Flocculation : A New Way to Treat the Waste Water

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ABSTRACT

Pure water is an essential requirement for the survival of human beings. To meet the requirements of potable, industrial and agricultural water, the immediate need is to treat waste water, particularly the sewage sludges and slimes from the municipal and industrial effluents respectively. These effluents are highly undesirable and unsafe. The removal of contaminants from waste water is a must before they can be reused. The removal of contaminants from these effluents involves the process of flocculation and coagulation. The purpose of the present article is to clarify and explain the processes in details along with the materials involved in the processes. This will be essential for the present day life.

1.   Coagulation and Flocculation

Colloidal particles in nature normally carry charges on their surface, which lead to the stabilisation of the suspension. By addition of some chemicals, the surface property of such colloidal particles can be changed or dissolved material can be precipitated so as to facilitate the separation of solids by gravity or filtration. Conversion of stable state dispersion to the unstable state is termed destabilisation and the processes of destabilisation are coagulation and flocculation[1,2]. Often the terms coagulation and flocculation are used synonymously inspite of existing a subtle difference between the two[1,3]. If destabilisation is induced through charge neutralisation by addition of inorganic chemicals, the process is called coagulation. On the other hand, the process of forming larger agglomerates of particles in suspension or of small agglomerates already formed as a result of coagulation through high molecular weight polymeric materials is called flocculation. No substantial change of surface charge is accomplished in flocculation. The agglomerates formed by coagulation are compact and loosely bound, whereas the flocs are of larger size, strongly bound and porous in case of flocculation. In mineral processing industries, the scope of application of flocculants is much greater than the coagulants. Coagulants find use in the processing of coal, taconite, soda ash,

sand and gravel and to some extent in the uranium industry. Flocculants are widely used in the processing of coal, bauxite, phosphate, potash sand, gravel, cement, soda ash, copper, silver, gold, beryllium, lead and zinc.

1.1. Stability of colloidal suspension

The attractive force between particles, known as Van der Waal force exit in case of colloidal particles in suspension. But the electrostatic repulsion of surface charges opposes the particles to come closer and form agglomerates. The principal mechanism controlling the stability of both hydrophobic and hydrophilic particles is the electrostatic repulsion[4]. Hydrophobic surfaces may acquire an excess of anions or cations at the interface producing an electrical barrier that can repulse particulates of similar surface potential. Hydrophillic particles acquire surface charge from dissociation of inorganic groups (carboxylic or other organic acid groups) located on the particle surface or interface. Besides electrical repulsion, a suspension may be stable due to the presence of adsorbed water molecules that provide a physical liquid barrier preventing particulates from making collisions and destabilisation. Particles may acquire surface charges due to unequal distribution of constituent ions on the particle surface, preferential adsorption of specific ions, ionisation of surface groups, crystal imperfection, or any combination of these.

1.2. Electrical double layer

Oppositely charged ions in an electrolytic solution are attracted to the surface of a charged particle and can either be closely associated with the surface or distributed some way into the solution[5]. Thus the two opposite forces, electrostatic attraction and ionic diffusion, produce a diffuse cloud of ions surrounding the particulate, which can extend up to 300 nm. This co-existence of original charged surface and the neutralizing excess of counter-ions over co-ions distributed in a diffused manner are known as the electrical double layer[6]. Fig.1 gives a schematic diagram[114] showing the nature of electrical forces around a colloidal particle in bulk solution and the various electrical potentials thus developed in the double layer. The double layer consists of two major regions, an inner layer (called Stern layer) where the initial layer of adsorbed ions and molecules are located at the particle surface; and the outer layer (called Gouy-Chapman layer) of oppositely charged counter-ions. The stability of colloidal suspension is greatly influenced by the potential of the Stern layer. Though this potential cannot be measured directly, it is approximated to the zeta potential representing the electrical potential between the shear plane and the bulk solution[7]. According to Deryagin and Landau[8], Verwey and Overbeek[9], if the kinetic energy of the particle is larger enough to surmount the potential hump created between them by way of double layer formation, the particles would coalesce otherwise they would remain as a stable suspension. This theory is popularly known as DLVO theory.

