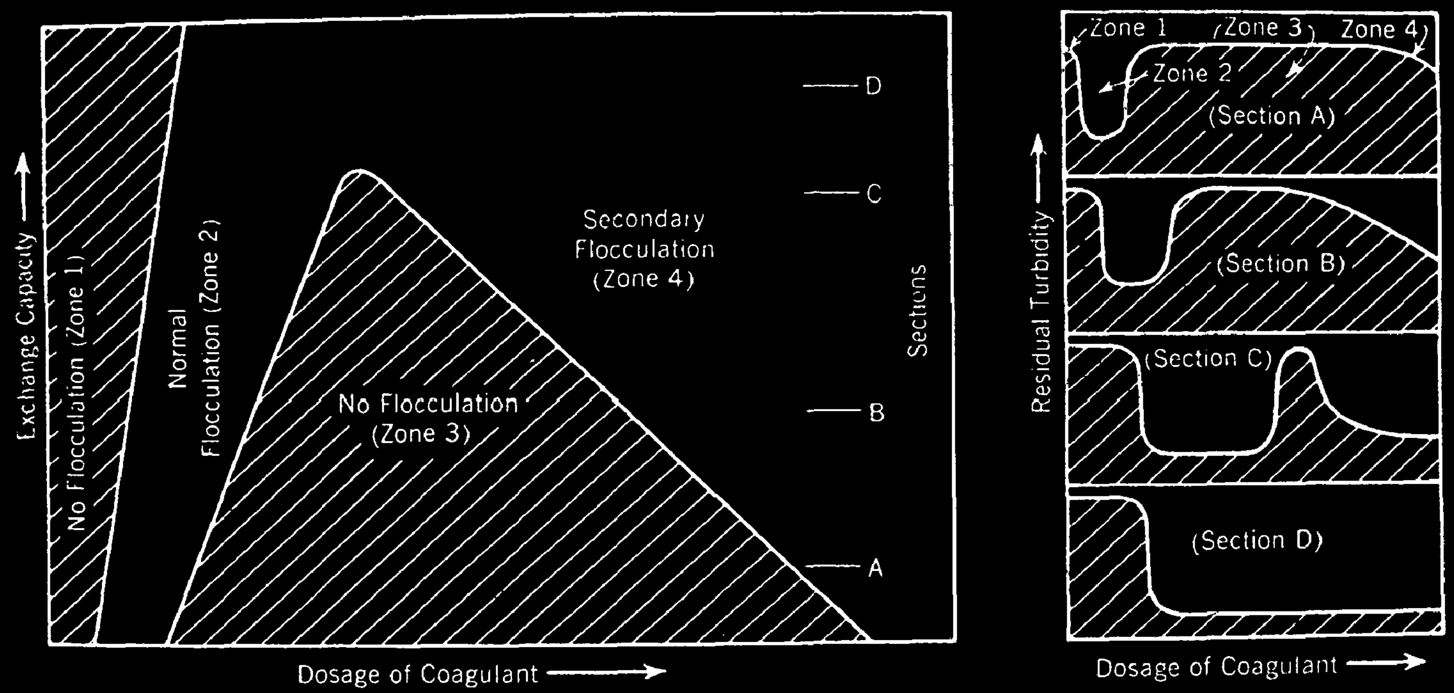
3.1 General Considerations

Inorganic turbidity in natural waters consists of clay particles originated from soil. The particle size ranges upto 5 μ in diameter; but the colloidal particles, the size of which is less than 1 μ are most stable and are of controlling importance in rapid flocculation. As it is explained, such colloids derive their stability from an electric double layer surrounding each particle. This electric double layer consists mainly of exchangeable cations such as Na^+ , K^+, Ca^{++}, $Mg^{++}$and H^+. The layer is assumed to be diffused into the surrounding medium. The other cations present in the medium may also enter into ion exchange mass action. The principle function of coagulation is the destabilization, agglomeration and binding together of these colloids. The addition of polyvalent cations to the whole system represses the double layer. If their concentration is further increased they lower the zeta potential due to their preferential adsorption among all the ions present in the medium; or they are exchanged for the initially present univalent or bivalent cations like Na^+, K^+, Ca^{++}, Mg^{++}etc. Thus the stability of the particle is lowered until a point is reached when the particles begin to coalesce very slowly to form aggregates. These aggregates will take a long time to settle.✓ Destabilization to a greater degree will increase the rate of coalescence so that finally visible reduction in turbidity is possible within a practicable short settling period. In water works practice it is achieved by the addition of a floc forming substance.✓ Common substances in use are the iron and aluminium compounds which after dissociation give polyvalent cations. ✓

The process is quite complex and sensitive to the change in the initial properties of waters, imparted to it by impurities present and also properties of coagulating agent. Here the flocculation phenomenon is discussed giving particular attention to the role of turbidity particles.✓ Optimum flocculation requires the equillibrium in which different variables play important part, including turbidity, particle size distribution, exchange capacity, pH, alkalinity etc. ✓

The more important factor affecting the rate of agglomeration is the total exchange capacity of the turbidity particles. Exchange capacity is the measure of the tendency of the particles for replacement of low valence cations with ones of high valence (18). Soil technologists have shown that practically all of the exchange capacity of the clay particles is due to the presence of suspensions smaller than 1.5 μ diameters. The waters having very high exchange capacities exceeding critical limits, exchange polyvalent cations formed by the addition of coagulant, for low valent cations very rapidly. Thus agglomeration following destabilization is also rapid, resulting large flocs and rapid clarification. Any electrolyte dissociating into active polyvalent cations will produce this effect and hydrolyzing coagulant is not essential. Under this condition rapid agglomeration of the destabilized colloidal particles also induces agglomeration of larger particles, and mutual coagulation is not involved in this type of flocculation (19).

But in most of the natural waters exchange capacity is less than the critical one; and so the aggregates formed after destabilization are too small to settle rapidly. So in order to effect rapid clarification the suitable binder material or agglomerating agent is essential. It will bind the various small aggregates into large flocs which will rapidly settle. In practice a properly adjusted dosage of a single hydrolyzing agent will effect both the actions. For example, when alum is used as a coagulant, a portion of Al^{+++} ions are effective in destabilizing the turbidity colloids and remaining of the ions will form insoluble hydrous oxide binder material (20). Thus the dosage of alum required comprises the destabilization and binder demand.



(*a*) GRAPHICAL REPRESENTATION OF FLOCCULATION PHENOMENA AS RELATED TO EXCHANGE CAPACITY

(*b*) SAME DATA SHOWING TURBIDITY REDUCTIONS

—FLOCCULATION PHENOMENON RELATED TO EXCHANGE CAPACITY AND TURBIDITY REDUCTION

Fig. No. 6.

Graphical Representation of Flocculation Phenomena, as related to Exchange Capacity.

Fig. No. 6 gives the representation of the practical results which is in support of the above concept (19). For ordinary waters having low exchange capacity, there are two flocculation zones possible : (i) primary or normal flocculation, and (ii) secondary or high range flocculation. In normal flocculation coagulant is required for both exchange and hydrolysis reaction. While in the secondary flocculation i.e., in the presence of excess of coagulant, the high concentration of active cations are mainly responsible for destabilization and flocculation. The zone of normal flocculation moves to the right and becomes wider with increase of exchange capacity. At the same time, secondary flocculation also occurs in correspondingly less coagulant. While at and above a certain critical exchange capacity, two flocculation zones merge. At higher exchange capacities secondary zone supercedes the primary one and excellent flocculation and clarification occurs in the absence of hydrolysis. The exchange capacity of a given water, if less than critical one, can be increased by the addition of negatively charged colloids, as for example activated silica, bentonite, which may greatly increase flocculation and clarification within normal range (21). Also added particles may improve the buffer capacity, which is valuable if the chemical alkalinity of the system is low.

Since middle of the eighteenth century, flocculation phenomenon is the subject ofinvestigation. The effect of each variable on optimum flocculation has been studied, keeping other variables constant. Alum or ferric compounds are almost invariably taken as coagulating agents for experimental determination, as they are normally employed in water works practice. Natural waters derive their buffer capacity from turbidity particles. A buffer solution commonly contains a weak acid plus a sodium or potassium salt of that acid; or a weak base plus a suitable salt of the base. Carbonic acid (carbon dioxide) and the bicarbonate ions of the turbidity particles comprise a buffer mixture of almost universal occurrence in natural waters (22). Experimental results state that alkalinity in excess of optimum results in waste of an equivalent amount of coagulant. In treatment of these waters it may be advantageous and economical to neutralize a portion of the alkalinity with strong acid. A probable explanation given is that in the presence of hydroxyl ions the added aluminium ions form a soluble complex. Thus when initial pH is greater than the optimum, alum first added to the water instead of forming hydrous oxide, results in complex aluminate ions, liberating H^+ ions. Continuous liberation of these H^+ ions lower the pH to optimum, and at this point further addition of alum effects normal reaction. Thus alkalinities in excess of optimum results in waste of an equivalent amount of coagulant. While at alkalinities less than optimum, hydrous oxide produced is not sufficient to satisfy the binder demand of the particles. In waters of low turbidity pretreatment with lime is advisible for optimum flocculation. Each coagulant has its own range of pH, called optimum pH for good flocculation. If the initial pH is not in its optimum range, it is advisible to adjust the same by the addition of an acid like sulphuric acid or alkali like lime. ✓

Effective flocculation of a turbid water requires, in addition to suitable pH and alkalinity, turbidity particles both finer and coarser than approximately 1 μ diameter.✓ Smaller particles have colloidal properties, and some of them are necessary to neutralize positive charges of the hydrous oxide binder material through mutual coagulation.✓ The aggregation of the colloidal particles after destabilization induces agglomeration of larger non-colloidal particles. The ✓ particles greater than 1 μ serve as suitable nuclei for binding up dense rapidly settling flocs.✓ If in any given water, there is a shortage of either of the finer or coarser particles, the addition of missing material will result in more efficient flocculation and clarification. As quoted above, the addition of bentonite or other clay colloids may improve the flocculation behaviour of waters, initially deficient in colloids.✓ They may also provide buffer capacity to the water initially low in bicarbonate alkalinity.✓

Detergency is the opposite of flocculation and the presence of detergents or surface active agents, which are now-a-days in use, both in home and industry, inhibits flocculation in varying degrees.✓ They may peptise the turbidity particles, increasing their stability and thus inhibiting flocculation or preventing it altogether. The presence of detergents increases coagulant demand.

3.2 Coagulation is the subject of investigation for many years, dealing with different aspects. The problem is attacked in different ways. Recent and more reliable methods confirm the previous results and also throw light on previous ideas (23, 24, 25, 26, and 20). In support of the above discussion a brief review of these experimental studies is inevitable. Flocculation experiments, with dilute suspensions prepared from known types of clay, carried out especially by Langelier, W.F., and Ludwig, H.F., give detail information about different variables and their bearing on flocculation phenomena (26).

Experimental Procedure

For studying the effects of flocculation variables, the experimental procedure followed by Langelier and his associates was as follows : (19).

The Table No. 2 gives the properties of six turbid waters prepared from six different representative types of soil. These suspensions were made by dispersing the soils in distilled water and allowing them to settle for 24 hours; after this, a proper depth of supernatant was siphoned off to include only particles of approximately 1.40 μ diameter or less. The turbidities range from 45 to 63 ppm. The initial buffer capacity given in the table is the acid titre of the

TABLE NO. 2.

Properties of Synthetic Turbid Waters

Soil type used.	Initial turbidity ppm	pH	Initial buffer capacity ppm as $CaCO_3$	Approximate exchange capacity (Mili Equi. per litre.)
Yelo silty clay loam.	60	7.0	4	80
Aiken clay loam.	62	7.0	4	15
Dublin clay.	60	6.9	3	100
Fresno sandy loam.	45	7.3	5	50
Panoche fine sandy loam.	62	7.3	4	20
Holland sandy loam.	58	7.0	4	10
Average.	58	7.1	4	45

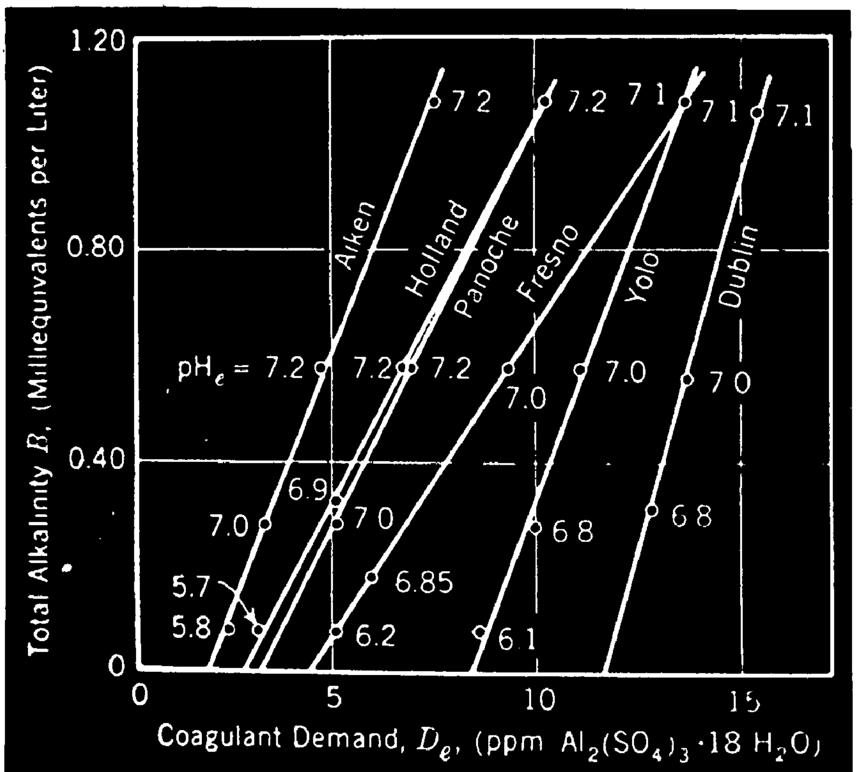
suspension; while exchange capacity is the property of suspension obtained by multiplying the weight of the suspended particles (obtained by evaporation) by their exchange or saturation capacities as measured by the standard procedure employed in soil technology.