1.3.   Zeta potential

A charged particle dispersed in an ionic medium tends to have a concentration of opposite ions attracted towards it. For example, a negatively charged particle collects a number of positive counter-ions. As one move further away from the particle, concentration of counter-ions decreases due to diffusion until ionic equilibrium is reached. A plot of the charge contributed by these ions versus distance from the particle surface (Fig.1) reveals the familiar exponential decay. Now, if the particles were imagined to be moving, it would tend to drag its counter-ions along with it while leaving behind the ions that are further away from its surface. This would set up a plane of shear – the potential difference at which is called the zeta potential (ζ).

1.3.1. Principle of measuring zeta potential

Zeta potential is measured[10] using the technique of micro-electrophoresis, which was invented by Ware and Flygare and independently by Uzgiris in the early 1970s. However, as per Friend and Kitchener[11], zeta potential was calculated using Smouluchowski equation as early as 1903. The sample to be measured is dispersed in suitable liquid phase and placed in the path of a beam of laser light. A pair of electrodes is introduced into the sample. Charged particles in the sample will move under the influence of an electric field applied across the electrodes. The direction of the motion indicates the sign of the charge on the particles: negatively charged particles will gravitate towards the positive electrode and vice versa. The velocity of particles, per unit electric field, can be measured and is called the electrophoretic mobility (u). Thus,

$$u = v / E \qquad (2.1)$$

Where v is the particle velocity and E is applied field strength. The equation used for converting the observed mobilities into effective electrokinetic potential depends upon the value of dimensionless quantity 'ka' in which 'a' is the radius of the particle (assumed spherical) and 'k' is the quantity given by[12].

$$k = \frac{4\pi e^2 \sum nZ^2}{\varepsilon KT} \qquad (2.2)$$

where, e = Electronic charge,
ε = Electrical permittivity of the solvent
K = Boltzman constant
T = Absolute temperature.

From the expression given, $k = 1 \times 10^6$ cm at 25°C in water ($\varepsilon/\varepsilon_o = 78$) containing 1 mM of 1:1 electrolyte. Values of 'k' at other concentration follow by simple proportion. If 'ka' > 200 it will be usually sufficiently accurate to use the Smoluchowski formula which in the original unrationalised form is $u = \varepsilon\zeta/4\pi\eta$, where ε is the permittivity of the suspending medium and η is the viscosity.

Typical units would be to have u in micron per second under one volt per cm, in which case for water at 25°C, zeta potential in mV would be given by

$$\zeta = 12.83\,u \tag{2.3}$$

1.3.2.   Significance of the measured zeta potential

The zeta potential is best seen as the potential at the surface of the 'electrokinetic unit' moving through the solution. This will not be the mean 'wall potential', often called W_o, but can be taken as the mean potential at the 'outer Stern plate' (OSP). The OSP is seen as removed from the surface by one hydrated radius of the principal counter-ions (0.2 to 0.5 nm). The electrokinetic entity may well include ions specifically adsorbed from the solutions and this will be reflected in the value of zeta potential. Certainly the double layer on the solution side of zeta potential will be purely diffused so that zeta potential is the relevant potential for all the effects that depend on diffuse layer effects (e.g., inter plate repulsion). Calculation of particle charge from zeta potential is also possible[12].

1.3.3.   Zeta potential and suspension stability

Knowledge of zeta potential can be used to predict and control the stability of colloidal suspensions or emulsions. Greater the zeta potential, more likely the suspension is to remain in stable form.

Zeta potential is very much dependent on the pH of the suspension. A plot of zeta potential vs pH is called an iso-electric curve. The pH for which zeta potential is zero, is called the 'iso-electric point' or 'point of zero charge' (PZC).

It has been already pointed out that if the particle surface charge is strong, it results in significant mutual repulsion prohibiting the particles to come closer. If the charge on these particles is reduced to zero, these repulsion forces are eliminated. Gentle mechanical agitation will then create numerous particle collisions instead of 'near misses'. The forces of adhesion, cohesion, and mechanical interlocking by 'polymer bridging' will result in agglomeration[13].

Turbidity (representing suspended particulate matters) consists of two distinct fractions: a coarse fraction (1 mm to 1 μm) and a colloid fraction (1 μm to 10°A). The coarse fraction may be successfully removed by conventional coagulation/flocculation treatment, but the colloid fraction cannot. As the floc forms during coagulation/flocculation is also of the same charge as that of the particles before treatment, a mutual repulsion exists between the floc particles and the colloids, and these repelling forces prevent the colloid from making permanent contact with the floc, regardless of agitation. Such colloids can effectively be removed by lowering the zeta potential of both the floc and colloid to a value of approximately zero plus or minus 5 mV[12]. This can be done by simultaneously employing the proper dosage of an inorganic coagulant coupled with an appropriate organic polyelectrolyte. The water treatment plant at Waterford, New York, is believed to be the first to demonstrate purification of water based on the principle of continuously controlled zeta potential.

1.4.   Flocculation mchanism

As discussed earlier, the charge structure surrounding the particles is called the electrical double layer, which, for convenience is divided into Stern, and Gouy-Chapman layers. The former is the initial layer of adsorbed ions and molecules located at the particle surface. The charge presented to the solution at the Stern layer naturally attracts a diffuse layer of free ions with a net different opposite charge, i.e., the Gouy-Chapman layer. For particles to make contact and aggregate, the potential at the stern layer must be overcome. Unfortunately, this potential, which is of interest in determining particle stability, cannot be measured experimentally. In order to cause the particles of a stable dispersion to flocculate, it is necessary to provide enough kinetic energy to particles to overcome the potential energy barrier. Alternatively, the barrier can be eliminated by surface-charge neutralization. This may be accomplished either by double layer compression (charge neutralization mechanism) or adsorption of flocculant onto the particle surface (bridging mechanism).

1.4.1.   Charge neutralization mechanism

Charge neutralization[14,15] by double layer compression is accomplished when flocculation is effective through an increase in solution ionic strength. The expression for the Debye-Huckel length, as derived from the Gouy-Chapman model of the electric double layer, is given as

$$K \; = \; (4 \times 10^{-3}e^2NI/\varepsilon kT)^{1/2} \qquad\qquad (2.4)$$

where, e = electronic charge

      N = Avogadro's number

      I = Ionic strength

      ε = Electrical permittivity of the solvent

      k = Boltzman constant, and

      T = Absolute temperature.

Since the double layer thickness is approximated by 1/K, increase in ionic strength (I) decreases the thickness of the double layer. This compression allows the approach of the colloidal particles to where short-range attractive forces predominate over electrostatic repulsive forces. In the presence of hydrolyzable metal ions such as Al^{3+} and Fe^{3+} or polyelectrolytes of opposite charge to colloid surface (see electrostatic patch mechanism), the charge is neutralised by adsorption of these species onto the particle surface. An important case of this is the flocculation of negative colloidal particles with cationic polymers. In fact, in many cases, the action of cationic polymers can be explained in terms of their strong adsorption on negatively charged particles and consequent reduction of double layer repulsion, allowing aggregation to occur. It may be noted that the most effective cationic flocculants are often

those of high charge density, with molecular weight playing only a minor role. That charge neutralization in fact occurs is reported by comparison of zeta-potential measurements with flocculation results, when it is found that optimum flocculation occurs at the point of total charge neutralization. For flocculation to proceed with pure charge-neutralization mechanism, it is neutral to expect that zeta-potential will be zero at the point of optimum flocculation. But in practice, the zeta potential tends to become negative at optimum flocculation with an increase in molcular weight of the polyelectrolyte. This is because increasing molecular weight of flocculant favours bridging relative to charge neutralization mechanism. Thus in any system where flocculation is affected by the addition of electrolyte or oppositely charged polyelectrolyte, it is likely that some degree of charge neutralisation occurs, the extent depending upon the system characteristics.

1.4.2.   Bridging mechanism

Long chain polymers[14,15] when added in small dosage to a suspension of colloidal particles, adsorb onto them in such a manner that an individual chain can become attached to two or more particles thus "bridging"[14] them together (Fig.2.a). But interestingly this phenomenon is observed up to a particular optimum polymer dosage beyond which flocculation diminishes, a process being known as steric stabilization (2b). The essential requirements for polymer bridging are that there should be sufficient unoccupied particle surface for attachment of polymer segments from chains attached to other particles and that the polymer bridges should be of such an extent that they span the distance over which interparticle repulsion prevails. Thus, at lower dosages, there is insufficient polymer to form adequate bridging links between particles. With excess polymer, there is no longer enough bare particle surface available for attachment of segments and the particles become destabilized, which may involve some steric repulsion. On average, bridging flocculation gives aggregates (flocs) which are much stronger than those produced by addition of salts (i.e., by reduction in electrical repulsion). However, such stronger flocs produced by the bridging mechanism may not reform once broken at high shear rates.