The flocculation tests were conducted in 200 ml. jars, each jar being equipped with a slowly revolving paddle. Ten minutes of stirring followed by 15 minutes of quiscence were allowed. Then top 100 ml. were taken off for turbidity and pH measurements. The tests data also included several other results such as floc quality and size, time of floc formation, rate of floc settling. But it is worth noting that almost invariably it was found that turbidity reduction alone was an adequate criterion for optimum flocculation, because in order to have low turbidity, each of the other factors had also to be at or near its respective optimum conditions.

CONCLUSIONS FROM EXPERIMENTAL OBSERVATIONS

3.3 Effect of Bicarbonate Alkalinity

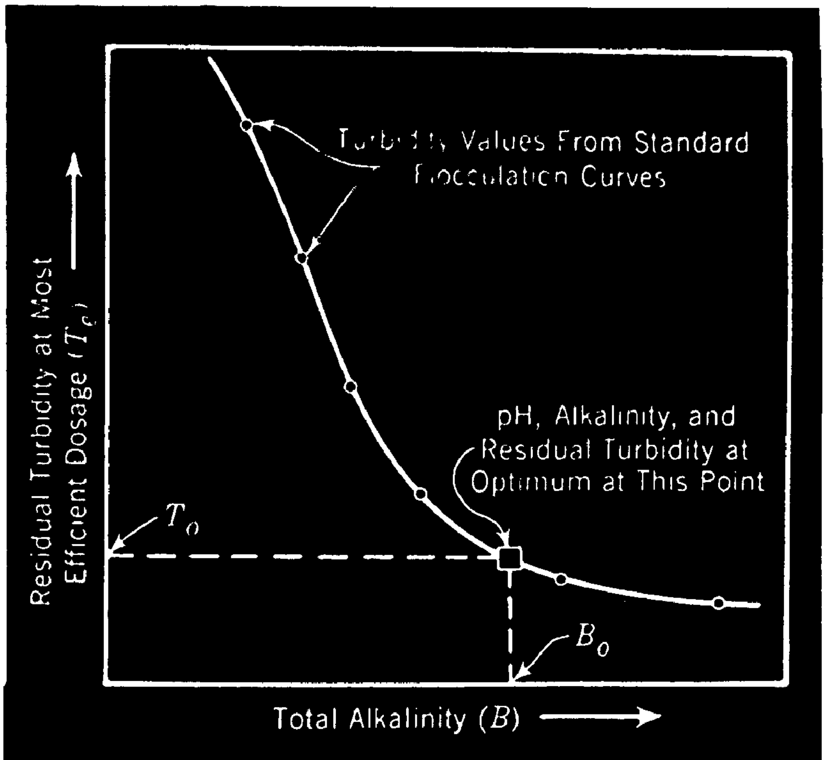
Series of tests were performed, adding $NaHCO_3$ as buffer in amounts of 0.00, 0.20, 0.50 and 1.00 milliequivalents per litre. The results are plotted in Fig. No. 7 (19). For each water, plotted point represents most efficient dosages (D_e) for total alkalinities (B). This total alkalinity also includes the titrable alkalinity of turbidity particles. It also gives the final pH value (pH_e), corresponding to most



—Coagulant Demand of Soil Suspensions in Waters of Varying Total Alkalinity

Fig. No. 7.

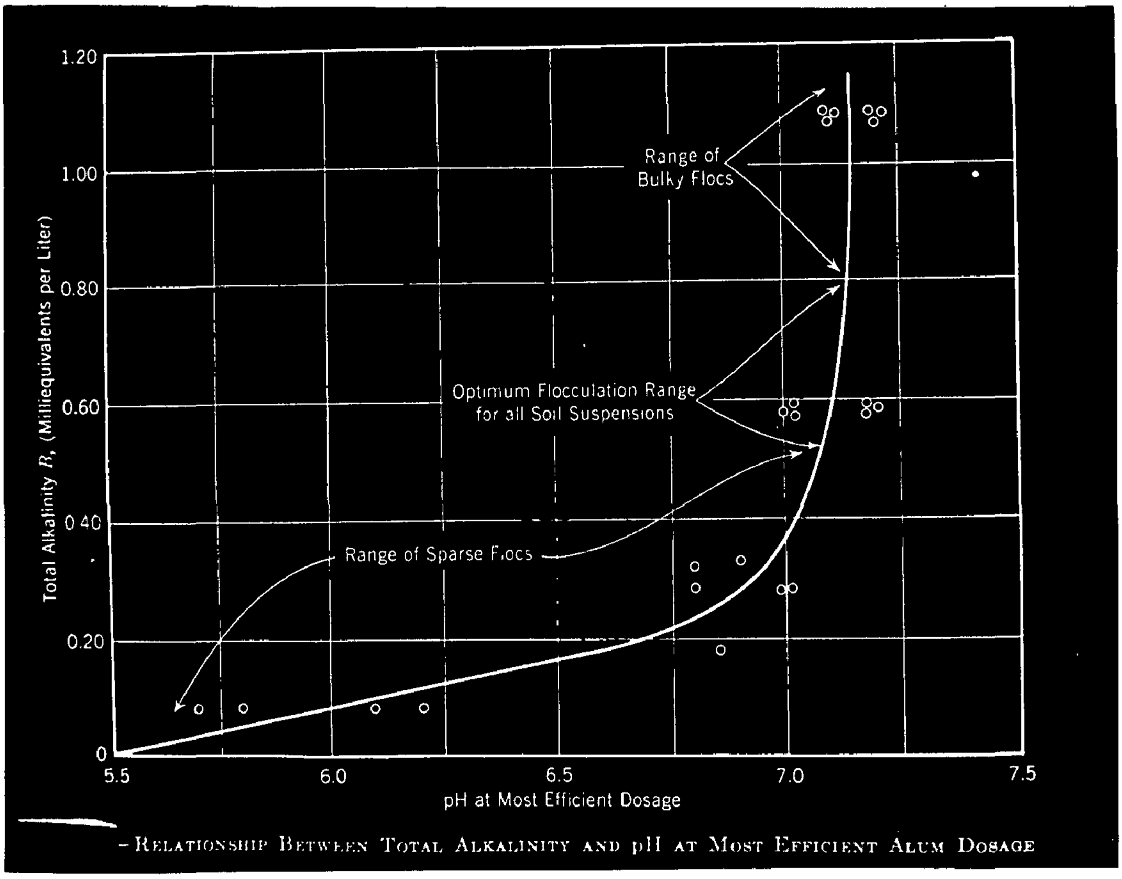
Coagulant Demand of Soil Suspensions in Waters, of Varying Total Alkalinity.



—Optimum Flocculation Conditions for a Given Water

Fig. No. 8.

Optimum Flocculation Conditions for a Given Water.



– Relationship Between Total Alkalinity and pH at Most Efficient Alum Dosage

Fig. No. 9.

Relationship between Total Alkalinity and pH at Most Efficient Alum Dosage.

efficient dosage. These are series of straight lines showing :

(a) that different soil suspensions exhibit different coagulant demand, ✓

(b) that an increase in the buffer capacity results in a proportionate increase in coagulant demand; and ✓

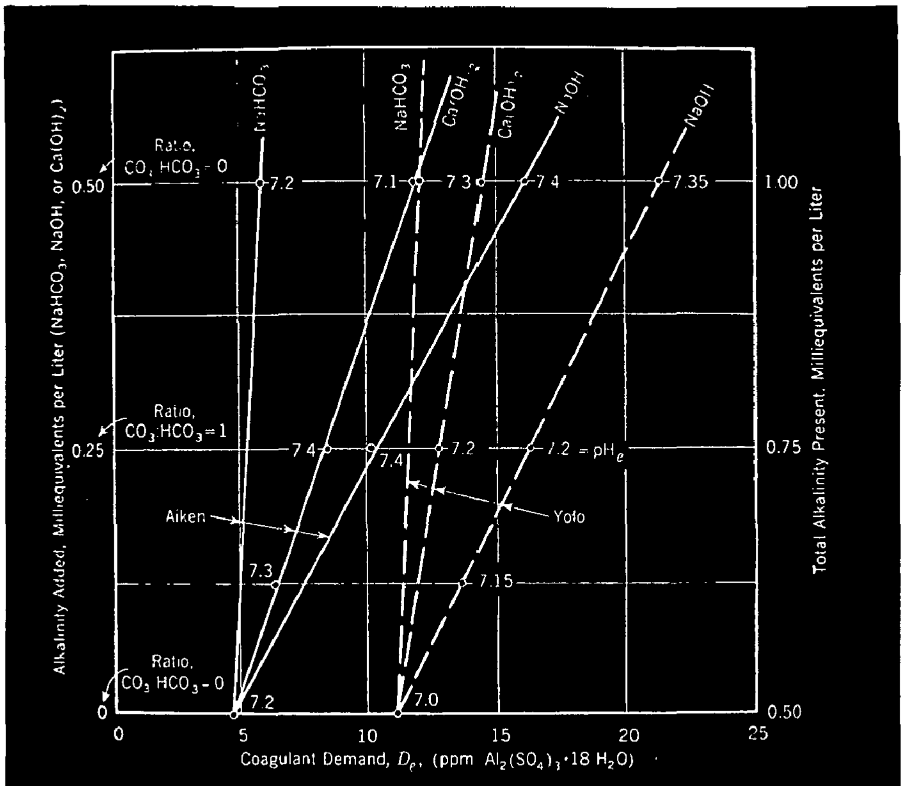
(c) pH_e increases with total alkalinity within test limits.

If for a given suspension various values of total alkalinities are plotted against the corresponding residual turbidities (T_e) at most efficient dosage, curve shown in Fig. No. 8 is obtained. Examination of this curve gives the minimum value of total alkalinity at which good clarification occurs. This alkalinity can be termed as optimum alkalinity, as it gives greatest turbidity reduction with an economical coagulant dosage. The optimum alkalinity for the six suspensions was from 0.5 to 0.8 milliequivalents per litre. ✓

3.4 Effect of pH

The pH_e value associated with the optimum value of alkalinity can be termed as the optimum pH (pH_o), and the most efficient dosage at that alkalinity is the optimum dosage (D_o). For the six suspensions optimum pH varies in narrow limits of 7.0 to 7.2. ✓

The Fig. No. 9 (19) has been plotted to show the typical values of pH_e, with increasing bicarbonate alkalinity. It is interesting to note that the value of pH increases with total alkalinity until reaching a maximum of 7.1, indicating



Effect of CO_3 — HCO_3 Ratio on Alum Demand at Constant Total Alkalinity

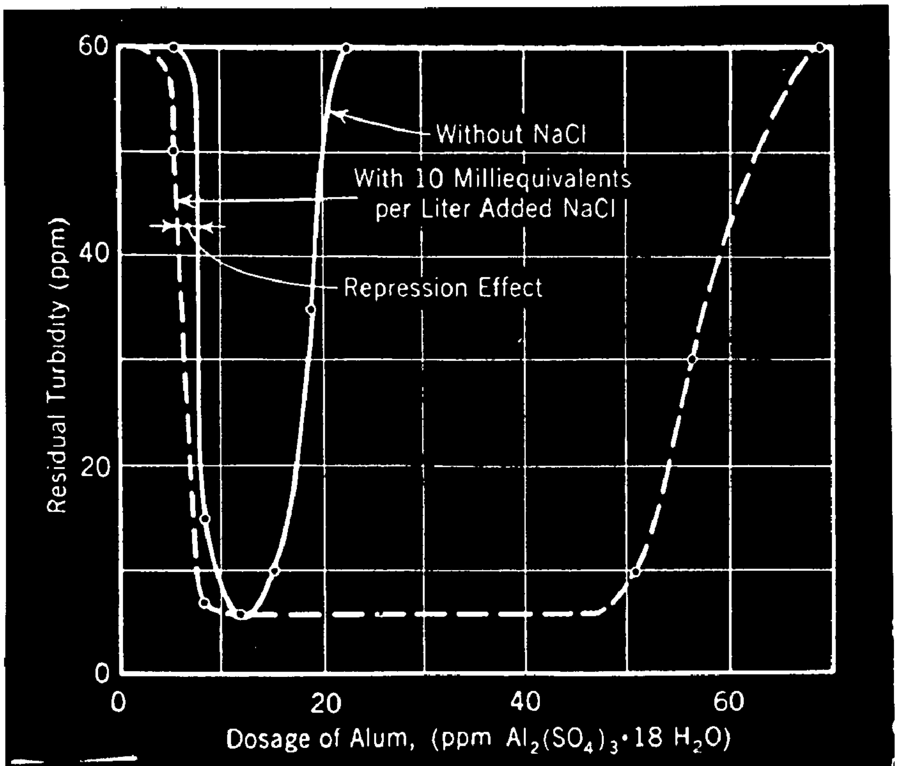
Fig. No. 10.

Effect of CO_3-HCO_3 Ratio on Alum Demand at Constant Total Alkalinity.

that alkalinity in excess of optimum results in the waste of an equivalent amount of coagulant. In the treatment of such waters it is advantageous to neutralise the excess portion of alkalinity with a strong acid before the coagulant is added. The probable explanation is that in the presence of hydroxyl ions at pH greater than optimum, the alum first added to the water combines with OH^- ions to form soluble aluminate liberating H^+ ions. Thus pH is lowered. When it reaches the optimum, normal reaction takes place.

3.5 Adjustment of pH and Buffer Capacity

To determine the effect of variable ratios of carbonate to bicarbonate alkalinity, varying increments of either sodium or calcium hydroxide were added to the bicarbonate suspensions (19). The typical results of two suspensions are shown in Fig. No. 10. It indicates that the coagulant demand for a given total alkalinity increases as the ratio of carbonate to bicarbonate increases. The reason for this is apparent, as it is noted that the sufficient alum should be added to lower the pH to an approximately constant value of 7.1 to 7.2 for efficient coagulation. Naturally the amount of alum or acid required for this is a function of both the total alkalinity and buffer capacity. The separate effects of total alkalinity and buffer capacity in the region above pH 7.2 are indicated by the relative slopes of the NaOH and $NaHCO_3$ curves. The $Ca(OH)_2$ curve falls to the left of NaOH curve and it is partly due to the destabilizing effect of divalent calcium



—Effect of Sodium Chloride on Alum Demand and Residual Turbidity

Fig. No. 11.

Effect of Sodium Chloride on Alum Demand and Residual Turbidity.

ions upon the turbidity particles and partly due to the formation of colloidal calcium carbonate.

In waters of low turbidity and alkalinity, the pretreatment with lime may be useful or even essential in effecting a better balance between two effective equillibria in normal flocculation.

3.6 Anion or Salinity Effect

The series of tests were conducted to study the effect of salts of strong acids and bases on the flocculation (19). To the six suspensions varying amount of NaCl (and in other test group Na_2SO_4) were added for each water and values of D_e and pH_e were determined. Typical results are shown in Fig. No. 11. Two effects are noted due to the presence of NaCl or Na_2SO_4 in appreciable concentrations.

(i) Na^+ ions have a slight destabilizing effect, thus there is a slight decrease in the coagulant demand. This is in agreement with colloid theory, and may be due to a repression rather than an exchange effect caused by the high concentration of cations in the water medium with colloids.

(ii) The zone or range of effective clarification is also widened. The effect is similar to that obtained by increasing the buffer capacity, but must be due to different cause. This phenomenon has also been noted and discussed by B.H. Peterson and Edward Bartow (27),

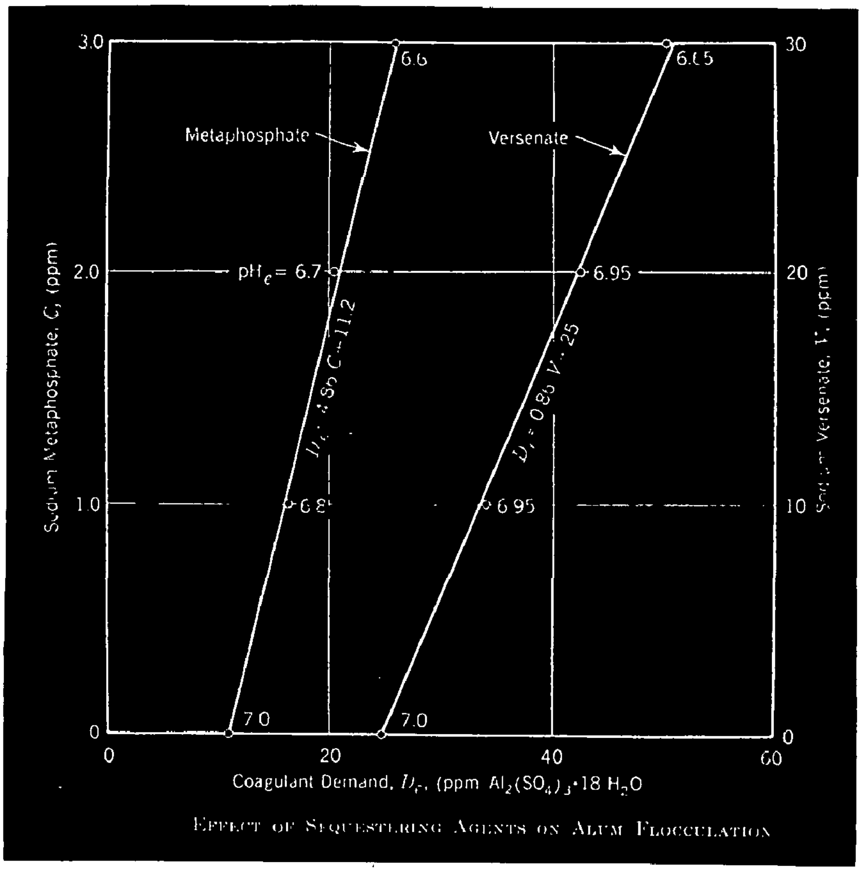


Fig. No. 12.

Effect of Sequestering Agents on Alum Flocculation.

and by Bartow, A.P. Black and Owen Rice (28).

Similarly it is also observed that large dosages of either NaCl or Na_2SO_4 beginning at 400 ppm or so, had a detrimental effect and results in a fine, slow settled floc. One of the reasons may be that Cl^- ion has a dispersing action on hydrous oxide micelles and thus prevents their formation.

3.7 Effect of Sequestering or Chelating Agents

In the series of tests sodium metaphosphate and Sodium versenate were used as the representative chelating substances (19, 29). The observation made with 'yellow' suspensions of 0.5 milliequivalents per litre alkalinity and 60 ppm initial turbidity are shown in Fig. No. 12. The alum dosage increases linearly with the concentration of metaphosphate or of versenate. It is also noted that the quality of the floc produced at most efficient dosage decreases with the concentration of metaphosphate.

The basic reaction, which causes this detrimental effect is not given. But the explanation given is that the metaphosphate, through its sequestering effect, interferes with the flocculation. At its low concentrations the effect can be overcome by simply increasing coagulant dosage to provide the necessary excess alum to meet with the metaphosphate, but yet due to peptization of clay particles by metaphosphate the floc quality deteriorates. And at high concentrations, the peptization of clay particles may be so complete that no dosage of alum can affect their coagulation. The sodium versenate also gives the same results as the sodium metaphosphate, except that more versenate than metaphosphate is required for the same result.

3.8 Effect of Surface Active Agents

The series of tests give the effect of the synthetic surface active agents on the flocculation of different types of suspensions. In recent years these agents have come into wide use both in the home and in the industry. One of the properties of these agents is their ability to disperse colloidal particles and ultimately they achieve the opposite of flocculation or deflocculation. The various agents studied were the representatives of ionic, cationic and nonionic groups. The dispersion effect of cationics might be expected to interfere with sewage treatment processes involving flocculation. The dosage required for efficient flocculation were proportional to the concentration of the surface active agents and were different for different substances (29).

3.9 Effect of Particle Size

As coagulation deals with the colloids it goes without saying that important variable in coagulant demand should be the fineness of the particles. The experimental procedure consisted of preparing a stock suspension by dispersing Yellow silty clay loam in distilled water to a concentration of 1000 ppm (19). This water had an initial turbidity of 610 ppm.

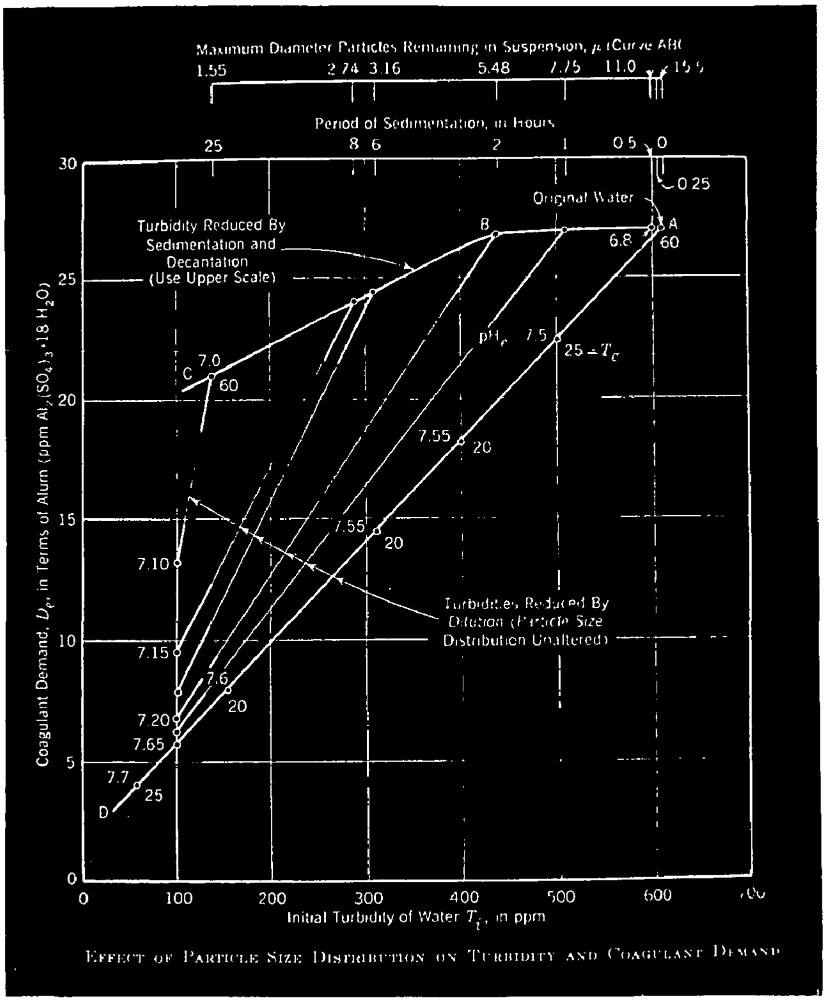
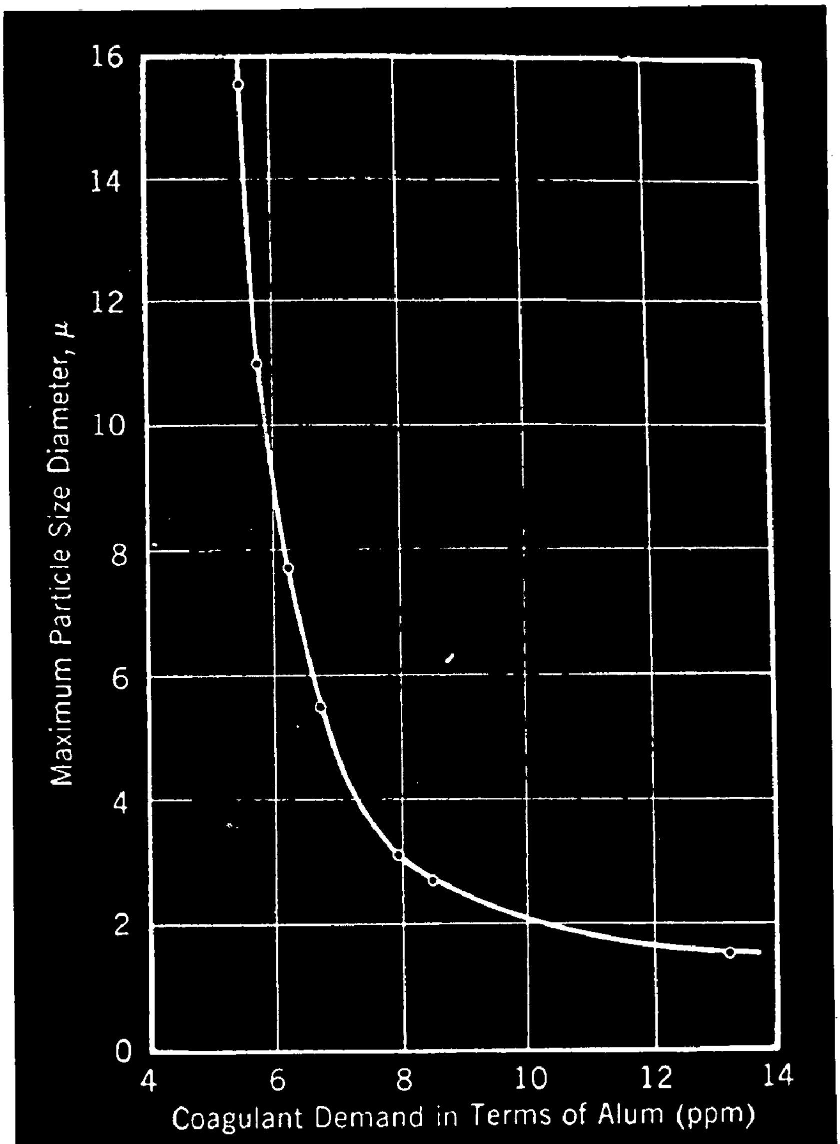


Fig. No. 13.