1.4.3.   Electrostatic patch mechanism

Although the bridging mechanism serves well to interpret the effects of nonionic and anionic polymers on the flocculation of colloidal particles, agreement with experiment is poor with respect to action of high-charge cationics on negatively charged colloidal particles particularly for molecules of low molecular weight in dilute suspensions. Of particular importance in determining the flocculation mechanism, is the equilibrium configuration[15] of the adsorbed polymer. It has been observed that for systems with a flocculant of high cationic[16] charge in anionic colloidal suspensions, the high interaction energy favours a flattened adsorbed configuration (Fig.3) that significantly reduces the formation of loops and trains, which can bridge the suspended particles. In such cases, each charged site on the particle surface cannot be neutralized individually by an oppositely charged polymer segment simply for

geometric reasons. Polymer chains then adsorb to give "islands" or "patches" of charge, surrounded by areas of opposite charge. Particles with polyelectrolytes adsorbed in this "patchwise" manner can interact in such a way that oppositely-charged areas of different particles come in contact giving rise to strong attraction[17,18]. Mabire[19] et al. give a semiquantitative interpretation of the role of molecular weight and cationicity through a patchwork model while studying the flocculation properties of some water soluble cationic copolymers toward silica suspension. However, Wang and Audebert[20] showed that the flocculation of a particle with strongly negative zeta potential such as silica, by cationic polyelectrolytes obeys mainly electrostatic mechanism for a cationicity > 0.15. On the contrary for low cationicity (< 0.15) the major effect is the interparticle bridging.

It may be noted that, the electrostatic patch mechanism should predominate in systems characterized by high cationic charge on the flocculant and anionic colloidal solids, especially at low particle concentration. However, bridging may occur in such systems if the particle concentration is high enough for collisions to take place on a time scale similar to that required for the polymer to attain a flattened configuration. The controlling mechanism of flocculation is then governed by the system and the flocculant.

1.5.   Flocculating materials

The vast categories of materials used as flocculating agents can be classified broadly into two categories inorganic and polymeric. (some of the inorganic materials exist in the polymeric form, e.g., poly (aluminium chloride), are not included in this classification). The polymeric materials are further classified into natural and synthetic. The synthetic materials may be cationic, anionic or nonionic. A new class of polymeric flocculants i.e., the graft copolymers have been developed which are synthesized from natural and synthetic polymers.

1.5.1.   Inorganic flocculants

Various chemicals[21,22] are used in coagulation depending on the characteristics of the water being used. In some waters, a combination of two or more chemicals produces better results than a single chemical. It is usually necessary to perform coagulation tests in the laboratory to decide which chemical or combination should be used. The inorganic flocculants are mostly based upon the hydrolyzable salts of iron and aluminium.

1.5.1.1. Aluminium compounds

Principal aluminium compounds that are commercially available for suspended solids removal are dry and liquid alum. Commercial dry alum most often used in wastewater treatment is known as filler alum and has the approximate formula $Al_2(SO_4)_3$, $14H_2O$ and a molecular weight of about 600. Activated alum contains about 9% sodium silicate, which improves the coagulation in some waters. Black alum is the alum containing activated carbon. Another aluminium compound in use is sodium aluminate. It is much more alkaline compound than alum. When added alkalinity is found to be necessary for the efficient coagulation, sodium aluminate may be substituted for all or part of the needed alum dose.

1.5.1.2. Iron compounds

Iron compounds possess pH coagulation ranges and floc characteristics similar to aluminium sulfate. The cost of iron compounds may often be less than that of alum. However, the iron compounds are generally corrosive and often present difficulties in dissolving, and their use may result in high soluble iron concentration in process effluents. The iron salts most commonly used as coagulants include ferric sulfate, ferric chloride and ferrous sulfate. These compounds often produce good coagulation when conditions are too acidic for best results with alum. Sometimes the particles are best removed under acidic conditions and iron compounds give better results.

1.5.2.   Polymeric flocculants

Polymeric materials used as flocculants/retention aids are mostly water-soluble linear polymers[23-27] of very high molecular weight. The cationic and anionic counterparts of these polymers are known as polyelectrolytes with many characteristic features of their own. Some of the nonionic water-soluble polymers at times bear some ionic groups as a result of inadvertent hydrolysis.