Effect of Particle Size Distribution on Turbidity, and Coagulation Demand.



—EFFECT OF PARTICLE SIZE ON COAGULANT DEMAND WITH A CONSTANT TURBIDITY OF 100 ppm USING YOLO SUSPENSION

Fig. No. 14.

Effect of Particle Size on Coagulant Demand with a Constant Turbidity of 100 ppm using Yellow Suspension.

(i) Tests were made to determine the coagulant demand for the initial turbidity and also for various dilutions of the stock solution down to 10 per cent or 61 ppm. In each case 0.5 milliequivalent per litre of $NaHCO_3$ was added as buffer.

(ii) Other test specimens of stock suspension were prepared by allowing it to settle for different periods ranging from 15 minutes to 25 hours and supernatant 20 cm. were tested for coagulation demand.

(iii) In addition settled waters were diluted to give uniform turbidity of 100 ppm and tested for coagulant demand.

The results are plotted in Fig. No. 13 and 14. ✓

The upper curve ABC of Fig. No. 13 with scales at the top shows the change in coagulation demand for varying turbidities obtained by plain settling and decantation. In AB range the demand is practically constant showing that particles greater than about 5 μ diameter have very little effect.✓ It is also noted during test that some of the particles were not incorporated into the flocs but settled rapidly to the bottom of test jar. While in range BC there was no separation of the particles noted, but coagulant demand decreased from 27 ppm to 21 ppm as a result of the absence of particles of diameters from about 5 μ down to 1.5 μ. Soil technologists have shown that practically all of the exchange capacity of a clay suspension is associated with the particles smaller than 1.5 μ diameters (30). So the coagulant demand at point C may be considered as comprising an exchange demand plus a binder demand. Now exchange demand is constant between points B and C and decreases in demand with lower turbidity is due to lower binder demand. Now this is expected since particles of 1.5 μ to 5 μ size are incorporated into the floc. ✓

The lower curve AD of Fig. No. 13 shows that coagulant demand of the diluted stock suspension, wherein particle size distribution is the same, decreases almost in direct proportion to the decrease in turbidity. The intermediate straight lines have the same interpretation. Thus the dilution decreases both the exchange and binder demands in equal proportions. ✓

The plotted points on vertical line of the Fig. No. 13 with the constant turbidity of 100 ppm show the effect of variation in particle size distribution over the coagulant demand. The same data is replotted in the Fig. No. 14 to show maximum particle size diameters. As the percentage of smaller particles becomes greater the coagulant demand also increases with it; and the increase is very great when the particles present are especially of diameters less than 2 μ. ✓

To gain additional information and also to confirm results a suspension of the Yellow silty clay loam was fractionated by means of repeated sedimentation and decantation. On the basis of Stroke's law the suspension was divided into groups containing only particles of following size : 0 to 1 μ, 1 μ to 2 μ, 2 μ to 5 μ, 5 μ to 15 μ, 15 μ to 25 μ, 25 μ to 60 μ, requires, in addition to suitable pH and alkalinity, turbidity particles both coarser and finer than approximately 1μ in diameter. The smaller particles possess colloidal properties and some of these are required for neutralizing the positive charges formed on hydrous oxide binder particles. After destabilization by suitable polyvalent cations the aggregation of colloidal particles takes place, which again induces the agglomeration of non-colloidal larger particles. The particles greater than 1μ serves as suitable structural units for binding up dense rapidly settling flocs, in the same manner in which larger aggregates are graded with smaller aggregates in the making of dense concrete. The practice of adding powdered limestone as a coagulant aid in reactor type flocculation units is an application of this principle.

If, in given water, (a) there is a shortage of either finer or coarser particles, the addition of missing particles increases the efficiency of flocculation, and in turn clarification. (b) While if it contains the particles with proper distribution of size of the particles, the addition of either will increase the coagulant demand without improving the flocculation. (c) The particles, which are too large to be taken up by the flocs, have no effect either on coagulant demand or on flocculation behaviour.

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CHAPTER IV

COAGULANTS

4.0 General Considerations

Since the coagulation is one of the old processes adopted for clarification of water, there are also very many substances used as coagulants. The role of coagulant to satisfy the exchange and binder demand is already discussed in the previous chapter. Here a brief review of different coagulants used, their properties, optimum conditions etc., is given.

The compounds of iron and aluminium are generally used for removing turbidity, bacteria, colour and other finely divided matter from water. They ionize in water producing cations and anions of high valence, and with alkalinity form insoluble hydrous oxide precipitates. The cations destabilize the negatively charged colloids and anions the positively charged hydrous oxide particles. The reactions are sensitive to the pH of water. Negatively charged particles particularly of colour colloids coagulate best at low pH values. Overdosing

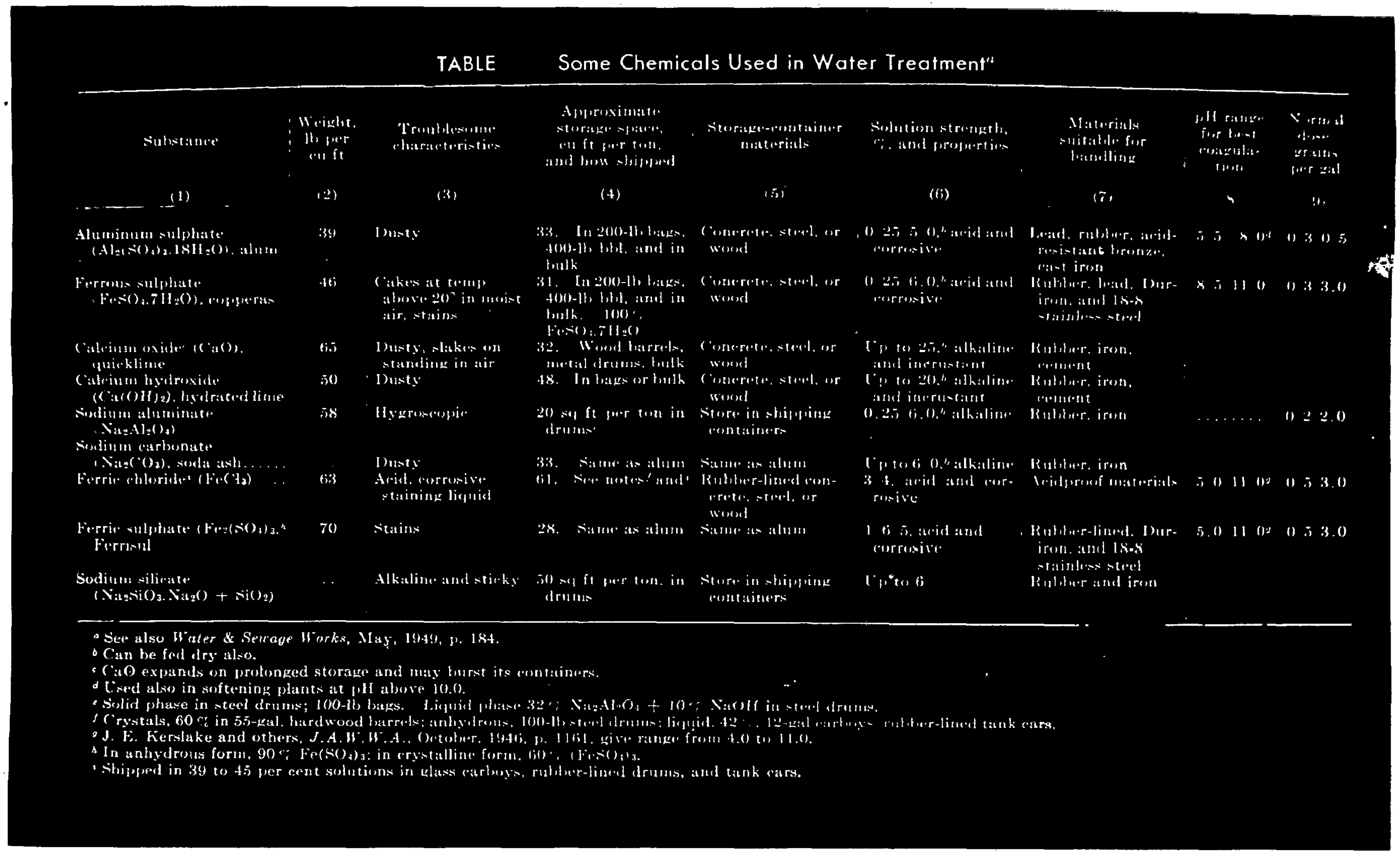

TABLE Some Chemicals Used in Water Treatment[a]

Substance	Weight, lb per cu ft	Troublesome characteristics	Approximate storage space, cu ft per ton, and how shipped	Storage-container materials	Solution strength, %, and properties	Materials suitable for handling	pH range for best coagulation	Normal dose grains per gal
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Aluminum sulphate ($Al_2(SO_4)_3.18H_2O$), alum	39	Dusty	33. In 200-lb bags, 400-lb bbl, and in bulk	Concrete, steel, or wood	0.25–5.0,[b] acid and corrosive	Lead, rubber, acid-resistant bronze, cast iron	5.5–8.0[d]	0.3–0.5
Ferrous sulphate ($FeSO_4.7H_2O$), copperas	46	Cakes at temp above 20° in moist air, stains	31. In 200-lb bags, 400-lb bbl, and in bulk. 100%, $FeSO_4.7H_2O$	Concrete, steel, or wood	0.25–6.0,[b] acid and corrosive	Rubber, lead, Duriron, and 18-8 stainless steel	8.5–11.0	0.3–3.0
Calcium oxide[c] (CaO), quicklime	65	Dusty, slakes on standing in air	32. Wood barrels, metal drums, bulk	Concrete, steel, or wood	Up to 25,[b] alkaline and incrustant	Rubber, iron, cement		
Calcium hydroxide ($(Ca(OH)_2)$), hydrated lime	50	Dusty	48. In bags or bulk	Concrete, steel, or wood	Up to 20,[b] alkaline and incrustant	Rubber, iron, cement		
Sodium aluminate ($Na_2Al_2O_4$)	58	Hygroscopic	20 sq ft per ton in drums[e]	Store in shipping containers	0.25–6.0,[b] alkaline	Rubber, iron	....	0.2–2.0
Sodium carbonate (Na_2CO_3), soda ash......	..	Dusty	33. Same as alum	Same as alum	Up to 6.0,[b] alkaline	Rubber, iron		
Ferric chloride[i] ($FeCl_3$) ..	63	Acid, corrosive staining liquid	61. See notes[f] and[i]	Rubber-lined concrete, steel, or wood	3–4, acid and corrosive	Acidproof materials	5.0–11.0[g]	0.5–3.0
Ferric sulphate ($Fe_2(SO_4)_3$,[h] Ferrisul	70	Stains	28. Same as alum	Same as alum	1–6.5, acid and corrosive	Rubber-lined, Duriron, and 18-8 stainless steel	5.0–11.0[g]	0.5–3.0
Sodium silicate ($Na_2SiO_3.Na_2O + SiO_2$)	..	Alkaline and sticky	50 sq ft per ton, in drums	Store in shipping containers	Up[b] to 6	Rubber and iron		

[a] See also *Water & Sewage Works*, May, 1949, p. 184.

[b] Can be fed dry also.

[c] CaO expands on prolonged storage and may burst its containers.

[d] Used also in softening plants at pH above 10.0.

[e] Solid phase in steel drums; 100-lb bags. Liquid phase 32% $Na_2Al_2O_4$ + 10% NaOH in steel drums.

[f] Crystals, 60% in 55-gal. hardwood barrels; anhydrous, 100-lb steel drums; liquid, 42%, 12-gal carboys, rubber-lined tank cars.

[g] J. E. Kerslake and others, *J.A.W.W.A.*, October, 1946, p. 1161, give range from 4.0 to 11.0.

[h] In anhydrous form, 90% $Fe_2(SO_4)_3$; in crystalline form, 60%, $(FeSO_4)_3$.

[i] Shipped in 39 to 45 per cent solutions in glass carboys, rubber-lined drums, and tank cars.

TABLE NO. 3.

Some Chemicals used in Water Treatment.

of electrolyte may reverse the zeta potential and interfere with the coagulation of colloids. However if very large amounts of electrolyte are added, zeta potential may again be driven to zero. Aluminium sulphates, iron chloride and iron sulphates are normally employed as coagulants because they are the cheapest available chemicals. A few of the many compounds used as coagulants, their properties and common dosages in American water works practice are listed in Table No. 3 (31).

4.1 Coagulation with Aluminium Sulphate $Al_2(SO_4)_3 \cdot 18H_2O$

x varies

Commercial alum is a dirty grey, yellowish, crystalline solid. It is available in lump, rice, granular or powdered form, containing about 17 per cent $Al_2(SO_4)_3$. It is an acid salt, corrosive to most metals and concretes. Its solubility is 86.9 parts in 100 parts of water at 0° C. Alkalinity is required when it is used as a coagulant.

It is most widely used chemical for coagulation of water, because of its excellent floc formation, its relative economy, its stability and its ease in handling. Due to the formation of calcium sulphate with natural alkalinity the hardness is increased to a slight extent. The presence of sodium and potassium anions have the dispersing effect on aluminium floc. The difficulty can be overcome by increasing the alum dose, if anion concentration is within the limits. (Refer to the previous chapter).

Black alum is a mixture of aluminium sulphate and about 4 per cent powdered activated carbon. It is used in coagulating waters for the removal of tastes and odours. A drawback to its use is the inability to vary carbon dosage if necessary.

Ammonia alum [$(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$] and potash alum [$K_2SO_4, Al_2(SO_4)_3, 24H_2O$] are not used at large water works, but primarily in the operation of pressure filters at industrial plants and swimming pools. The alum is placed in a 'pot' through which water is run under pressure to dissolve some of the alum. The solution so formed is injected into the raw water. These alums dissolve more slowly than aluminium sulphate, are less likely to cause clogging of pipes, and are therefore suitable for pot feeds.

4.2 Reactions with Alum

Aluminium sulphate requires the presence of alkalinity in the water to form the floc. In waters having bicarbonate alkalinity, the chemical reaction proceeds as follows, ✓

$$Al_2(SO_4)_3.\overset{x}{\cancel{18}}H_2O + 3CaCO_3.H_2CO_3 = \overset{2\,Al\,(OH)_3}{\cancel{Al_2(OH)_3}} + \overset{\checkmark}{3CaSO_4} + \overset{x\ \checkmark}{\cancel{18}}H_2O + \overset{\checkmark}{6CO_2}.$$

The aluminium hydroxide is the floc. The temporary or the carbonate hardness caused by calcium bicarbonate is reduced, but the permanent or noncarbonate hardness caused by calcium sulphate is increased. Another undesirable result is the addition of carbon dioxide, which is corrosive to metals. ✓

Some waters have insufficient natural alkalinity to react with the alum. In those cases lime is generally added.

$$Al_2(SO_4)_3 \cdot \overset{2}{18}\ H_2O + 3Ca(OH)_2 = Al_2(OH)_6 + 3CaSO_4 + \overset{2}{18}\ H_2O.$$

In some plants, sodium carbonate, frequently called soda ash, is added to form alkalinity.

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Na_2CO_3 + 3H_2O = \overset{2\ Al(OH)_3}{Al_2(OH)_6} + 3Na_2SO_4 + 3CO_2 + 18\ H_2O.$$

The advantage of using sodium carbonate is that it does not add to hardness, although it does increase corrosiveness to some extent. It is more expensive than lime and is therefore less used. Natural alkalinity is present in many waters, so alum is favoured by some plant operators, as it is the only chemical that is needed to be added.

Theoretically 1 grain per gal. commercial alum requires 7.7 ppm of alkalinity as $CaCO_3$; but practically the amount required may vary between 4 ppm for highly coloured waters upto 6 to 7 ppm. In actual practice more than theoretical amount is required because part of it combines directly with impurities in waters. The absence of sufficient alkalinity to complete reaction is generally unusual. In general, 8 to 10 ppm of alkalinity as $CaCO_3$ will react with 1 grain per gal. of alum. Where there is less than 20 ppm of natural alkalinity as $CaCO_3$ about 0.35 grain of lime or 0.5 grain of soda ash should be added per grain of alum. The chemical should be thoroughly mixed with the raw water for short time before alum is added. If it is added quite early before the coagulant, some softening action may occur, necessitating more chemical dosage. Doses of alum used in practice vary between 0.3 and 2.0 grains per gal. depending upon many factors.

4.3 Practical Difficulties with Alum

Difficulties with alum as already mentioned are a slight increase in sulphate hardness, the increase in carbon dioxide, and the formation of colloidal precipitate in the presence of sodium and potassium. If it is necessary to add alkalinity to improve coagulation there is a danger of fixation of colour to the water, if the alkalinity added is too strong (32). The reaction is seldom fully completed, and high concentration of colloidal matter sometimes hinders the reaction, and residual alum remains in the water that goes to the filters. As the optimum range of pH is very small (5.5 to 8.0), it is difficult to adjust coagulation through pH control. Where the optimum pH is low, 4.4 to 5.0, as in the case of some soft coloured waters, it is advisible to depress pH by the addition of sulphuric acid, so that smaller quantity of alum is used.

for what? turbidity or colour removal

Water coagulated with alum contains aluminium compounds in solution. The exact nature of these compounds is quite complex. Since aluminium hydroxide is also soluble in water to the extent of 0.3 to 0.5 ppm, some residual alumina is expected, but the amount should not exceed 0.3 ppm. Colourimetric tests are satisfactory for operation control (33).

(33).

4.4 Coagulation with Iron Salts

Ferrous Sulphate ($FeSO_4$), Ferric Sulphate $[Fe_2(SO_4)_3]$, Ferric Chloride ($FeCl_3$), and the mixture of Ferric Chloride and Ferric Sulphate known as Copperas, are the common iron compounds used as coagulants in water and sewage treatment works. Iron salts are said to produce a faster forming, denser, quicker settling, and less easily broken up floc than alum, especially at low temperatures. The wide optimum pH range of iron makes them useful in the removal of manganese at values of pH above 9.0 and in the coagulation of coloured waters at pH values below 5.0.

4.5 Coagulation with Ferrous Sulphate $FeSO_4 \cdot 7\ H_2O$

Ferrous Sulphate has an advantage over alum in that it may be less expensive and the floc is heavier and sinks more rapidly. But it needs the use of lime with it. Strict chemical control is required. Also there is a danger of after precipitation in the distribution system due to reaction of surplus lime and bicarbonate alkalinity for the treatment of soft coloured waters as they are best coagulated at a pH below 7.0, while optimum pH range for ferrous sulphate is pH 8.5 & 11 8.5 and above (34). Sometimes colour appears to become fixed by the addition of alkali to coloured waters. Hence its use is limited to those waters in which alkalinity will not interfere with the removal of colour. ✓

It is best suited for coagulating turbid waters of high natural alkalinity. There is usually insufficient alkalinity in natural waters thus necessitating the addition of lime, which otherwise leaves soluble compounds of iron in treated water.

4.6 Reactions with Ferrous Sulphate

Ferrous sulphate can react with natural alkalinity in water, but this reaction is much delayed and therefore not depended upon. Caustic alkalinity with the addition of lime to water, causes a speedy reaction. However chemical reactions depend on the order in which the chemicals are added to water.

When iron is added first, the reactions are,

$$FeSO_4.7\ H_2O + CaCO_3.H_2CO_3 = FeCO_3.H_2CO_3 + CaSO_4 + 7\ H_2O.$$

$$FeCO_3.H_2CO_3 + 2\ Ca(OH)_2 = Fe(OH)_2 + 2CaCO_3 + 2\ H_2O.$$

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

When the lime is added first, the reactions are,

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.$$

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

The ferrous hydroxide $Fe(OH)_2$ is a desirable, heavy, gelatinous precipitate. It is, however, oxidised to ferric hydroxide $Fe(OH)_3$, likewise a satisfactory gelatinous precipitate. It should be noted that the use of lime and iron adds less hardness to water and no corrosiveness.

The amount of ferrous sulphate required, which is mainly dependent on the turbidity, the natural alkalinity and the carbon dioxide present in the raw water, is commonly determined by the experience with the water being treated. While the amount of lime required depends in turn on the amount of ferrous sulphate added and also on the carbon dioxide present, which must be neutralized. The addition of slight excess of lime than required, say about 1 to 5 ppm, enhances the precipitation of ferric hydroxide, through the formation of calcium chloride crystals about the ferric hydroxide. There is a danger of afterprecipitation if too great in excess of the lime is added; so it should be avoided. ✓

4.7 Ferric Coagulation

Ferric Chloride ($FeCl_3$), Ferric Sulphate $Fe_2(SO_4)_3$ and Chlorinated Copperas are used as coagulants especially in sewage treatment. Advantages with ferric coagulants are as (35) :

(i) Coagulation is effective over a wider range of pH than with alum (pH ~~4~~5.0 and above).✓ pH 5 to 11 ✓

Page 53 Table 3.

(ii) The time required for floc formation, conditioning and settling is considerably shorter than that required for alum. ✓

(iii) Filter runs have been increased. ✓

(iv) It can be used for the removal of manganese at pH values above 9.0. ✓

(v) Very little iron is carried through effluent. ✓

(vi) Tastes and odours are reduced. ✓

$$Fe_2(SO_4)_3 + 3\ CaCO_3.H_2CO_3 = 2\ Fe(OH)_3 + 3\ CaSO_4 + 6CO_2.$$

$$Fe_2(SO_4)_3 + 3\ Ca(OH)_3 = 2\ Fe(OH)_3 + 3\ CaSO_4.$$

The floc is denser than that of alum, and it is precipitated over a wide pH range. It is useful in removing iron and hydrogen sulphide from well waters. But the solution of ferric sulphate is corrosive and staining; and dissolves readily only in warm waters.

4.10 Chlorinated Copperas

Chlorinated copperas is a mixture of ferric chloride and ferric sulphate prepared by adding chlorine to a solution of ferrous sulphate in the ratio of 1 part of chlorine to 7.8 parts of copperas. The salt is highly corrosive. It is claimed that the effectiveness of copperas is increased as a coagulant and necessity for high alkalinity is eliminated. The coagulant may be prepared in the plant by dosing a solution of copperas with chlorine. Among the advantages claimed for the use of chlorinated copperas, as a coagulant, are : (36),

(i) It produces a desirable floc formation with tough floc particles.

(ii) Floc formation settles well allowing to go only a small part to filter.

(iii) The coagulating effect has a wide range of pH from 8 or 9 to 6.

(iv) A compact ferric hydroxide floc is formed at all pH values above 3.5.

analysis of the best grade is Al_2O_3, 55 per cent; combined Na_2O_3, 34 per cent; Na_2CO_3, 4.5 per cent; NaOH (excess), 6.3 per cent. The advantages of sodium aluminate are that it itself is an alkaline salt and alkalinity need not be added to the waters. When used, it is generally used with aluminium sulphate for coagulation; reactions are :

$$6\ NaAlO_2 + Al_2(SO_4)_3 \cdot 18\ H_2O = 8\ Al(OH)_3 + 3\ Na_2SO_4 + 6\ H_2O.$$

$$2\ NaAlO_2 + CO_2 + 3\ H_2O = Na_2CO_3 + 2\ Al(OH)_3\ .$$

Some very cold waters have coagulated well with the addition of 0.2 g.p.g. of sodium aluminate. It does not increase the noncarbonate hardness and can be mixed with lime and soda ash solution, thus additional equipment for its application is not necessary. It is rather expensive but since it is only used in small amounts, its cost will be justified under special conditions. ✓

4.13 Electrolytic Coagulation

Coagulation has been effected by passing water through a series of aluminium sheets spaced about $\frac{1}{8}$ inch apart. Opposite electrical charges on alternate plates discharge trivalent ions into water, using a low-voltage, high - amperage current. Advantages claimed for the process include fast floc formation, independence from pH, better clarification, and touch floc. Costs are variable within wide limits. ✓

Experience with the process on the Potomac River Water indicates a consumption of electric power approximately 1,080 kwhr. per million gallons (37).

4.14 Coagulant Aids

These are the substances which effectively increase the efficiency in coagulation. They normally alter the initial properties of waters, adjust the pH, alkalinity, particle size distribution in initial turbidity so that coagulant dose is reduced.

Lime and soda ash are used for the adjustment of alkalinity or providing sufficient alkalinity. Acids like sulphuric acid and phosphoric acid have many uses, such as pH adjustment and regeneration of base exchange materials.

Activated silica is sodium silicate activated with aluminium sulphate, sulphuric acid, carbon dioxide, or chlorine. When placed in water, it produces a stable sol, having a high negative charge and hence neutralize the positive charge on aluminium hydroxide or other floc to make it denser and tougher (38, 39). It is especially used for waters having low turbidity which do not coagulate well with the usual processes. The sodium silicate is an opaque, viscous liquid. Activation requires proper equipment and good operation for success. It is generally produced on continuous basis (40).

Application of chlorine ahead of coagulation has been reported to be advantageous (41, 42). Chlorine may alter or destroy materials which inhibit floc formation and render other materials susceptible to coagulation.

Polyelectrolytes are the recent developments. These the carbon dioxide present in the raw water, is commonly determined by the experience with the water being treated. While the amount of lime required depends in turn on the amount of ferrous sulphate added and also on the carbon dioxide present, which must be neutralized. The addition of slight excess of lime than required, say about 1 to 5 ppm, enhances the precipitation of ferric hydroxide, through the formation of calcium chloride crystals about the ferric hydroxide. There is a danger of afterprecipitation if too great in excess of the lime is added; so it should be avoided. ✓

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(iii) Filter runs have been increased. ✓

(iv) It can be used for the removal of manganese at pH values above 9.0. ✓

(v) Very little iron is carried through effluent. ✓

(vi) Tastes and odours are reduced. ✓

(vii) There is a decreased tendency of forming mud balls compared with alum floc.

(viii) Under some conditions it is economical than alum, and

(ix) Ferric coagulants have been used with success also in waters containing hydrogen sulphide because, unlike alum, they are oxidising agents; while alum is a reducing agent. Ferric salts are reduced to ferrous state after which they behave like ferrous sulphate.

4.8 Ferric Chloride (Ferrichlor) $FeCl_3$ ✓

Ferric Chloride has been successfully used in a number of water treatment plants. The reaction with natural alkalinity and lime are as follows :-

$$2FeCl_3 + 3\ CaCO_3.H_2CO_3 = 2Fe(OH)_3 + 3\ CaCl_2 + 6\ CO_2.$$

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

It produces a heavy, quick settling floc, and at high pH values over 9.0 it is successful in removing manganese. Acidities that are encountered with some soft highly coloured waters make their coagulation with alum impossible, but they may be coagulated successfully with ferric compounds. It also removes hydrogen sulphide.