1.5.2.1. Cationic polymers

Water-soluble cationic polymers are a class of polyelectrolytes that derive their unique properties from the density and distribution of positive charges along the macromolecular backbone. Chain conformation and solubility of such flocculants depend on the extent of ionization and interaction with water. Cationic functional groups can strongly interact with suspended, negatively charged particles or oil droplets and hence are useful in many applications, including waste treatment and paper making process. Water-soluble polymers containing cationic charge can be divided into three categories: ammonium (including amines), sulfonium and phosphonium quaternaries.

Polyacrylamide-Based Cationics

Many types of cationic monomers can be home- or copolymerized with acrylamide to yield water soluble polymers with varying positive charge (1-100%). Some of the more widely used cationic monomers and their structure have been summarized in Fig.4 Cationic monomers are, in general, more expensive than acrylamide or anionic acrylic monomers.

Random copolymers of acrylamide and acryloyloxyethyltrimethyl ammonium chloride, formed by quaternization of dimethylaminoethyl acrylate with methyl chloride are exclusively used in water industry. The methacrylate analogue with variation of cationic content is also commercially available. The quaternized aminoacrylate copolymer having charge density (CD) of 30 mol% has been used for clay flocculation studies. In copolymers with acrylamide, hydrolysis of the ester groups has been investigated and found to be CD and pH dependent with hydrolysis increasing under more alkaline conditions.

$$\text{Pol-COOCH}_2\text{CH}_2\text{N}^+\text{Me}_3 \quad \rightarrow \quad \text{Pol-COO}^- \quad + \quad \text{HO CH}_2\text{CH}_2\text{N}^+\text{Me}_3$$

Cationic polyacrylamides can be prepared by post polymerization functionalization of polyacrylamide. In a Mannich-type reaction, polyacrylamide reacts with formaldehyde to form N-methylol groups, which can be treated with a dialkyl amine such as dimethyl amine to yield pendent amine groups[28]. The synthesis of a model cationic polymer based on the Mannich reaction of polyacrylamine[29] has been described. The amine groups can be quaternized subsequently. Another approach to introduce amino groups into polyacrylamide is by reaction with polyamines or by sodium hypochlorite degradation (Hoffmann reaction)[30].

Research continues on the synthesis and characterization of homo- and copolymers of quaternary ammonium monomers with acrylamide. Synthesis and characterization of homo- and copolymers of 2-acrylamido-2-methylpropanedimethyl ammonium chloride (AMPDAC) with acrylamide have been reported [31]. This monomer is the cationic analogue of the anionic monomer sodium 2-acrylamide-2-methylpropanesulfonate (NAMPS). Redox polymerization of a quaternary ammonium acrylic comonomer with acrylamide has also been reported[32]

One of the cationic systems that has been the subject of some basic research[33,34] is the poly (diallyldimethylammonium chloride) and its copolymer with acrylamide. The monomer has been referred to as DADMAC or DADAAC in the literature. Polymerization of a 50-70% aq. Solution of DADMAC, initiated with peroxide catalyst produces a linear water-soluble polymer known as poly (DADMAC). This first cyclopolymer is of low to medium molecular weight and in its chloride form has been used in many applications such as paper making process, water treatment etc. Butler and Angelo[33] have established that the free radical polymerization of DADMAC is intra-molecular and involves a cyclization mechanism to produce a five membered ring. The advantages of this polymer are that it is highly cationic, pH-insensitive, chlorine resistant and as such it is a major representative of cationic flocculants. The solution properties of poly (DADMAC) in water and salt and interaction with solids, such as silica, suggest the potentially of these polymers as coagulants and flocculants. High-molecular weight copolymers of poly (DADMAC) with acrylamide[35,36] have been synthesised which have found applications in sludge conditioning. Butler and Lin[37] have synthesised graft copolymers of acrylamide onto poly (DADMAC) by first making a copolymer of DADMAC with 1-10% of acrylic acid and esterfying it with 3-chloro-1, 2-propane diol to introduce the cis-diol groups. These cis-diol groups serve as grafting sites in presence of ceric ions. A later approach[38] via a copolymer with 3,4-dihydroxy cyclohexylmethyl acrylate acrylate gives higher molecular weight material and less homopolymer. Alternating copolymers of low to medium molecular weight have been prepared from DADMAC and sulfur dioxide and have been tested for clay flocculation[39]. Yulin et al[40] have studied the temperature-sensitive flocculation characteristics of a copolymer of poly (N-isopropyl acrylamide) and poly (DADMAC) with colloidal TiO$_2$.