✓4.9 Ferric Sulphate (Ferrifloc, Ferriclear) $Fe_2(SO_4)_3$ ✓

When ferric sulphate is added as coagulant it reacts with the natural alkalinity of water or with lime.

$$Fe_2(SO_4)_3 + 3\ CaCO_3.H_2CO_3 = 2\ Fe(OH)_3 + 3\ CaSO_4 + 6CO_2.$$

$$Fe_2(SO_4)_3 + 3\ Ca(OH)_3 = 2\ Fe(OH)_3 + 3\ CaSO_4.$$

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(iii) The coagulating effect has a wide range of pH from 8 or 9 to 6.

(iv) A compact ferric hydroxide floc is formed at all pH values above 3.5.

(v) The coagulant is particularly effective in colour removal compared with ineffectiveness of ferric and ferrous hydroxides on colloids having an isoelectric point below 7.0. ✓

4.11 Handling of Iron Coagulants

Ferrous and ferric coagulants are corrosive, staining and deliquescent. Sludge from settling basins and wash water will stain streams a typical brown iron colour. Thus they should be carefully handled. ✓

Ferric chloride is corrosive to metals thus necessitating its storage and transportation in nonmetallic material. Materials recommended includes rubber, glass, ceramics and stainless steel. Similarly it cannot be applied through dry feed device because of its hygroscopic characteristics. It is applied in aqueous solutions in a strength between 2 to 20 per cent as per requirements.

Ferric chloride is not deliquescent and is less corrosive than ferric chloride and can therefore be stored and handled with greater ease. It does not dissolve readily requiring special equipment for its successful application. Storage solutions should not be made in strengths less than about 1 per cent to prevent rapid hydrolysis of the coagulant. Hydrolysis is almost instantaneous and will occur at pH of 5.0 to 6.0. ✓

4.12 Sodium Aluminate $NaAlO_2$.

Sodium aluminate is an alkaline compound, a typical are generally synthetic organic compounds and are said to be useful in flocculation (43). They have been used in the treatment of industrial wastes and some of them have been approved by the U.S. Public Health Service for use in potable waters (44). Three types are available, (i) anionic, (ii) cationic and (iii) nonionic. Polyelectrolytes are used with common metal coagulants. They form large, dense, rapid settling floc. This may improve flocculation and reduce flocculation time. In some waters, their use reduces the metal coagulant doses, while in other waters they themselves act as coagulants. The cationic types rapidly coagulate algae, aid in removal of surface acting agents and detergents. The polyelectrolytes are expensive, but their use is justified where experiments indicate that small amounts will reduce the coagulant dosage.

Suspended particles assist flocculation in different ways (Refer to Chapter No. 3). Coagulation in (waters of low turbidity) some cases~~,~~ may be improved by the addition of small amounts of finely divided, insoluble particles. Clay, bentonite, and activated carbon are used for this purpose (45). Sometimes returned sludge from previously treated water helps in providing neuclei and thus induces early coagulation.

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CHAPTER V

FLOCCULATION BASINS

The inclusion of chapter V and VI in this dissertation should have been properly justified. Achand

In this chapter a brief review of the fundamental theory of the physical process of the floc formation, which is recently developed, is presented together with experimental verification. It also includes the practical applications of the theory, to the flocculation apparatus and basins.

5.1 Theory of Physical Flocculation

The chemical reactions in coagulation, described in the previous chapters, are almost completed instantaneously, if the chemicals are fully mixed. The precipitates formed immediately after these chemical reactions, are of molecular size. These colloidal particles are in 'Brownian Motion', through which they come in intimate contact with one another and begin to coalesce. A stage comes when the size of the particles becomes too great to be acted upon by Brownian Motion. At this stage the size of the particles is so small that it is not even possible to see the particles - called 'microflocs' - with naked eye. For further increase of colloidal particles through coagulation and aggregation requires gentle turbulent mixing of suspensions. For this mixing, so called flocculation begins with efficient mixing accessories are used in practice. It has been previously shown by Camp, Root and Bhoota that above mentioned Brownian Motion stage is completed in a few seconds (46), and thus it is of negligible importance in the design of flocculation tanks.

It has been previously demonstrated (47, 48), that the rate of flocculation at a point in a fluid, which is caused by the motion of the fluid, is directly proportional to the absolute velocity gradient or space rate of change of velocity at the point and is also directly proportional to the concentrations of flocculable particles at the point. This relation is derived independently by the others (49), and experimental verification is obtained in stream line motion with small glass spheres of average diameter of 137 microns. why this particular size?

It has also been further demonstrated (47) that the absolute velocity gradient at a point in a fluid in motion is equal to the square root of the ratio of the power loss by shear per unit of volume of fluid to the viscocity of the fluid. The velocity gradients throughout the flocculation basin vary considerably in magnitude. It is greatest at the solid boundaries of the paddles or other devices used in basins for creating motion. Similarly velocity gradients in the coagulation conduit are greatest at the walls. It is found that under steady conditions of input of work there is a mean velocity gradient which is corresponding to the mean value of the rate of power dissipation, throughout the conduit or the basin.

Strokes (50) used the term 'dissipation function' for the rate of power dissipation i.e., the work of shear per unit of volume per unit of time at a point. The root mean square velocity gradient is given by the following relation :-

$$G = \sqrt{\frac{W}{\mu}} \quad . \; . \; . \; . \; . \quad (i),$$

in which,

G = root mean square velocity gradient,
W = mean value of the dissipation function, and
μ = absolute viscocity of the fluid.

As the rate of flocculation is directly proportional to the velocity gradient G, greater the magnitude of G, less is the time required for floc formation. So for economy in the size of flocculation chamber, velocity gradient should be as large as practicable. And it is the size of the particle which fixes the practical limit for velocity gradients, because there is a maximum size of floc particle with each velocity gradient, which can be proved easily as follows :

The viscocity constant is the proportionality constant between the unit shearing force T, and a velocity gradient at a point G' (46),

$$T = \mu G' \quad . \; . \; . \; . \; . \quad (ii).$$

Naturally from this equation, for the higher velocity gradient the greater are the shearing forces. But as particle size increases they become weaker and can be easily sheared apart. So for forming small floc particles relatively high velocity gradients may be used and for large floc particles lower velocity gradients are required. Experience in water and sewage treatment plants also shows that too violent mix in flocculation basin prevents the formation of floc particles large enough to settle out. If the flocculation is carried out in several stages in a series of tanks with the velocity gradients progressively decreased with the increase of floc size, it should give an economical design. The procedure is firstly given by Langelier and thus known as 'Langelier process.'

Very little data is available in Water Treatment fields regarding limiting velocity gradients. But existing water treatment plants data can be used for computation of the mean velocity gradient in flocculation basin. For this purpose the data given in Associated Society of Civil Engineers' Manual No. 19, "Water Treatment Plant Design", Table No. 2 were used, by Camp T.R. (45). The velocity gradients have been calculated for 20 flocculation basins, having complete data or detention period greater than 10 minutes. Computations are shown in Table No. 4. The velocity gradients are at temperature of 50^{o} F., at which the absolute viscocity is 0.273 X 10^{-4} lbs. per second per sq. ft. The values for the velocity gradients and dissipation functions W are based on the capacity of plant.

Plant	Capacity, in million gallons daily	Date built	Type of agitation	Velocity, in ft per second	Retention period, in minutes	Head loss for mixing, in feet	HP per mgd	W ft lbs per sec per cu ft	G sec^{-1}	GT (T in sec)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Albany, N. Y. (Helderberg)	40	1932	Over and under, around end baffles	0.9	20	3		0.156	74	88,800
Atlanta, Ga.	42	1923	Around end baffles	2.0	25	1		0.041	39	58,500
Baltimore, Md. (new)	112	1928	Around end baffles	1.3	30	3		0.104	61	110,000
Cleveland Ohio (Division Avenue)	140	1918	Over and under baffles	0.4	39	0.4		0.011	20	46,800
Denver, Colo.	60	1924	Around end baffles	0.3	20	0.5		0.026	31	37,200
Detroit, Mich. (Springwells)	272	1931	Around end baffles	0.4	17	0.5±		0.030	33	33,600
Erie, Pa. (Chestnut Street)	37	1925	Vertical baffles	0.1	19	1.3		0.068	50	57,000
Flint, Mich.	28	1924	Over and under baffles	0.6	35	1.2		0.036	36	75,600
Fort Worth, Tex.	20	1923	Around end baffles	0.5	40	1±		0.026	31	74,400
Grand Rapids, Mich.	40	1924	Around end baffles	1.0	45	1.0		0.023	29	78,000
Kansas City, Kans.	25	1927	Around end baffles	1.1	10	0.4		0.041	39	23,400
Kansas City, Mo.	100	1928	Spiral flow	---	30	3.5		0.121	67	121,000
Knoxville, Tenn.	15	1927	Mechanical agitators	1.5	20	(6 hp)	0.4	0.120	66	79,200
Miami, Fla.	20	1926	Mechanical agitators	1.0	20	(3 hp)	0.15	0.045	40	48,000
New Orleans, La.	(40 (72	1909) 1928)	Around end baffles	0.8	60	1±		0.017	25	90,000
Oakland, Calif.	12	1927	Mechanical agitators	1.7	20	(4 hp)	0.33	0.098	60	72,000
Oklahoma City, Okla.	16	1923	Over and under baffles	0.6	30	2		0.071	51	92,000
St. Louis, Mo. (Howard Bend)	80	1929	Spiral flow	0.7	16	0.5±		0.032	34	32,600
Tampa, Fla.	14	1926	Mechanical agitators	0.8	100	(8 hp)	0.57	0.034	35	210,000
Washington, D. C.	80	1927	Around end baffles	1.5	27	0.5 to 2		0.077	53	86,000

TABLE NO. 4.

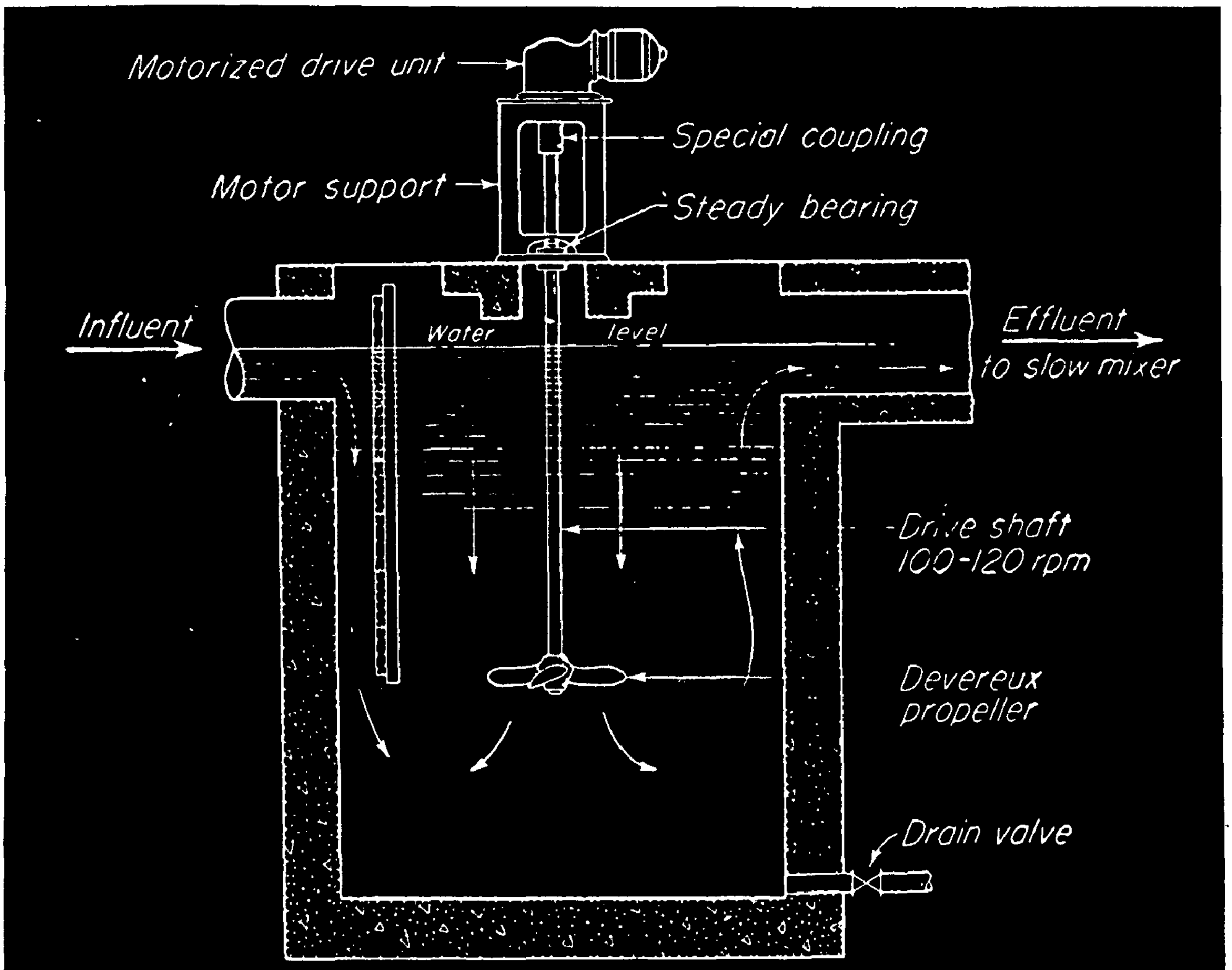
Detailed Information about some Existing, Flocculation Basins in America.