Polyamines, Polyimines and Polyvinylpyridines

Four types of cationic monomers are involved in this class:

- Polyamines that are condensation products of amines and halogenated compounds.
- Polyamidoamines that result from the formation of a polyamide followed by reaction with a halogenated compound (e.g. epichlorohydrin).
- Polyethylene imines made by ring-opening polymerization of aziridine and
- Polyvinylpyridinium systems.

Polyamines

Polyamines are the step-growth polymerization products of polyfunctional amines and alkyl halides or bifunctional alkyl epoxides and alkyl epoxide derivatives. They are relatively of low molecular weight ($< 10^5$) but have high level of cationicity. Typically in the first case, a poly (ethyl amine) is produced by the reaction of ammonia or low molecular weight alkyl polyamine with ethylene chloride in the presence of aqueous base. This is sometimes followed by reaction with epichlorohydrin. Reaction variables need to be controlled carefully to meet the molecular weight requirements.

A second family of polyamines is usually prepared from epichlorohydrin and ammonia or monomethylamine or both under basic conditions. The reaction involves a series of nucleophilic ring-opening additions and condensations. Depending on reaction conditions, these polyamines tend to be branched, particularly the high molecular weight products.

Polyamidoamines

These are produced by reaction of adipic acid with diethylene triamine, yielding a polyamide with secondary amine groups that react further with epichlorohydrin. The pendent epoxide group may react with the secondary amine group of another polymer chain resulting in cross linking. This must be controlled to render the polymer water-soluble.

Poly (Ethylene Imine) (PEI)

This is a special poly (ethyl amine) produced commercially from ethylene amine (azidine) in an aqueous medium by ring-opening polymerization using CO_2, a mineral acid or ethylene dichloride as initiator. This product (PEI or polyaziridine) is highly branched, with primary, secondary and tertiary amine groups. PEI has been used in a number of model investigations of flocculation[41].

Poly (2-Vinyl Pyridine) and Poly (4-Vinyl Pyridine)

These can be prepared by conventional free radical techniques. The polymers are quaternized with alkyl derivatives to form strong polyelectrolytes in solution. Cardoso et al[42] have studied the flocculation characteristics with bentonite clay suspension of a N-oxide type zwitterionic polymeric flocculant derived from isomers of poly (vinyl pyridine) and poly

(N, N-dimethylaminoethylmethacrylate) by oxidation. The resulting polymers have high water solubility, chemical stability and ability of chain expansion with increased ionic strength, a property highly desirable in the process of flocculation by polymers. In a related communication, Asanov et al.[43] have studied the flocculation characteristics of an aqueous suspension of bentonite with a water-soluble polyelectrolyte based on 2-methyl-5-vinyl pyridine, methacrylic acid and its amides to show that the presence of functional groups like amines and amides strengthen the flocculation attributes.

1.5.2.2. Anionic polymers

In anionic flocculants, 1-100% of the monomer units contribute to the charge. Molecular weights tend to be in the high or very high range. Although several types of anionic sites in a polymer are possible, the major type in commercial flocculants is the polymers having carboxylate ions.

Polymers Containing Carboxyl Groups

High molecular weight carboxylic acid polymers based on polyacrylamide are extensively employed as flocculating agents in the water and various process industries, where a low charge density is the general rule. One exception is the separation of red mud from alumina where a high charge density polymer performs better. Homopoly (acrylic acid), poly (acrylic acid-co-acrylamide) and hydrolyzed polyacrylamide dominate the anionic flocculant market. Hydrolyzed polyacrylonitrile has been found to be playing a lesser role.

Poly (Acrylic Acid) and Its Salts

Anionic poly (acrylic acid) (PAA) can be synthesized in two ways direct polymerization or hydrolysis. In the direct method, salts of acrylic acid are homopolymerized or copolymerized by free-radical initiation in aqueous media. Usually the rate of polymerization of the ionic monomer is slower than the corresponding nonionic monomer, presumably owing to charge repulsion between the growing chain and the incoming ionic monomer. Direct polymerization of acrylic acid salt solutions has some advantages because the non-volatility of acrylic acid salts allows simultaneous polymerization and spray drying to produce high molecular weight polymers directly.

Hydrolysis (saponification) is the alternative method for producing anionic poly (acrylic acid). Copolymers with variation in the percent of amide and carboxylic acid groups can be prepared either by copolymerisation of acrylamide and acrylic acid or its salts, or by polymerization of acrylamide followed by partial hydrolysis. The former route gives random copolymer, whereas some clustering can occur in the alkaline hydrolysis approach. Polyacrylamide is hydrolyzed readily with alkali (usually sodium hydroxide or sodium carbonate) in an aqueous medium. The hydrolysis is relatively rapid upto about 50% conversion of amide groups and then shows down considerably, probably due to neighbouring group effects. High molecular weight anionic flocculants with 2-50% of the amide groups hydrolyzed

by stoichiometric amounts of alkali are prepared conveniently in this way. Addition copolymerisation of acrylic acid with acrylamide covers the entire range of anionicity. The rate of copolymerisation is pH dependent and the reactivity ratio for acrylic acid copolymerisation with acrylamide decreases with increasing pH. Use of anionic polyacrylamide in flocculation has also been reported[44].

Although the carboxyl grouping is a relatively strong acid, the extent of ionization is a function of pH in acidic substrates. Both the inherent acidity of the carboxyl group and the effect of neighbouring carboxyl groups in the same molecule (electrostatic and statistical) influence ionization. Electrostatic effects are moderated by ionic strength of the medium and all these factors influence the conformation of the molecules in solution, which in turn affects the polymer properties.

Polymers Containing Sulfonic Acid Groups

The sulfonic group is an inherently stronger acid than the carboxyl. Polymers with sulfonic acid moieties, therefore, retain their anionic charge in media with low pH. The major representatives of polymers containing sulfonic acid are poly (vinyl sulfonic acid) (PVSA) and poly (styrene sulfonic acid) (PSSA).

Poly (Vinyl Sulfonic Acid) (PVSA)

It is the simplest example of this family of fully ionized strong electrolyte polymers. It is prepared by polymerization of ethylene sulfonic acid or its sodium salts under free radical conditions and purified by precipitating aqueous solutions of the sodium salt form with methanol or dioxane. The ion binding selectivity of the polymer with alkali metals has been observed in viscosity and phase separation studies. The homopolymers and its copolymers with methacrylic acid are reported to be useful in deposit control as are the copolymers of allylsulfonic acid and fumaric acid.

Poly (Styrenic Sulfonic Acid) (PSSA)

Poly (styrenic sulfonic acid) may be prepared by free-radical polymerization of the monomer in solution using the acid, sodium salt or potassium salt form. PSSA may also be prepared by sulfonation of polystyrene or by hydrolysis of poly (n-propyl p-vinyl benzenesulfonate). The sulfonation route requires a careful choice of the sulfonating conditions necessary to minimize crosslinking and the formation of insoluble gels. The best reagent appears to be a sulfur trioxide-trialkyl phosphate complex, with the para-isomer as the major product. Very high products of PSSA have been investigated as flocculants for the so-called red muds in the Bayer process for bauxite to demonstrate the effect of molecular weight on that substrate[45].

Several acrylate or acrylamide polymers containing sulfonate groups are commercially relevant as high molecular weight flocculants or low molecular deposit control agents[46]. These include homopolymers of sodium 2-methacryloyloxyethyl sulfonate (SEM)[47] and sodium 2-acrylamido 2-methyl propyl sulfonate (AMPS)[46] (Fig.5). Of these monomers,

2-sulfoethyl methacrylate is of limited commercial value owing to the hydrolytic instability of the ester linkage. The same factor has been a major drawback with 3-sulfo-2-hydroxylpropyl methacrylate (SHPM).

However, 2-Acrylamide-2-methyl propyl sulfonic acid (AMPS) prepared by the reaction of SO_3 with isobutylene followed by Ritter reaction with acrylonitrile[48,49] is hydrolytically quite stable. AMPS is highly reactive in both homo- and copolymerisation and can be incorporated by homogeneous, solution or emulsion polymerization technique. Its applications include improving emulsion stability, flocculation, improving dry strength of paper, sludge disposal in boil-water treatment etc. Qin et al.[50] have copolymerized sodium allyl sulfonate onto acrylamide in an aqueous solution using ammonium persulfate as initiator and studied their flocculation behaviour in kaolin suspension in presence of calcium ion.