For the baffled basins the value of W has been based on detention period and head losses, are calculated for plant capacity. At lesser rates, head loss will be less and detention period greater. Thus the range of values for mean velocity gradient are maxima, and optimum values are probably much smaller.

Since rate of flocculation is directly proportional to velocity gradient G, satisfactory flocculation should be produced with particular values of the product G X T, where T is flocculation period. If G and T are expressed in seconds, G X T is a dimensionless number. The Table No. 4 indicates that maximum velocity gradients used in the American practice range from about 20 Sec^{-1} to 74 Sec^{-1}, and that values of the product G X T at plant capacity range from 23,000 to 2,10,000. Camp also found that G varied from 35 Sec^{-1} to 66 Sec^{-1}, where paddle wheels are used and with values of G X T from 48,000 to 2,10,000. In baffled basins, values varied from 20 Sec^{-1} to 74 Sec^{-1} and 23,000 to 1,21,000. As these basins are in practice, assumption can be made that these values represent coagulation basins which give some degree of satisfaction.

5.2 Practical Means of Producing Velocity Gradients

The aim in designing the flocculation basins is to secure as nearly and as quickly as possible a thorough diffusion of chemical throughout the incoming water and to bring about physical flocculation. The duration of period also



Flash mixer. (*Courtesy of Link-Belt Co.*)

Fig. No. 15.

Flash Mixer.

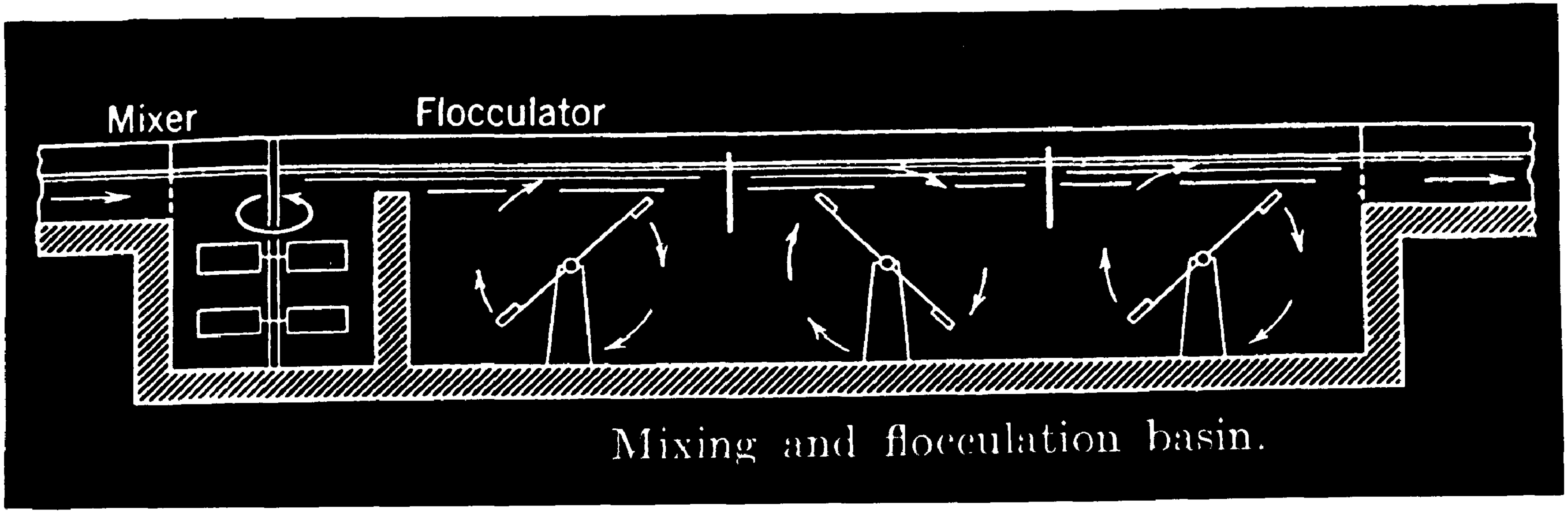


Fig. No. 16.

Mixing and Flocculation Basin.

depends upon the condition of raw water, the kind and amount of chemical coagulant used for the desired result. Considering all the points for chemical flocculation at their optimum value, naturally velocity gradient is the guiding factor for flocculation basin design.

Efficient coagulation as discussed in chapter No. 2 requires thorough and quick mixing of coagulant throughout the raw water and gentle mixing or 'conditioning' to allow the floc formation. Then onwards the water is taken to the sedimentation or settling tanks for clarification. In old plants mixing of chemicals was frequently combined with flocculation as in baffled basins. Later designs favour a separate mixing device, called 'flash mixer'. One type of a flash mixer is shown in Fig. No. 15 (51). Generally paddles, operating on vertical shafts with high speeds, are provided in the flash mixers. Detention periods are short, ranging from 10 to 60 seconds. Combination of mixer and flocculator is shown in Fig. No. 16. While in modern practice mixing, flocculation and clarification are achieved in a single compact unit, called 'Vertical Flow Units', discussed at the end of this chapter.

Thus mixing and flocculation devices normally in use, include (i) baffle basins, (ii) spiral flow basins, (iii) basins with mechanically driven paddles, (iv) air agitation and (v) hydraulic jump. Modern practice adopts mechanical means of agitation for flocculation, usually employing rotating paddles, wheels and occasionally reciprocating blades or compressed air.

Mechanical stirring devices are usually found most satisfactory. The speed of the paddle and length of mixing period should be adjustable to permit the flexibility in operation, to make to suit for the frequent change in quality of water. In practice the flocculation period varies from 10 minutes to 60 minutes depending upon the type of flocculator.

5.3 Baffled Basins

In baffle basins water flows horizontally, back and forth, past around the end baffles placed 2 to 3 ft. apart; or in which it flows up and down, past under and over baffles about 2 to 3 ft. apart. They may serve as combined mixing and coagulation basins. These are earliest flocculation basins and are designed with a channel velocity from 0.3 to 1.0 ft. per second. Detention period in basins of these types varies from 20 to 30 minutes. For baffle mixing channels or conduits, the value of the dissipation function W may be computed from the discharge and head loss as follows :

$$W = Q\rho hf/V = \rho h_f/T \; . \; . \; . \; . \; . \quad \text{(iii)},$$

where,

Q = discharge,

ρ = unit weight of the fluid,

h_f = head loss,

V = volume of conduit or chamber, and

T = detention period in seconds.

These devices are not satisfactory for flocculation purpose because most of the head loss occurs at 180° bends so that velocity gradients are too high at the bends and not high enough in the straight channels. Also the magnitude of dissipation function and thus that of velocity gradients is directly proportional to the rate of discharge and cannot be varied at will by the operator.

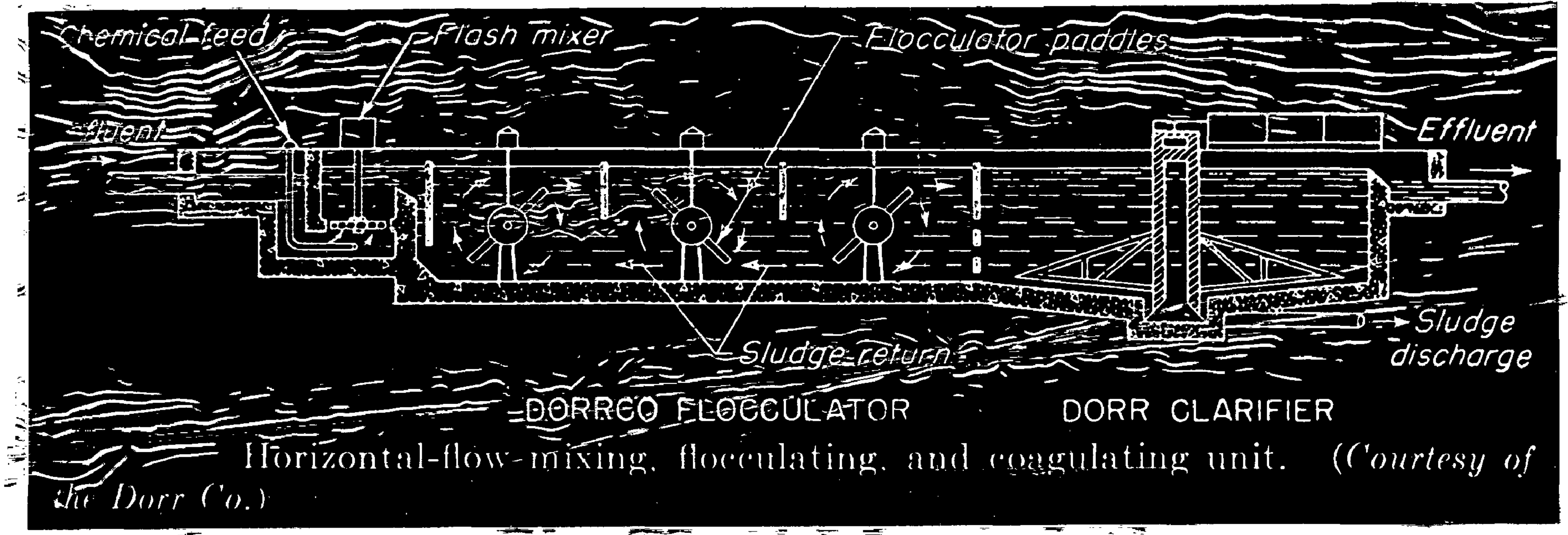
5.4 Spiral Flow or Tangential Flow Basins

In some treatment plants, turbulent mixing for coagulation has been introduced by bringing the water into the basins tangentially so as to create spiral flow. The average rotating velocity in such tanks, which are generally circular and not exceeding 40' in diameter, lies in between 0.5 to 0.75 f.p.s., with an energy requirement equivalent to about 1 ft. of head loss. The depth is usually equal to or greater than the diameter.

The values of dissipation function may be calculated by the use of equation No. 3, with h_f taken as velocity head at inlet. In such basins the turbulence is not uniformly distributed since it is introduced only at one point. Also these are not satisfactory in series as the floc breaks up while passing from one basin to the next. There is always a possibility of short circuiting. Inflow variation affects the intensity of agitation and thus not under control.

5.5 Mechanical Flocculators

In the modern plants mechanical stirring devices are used in which case the velocity gradients are independent of the rate of discharge. The velocity gradient may be changed by the



Horizontal-flow-mixing, flocculating, and coagulating unit. (*Courtesy of the Dorr Co.*)

Fig. No. 17.

Horizontal-flow Mixing, Flocculating and Coagulating Unit.

operator, in the plants provided with variable speed drives.

Mechanical flocculators may be either circular tanks with paddles revolving on a vertical shaft or rectangular tanks with paddles revolving on a horizontal shaft. A combination of chemical feed, flash mix, flocculator and clarifier is shown in the Figure No. 17 (51). The 'Walking Beam' flocculator alternatively raises and lowers inverted V shaped troughs called 'dashers' which have adjustable slots to change the degree of agitation. Circular basins are common with paddles revolving about a vertical shaft with the direction of rotation of adjacent paddles opposed or with some fixed and some revolving paddles. Detention periods in basins of these types are 30 to 60 minutes with the longer periods becoming more popular.

The horizontal, continuous flow rectangular basin is also used in practice. Water enters from one side at the bottom, and leaves at the opposite side; and encounters one or more slowly revolving paddles. The length of the horizontal shaft is placed at right angles to the direction of the flow of the water, and paddles are so placed that shortest distance between their tips is not greater than 2 to 3 ft. The clearance between bottom and side walls may be 6 inches, although 12 inches is sometimes allowed. Paddles revolve so that top layer of water moves towards the outlet, with their tips just below or projecting an inch above the water surface. Depending upon the type of paddle and other conditions, the total area of each paddle may be between 10 to 25 per cent of the vertical cross sectional area of the basin (52). The velocity is controlled by velocity gradient, the peripheral speeds varying between 1 to 2 f.p.s., without breaking the floc. Some designs have adjustable speeds to permit tapered flocculation, with increase in the floc size, consistent with the Langelier's Process previously mentioned. Fixed blades may also be used to intermesh between the moving blades and thus increase the velocity gradients. Velocities of flow recommended lie between 0.5 to 0.7 f.p.s. (53).

The value of the dissipation function W may be estimated from the drag force of the stirring blades and the distance moved per second. The drag force for any body immersed in still water is given by Newton's Law as follows :

$$F_D = C_D\ A\ v^2/2g \quad . \ . \ . \ . \quad (iv),$$

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where,

C_D = the drag coefficient,

A = Cross sectional area of the submerged object perpendicular to the direction of motion, and

v = relative velocity of the object with respect to the fluid.

The distance moved by submerged blade is equal to the velocity with respect to the water. Thus the power required to overcome the drag of a single rotating blade will be the drag force times its velocity relative to the water. So W is given by the following equation,

$$W = F_D.v = C_D.A.\rho.\frac{v^3}{2g} \quad . \ . \ . \ . \ . \quad (v).$$

Unfortunately it is difficult to find out the relative velocity of the stirring blade and liquid immediately surrounding it, for most types of stirring devices. With rotary stirring devices the liquid is set in spiral motion, thus its average angular velocity is less than the velocity of the rotars and velocity diminishes somewhat with the distance from the centre. With reciprocating devices such as 'Walking Beams' the velocity of the blade with respect to the tank varies throughout. Similarly relative motion of the blade and the tank is not the same as that of the blade and the surrounding liquid.

5.6 Flocculation with Diffused Air

Flocculation can be achieved by blowing air from a grid of perforated pipes or other diffusers placed on the bottom of the basin, through which water is flowing (54). Depth varies from 7' to 12' with a maximum practical depth of about 15'. Porous tubes, porous plates or perforated pipes may be used for air distribution. In perforated pipes laterals may be spaced 3' to 5' apart with 1/16" diameter perforations on 3" to 6" centre to centre distance. Distribution system should be placed in valleys with concrete ridges in between them.

The drag force and in turn the value of dissipation function W may be calculated by using the equation No. 4. The same difficulties are there in calculating the relative velocity.

5.7 Coagulation with A Sludge Blanket ✓

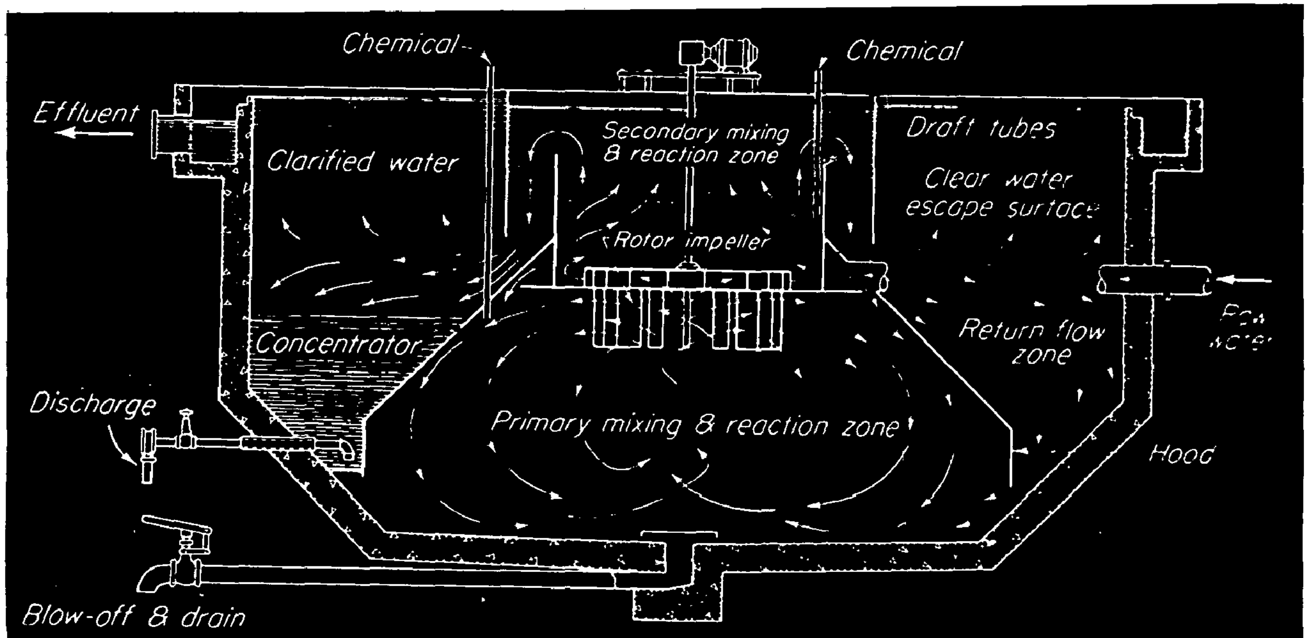
These units are also known as upward flow units. They were originally used for the lime-soda process of softening clear waters. But now they are also used with success for coagulation and clarification as a primary treatment in rapid sand filter plants and treatment of process waters without filtration for industrial plants.

These upward flow units combine mixing, flocculation and clarification in the same structure. In general, their operation is as follows :-

(a) The raw water enters a central chamber which also receives the chemicals. In this chamber there is a provision for agitation and circulation of chemicals and water as shown in Fig. No. 18 (51), and mixing and reaction zones are formed.

(b) Water, precipitated chemicals, floc and turbidity pass to a clarification chamber. In most types, the effluent passes upward through a blanket of suspended floc, called 'sludge blanket', before leaving the tank. There may be provision for some of the floc to recirculate back into the mixing chamber.

(c) There is a sludge hopper or concentrator from which the sludge is discharged continuously or intermittently as required.



An Accelerator, combining chemical mixing, reaction, floc concentration, and clarification. (*Courtesy of Infilco.*)

<u>Fig. No. 18.</u>

An Accelerator combining Chemical Mixing, Reaction Floc Concentration, and Clarification.

In these plants, chemicals are introduced, not into the raw water, but into the water which already has some previously formed precipitates. Precipitation of the newly arrived chemicals will take place on the old particles, which act as neuclei, thus resulting in larger and quicker floc. The raw water is introduced into this larger amount of water containing previous floc and it is slowly agitated. The result is that the reactions between turbidity and floc are quickly accomplished. After this, the water with floc goes to the clarifying portion of the tank. As the water rises, vertical velocity decreases and suspended material falls. The rising water passes through a suspended filter and clarification is thus aided.

Treatment rates vary from 1.5 to 2.25 gal. per sq. ft. per minute, at the sludge blanket level; detention periods from 1 to 2 hours. Since these units should not be overloaded, it is necessary to provide multiple units. Records from many industrial plants and cities indicate that, in general, they are satisfactory (55). They require careful and skilled operations.

In selecting a particular device for a particular treatment plant, ~~so~~ many factors are involved, which are already discussed. The coagulation is a complicated phenomenon, comprising not only physical but also chemical flocculation. So firstly, considering the required final result the optimum conditions should be obtained for chemical flocculation to take place first and then for the physical flocculation. While in the design of flocculator the main problem is the availability of funds for whole treatment plant - definitely a now and then meeting question in India - comprising not only the initial cost but also the maintenance of the device. For example, the baffled type basins have the least maintenance as compared with other devices. While mechanical devices are most efficient and permit a good control over the process to meet with the flexibility of incoming water. Thus they form better floc; results reduction in the coagulant demand, also in capacity of flocculator, and relatively less head or power loss. But they require the external driving power and skilled maintenance, even though the initial cost of installation may be less. So only detailed study of the environmental conditions prevailing at the time of design with the expected result, controls the selection and the design of the flocculation basins.

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CHAPTER VI

SUMMARY AND CONCLUSIONS

Visible material in suspensions imparts the turbidity to the water. This turbidity may result from living or dead algae or other organisms, but it is generally caused by silt and clay. The amount and character of turbidity will depend upon the type of soil over which the water has run and the velocity of the water. When this turbid water is given quiet conditions, the heavier and larger particles settle quickly, while the lighter and more finely divided particles settle slowly. Very finely divided clay may require months for settlement. It is necessary, therefore, to devise means to coagulate the very small particles into larger ones with higher settling values. These particles may be as big as 5 μ in diameter but it is the less than 1 μ diameter colloidal particles that are most stable and of controlling importance in coagulation. Such colloids derive their stability from electrical double layer surrounding each particle (Na^+,K^+,Ca^{++},Mg^{++} or H^+) that diffuse into the surrounding water medium. Other cations present in the dispersion medium may enter into ion exchange mass action. The addition of polyvalent cations to the system will repress the double layer and thus lower the stability of the particle until a point will reach at which the particles begin to coalescence very slowly to form aggregates. Destabilization to a greater degree will increase the rate of coalescence until finally a visible reduction in turbidity will be possible with <u>short</u> settling periods. The rate of coalescence will be greater for particles having initially adsorbed cations like Na^+ or K^+ rather than Ca^{++}, Mg^{++} or H^+.

A more important factor affecting the rate of agglomeration is the total exchange capacity of the turbidity particles, i.e., the total concentration of adsorbed or exchangeable cations. Most natural waters contain less than critical concentrations of exchange capacity and for these waters aggregates formed after destabilization are too small to settle in a reasonable time. To effect rapid clarification it is necessary that a suitable agglomerating agent or binder material be present which will bind the small aggregates into a large rapidly settling flocs. In practice, a properly adjusted dosage of a single hydrolysing coagulant, such as aluminium or ferric salts, will effect both actions. Say, in alum flocculation portion of the Al^{+++} ions are effective in destabilizing the turbidity particles and the remainder of the ions, through hydrolysis, forms insoluble hydrous oxide binder material. The hydrous oxide required will depend upon the concentration and particle size distribution of the turbidity.

Thus optimum coagulation involves a complex equilibrium of many variables. This necessitates the careful study of initial properties of waters such as turbidity, particle size distribution, exchange capacity, pH and alkalinity and also the proper selection of the coagulant. Alkalinities in excess of optimum results in the waste of equivalent amount of the coagulant, while alkalinities less than optimum will not give sufficient binder material. Also for optimum flocculation, water must contain a suitable number of colloidal particles of size less than 1 μ and also of size in between 1 μ to about 5 μ. If the water is initially deficient in colloids, coagulation can be improved by the addition of bentonite or other clay colloids of high exchange capacity, activated silica or other negatively charged material. Addition of colloidal clay, like bentonite may also be helpful in providing buffer capacity to a water, if initially low in bicarbonate alkalinity. These substances, the pre-addition of which, aids the coagulation are called 'coagulant aids'. They adjust pH alkalinity, particle size distribution, buffer capacity in their optimum range, thus reducing coagulant dosages and also improving the efficiency of the process.

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The sulphates of aluminium and sulphates and chlorides of iron are normally employed as coagulants because they are the cheapest available chemical coagulants. The following points give in nut shell the practical aspect of the properties of colloids, the dosage and the behaviour of common coagulants :

(i) pH range of relative insolubility is 5 to 8 for alum, above 4 for ferric iron, and above 8.5 for ferrous iron.

(ii) With copperas, best precipitates obtained at and above pH 9.5, thus it is useful coagulant in the highly alkaline waters. Otherwise lime must be added to raise the pH. The combined use of copperas and lime is known as the 'iron and lime process'. The hydrous ferrous oxide is oxidised to ferric state in the presence of dissolved oxygen. Oxidation may be effected by adding solution of chlorine to dissolved copperas. This renders the oxide less soluble at low pH values, being in ferric state and extend the range of usefulness of copperas down to a pH value of about 8.5. Aeration of the water prior to liming will make oxygen available and blow out lime consuming CO_2. The use of large amounts of lime renders the process uneconomical unless treatment includes lime softening. Also at high pH values natural coloured colloids are stabilized and $CaCO_3$ may be precipitated in further units. So far waters with high alkalinity, where there is a danger of fixation, it should not be used; and proper dose of lime should be given for checking after precipitation.

(iii) The presence or addition of negative ions extends the useful range of pH in acid region. Bivalent SO_4^{--} ions are more effective than monovalent Cl^-. Conversely the presence or addition of positive ions extends the useful pH zone in the basic region, bivalent Ca^{++} ions being more effective than monovalent Na^+ ions.

(iv) In soft waters negatively charged coloured colloids are coagulated most effectively at pH values of 4 or less.

(v) Colour removal is sometimes improved by prechlorination of alum - treated waters. This may be due to oxidation of ferrous ions, which impart the colour. Iron in organic combination in highly coloured water are also effectively oxidised and precipitated by potassium permanganate at a pH of 8.8 to 9.8.

(vi) Iron and manganese naturally present in water can be utilised as a coagulant and to speed their own removal (56).

The chemical flocculation is so to say, almost instantaneous, after the chemicals are properly mixed. The initial increase in the size of the colloidal particles is brought about by true diffusion or Brownion motion, until the size of the particles becomes too great to be influenced by Brownion motion. At this stage the particles are too small to be seen by naked eye. So the completion of coagulation process requires external turbulent mixing of the suspensions. Stirring increases the opportunity of contact and decreases the time for floc formation. It also promotes the floc growth. The main criterian in designing flocculation basins is to select the suitable mean velocity gradient for required floc size.

Coagulation is a very complicated process and sensible to a little change in the influent. Thus this process requires strict chemical and mechanical control for required efficiency for the expected result; and it necessitates the services of skilled workers and technical personnel. Moreover, it requires cheap availability of power also.

It goes without saying that the availability of funds for the installation and the maintenance costs, is the prominent figure, after all, in the designing of the plant. Water supply and also sanitation of most of the places in India are under the control of either private or semi-government bodies. The skilled personnel are not so easily available due to the lack of funds. Except some of the big cities, at present, most of the towns in India cannot afford costly and elaborate treatment plants. In such unavoidable circumstances, one is forced to adopt easy and smooth working plant with the sacrifice in the efficiency. In water treatment, there is a great field for investigation for clarification of water, suiting to its initial properties and the existing conditions. A Research Centre is established at Chandrawal Water Works at Delhi, under the auspices of the Central Public Health Research Institute. Now-a-days 'efficient coagulation and sedimentation tanks' is the subject for investigation. The different materials, available cheaply and locally, will also be under test investigations, in near future, for their suitability as coagulants.

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Accepted for the award of M.E. (P.H.)

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