1.5.2.3. Nonionic polymers

For the purpose of classifying as flocculants, a polymer is considered nonionic if less than 1% of the monomer units are charged. In aqueous systems such polymers function as flocculants primarily by the bridging mechanism. Hence, they must be of high or very high molecular weight for practical applications. Polyacrylamide is the most prominent member of this class followed by poly (ethylene oxide).

Polyacrylamide

Acrylamide monomer is polymerized by free radical initiators, e.g. azo compounds, redox catalysts, light and radiation. This monomer is unique among vinyl and acrylic monomers because it can be polymerized to ultra-high molecular weight (10^6-10^7). This extraordinary feature of acrylamide polymerization is attributed, in part, to the ease of purification of acrylamide monomer and to the unusually high ratio of its propagation to termination rate constants (K_p/K_t). In fact acrylamide has the highest K_p/K_t of any free radically polymerizable monomer. Polyacrylamide can be prepared via solution inverse emulsion, inverse microemulsion or precipitation techniques. Low temperature initiation, high monomer concentration and a small amount of added 2-mercapdtobenzimidazole, radical scavenger, are reported to be the optimal reaction conditions for preparing high molecular weight, soluble polymers. In case of polymers and copolymers made from acrylamide, some 1-3% of anionic groups are introduced due to the inadvertent hydrolysis of the amide groups.

However, polyacrylamide with less than 1% hydrolysis can be prepared by careful attention, the monomer concentration, pH, temperature and initiator, preferably a redox type. The chemical and physical properties of the polymers often are dependent on synthesis variables. One feature that has been the subject of many basic investigations is the stability of dilute aqueous solutions on ageing.

Poly (Ethylene Oxide) (PEO)

PEO resins are commercially made by the catalytic polymerization of ethylene oxide in the presence of one of the several existing catalyst systems. They are available with average molecular weight from as low as 200 up to 5×10^6. The products with a molecular

weight below about 25,000 are viscous liquids or waxy solids, commonly referred to as poly (ethylene glycols). Those with a molecular weight range from about 1×10^5 to 5×10^6 are called poly (ethylene oxide) resins. They are dry, free flowing, white powders completely soluble in water at temperatures upto 98°C and completely soluble in certain organic solvents. Aqueous solutions of PEO display increasing pseudoplasticity with increasing molecular weight. High molecular weight polymers of ethylene oxide are susceptible to severe auto-oxidative degradation and loss of viscosity in aqueous solution. The mechanism involves the formation of hydroperoxides that decompose and cause cleavage of the polymer chain. The rate of degradation is increased by heat, UV light, strong acids, and certain transition metals, particularly Fe^{3+}, Cr^{3+} and Ni^{2+}. Ethyl, isopropyl or allyl alcohols, ethylene glycol or Mn^{2+} ions are known to be effective stabilizers of aqueous PEO solutions. The major commercial uses of poly (ethylene oxide) include adhesives, water soluble films, textile sizes, rheology control agents and thickners, water-retention aids, lubricants, hydrodynamic drag reducing agents, flocculants[51], dispersants and additives in medical and pharmaceutical products. The unique combination of properties of these polymers had led to developing applications in detergents, solids transport, control of sewer surcharges, dredging and metal-forming lubricants.

1.5.3. Natural polymers

Several naturally derived substances are used as flocculants, most of them being based on a polysaccharide skeleton. Some of them contain anionic groups like carboxyl.

Starch

Among natural flocculants the most widely used are starch and its derivatives. Starches isolated from different sources are all used to some degree as flocculants, but some work better with certain substrates than others. It has been reported that the amylose fraction of starch is superior to amylopectin or native starch in red mud flocculation. Dosage efficiency and dispersibility of starch flocculants are improved by introduction of cationic and anionic substituents. Jaernstroem et al;[52] have studied the effect of temperature and ionic strength on the flocculation of a kaolin suspension with cationically modified and converted starch and compared[53] its efficiency with that of poly (vinyl alcohol) and carboxymethyl cellulose. Weissenborn et al.[54,55] have investigated the mechanism of adsorption of wheat starch and its components (amylopectin and amylose) onto hematite ore. It was observed that wheat starch and amylopectin adsorbed onto hematite strongly which was proposed to be due to the formation of a surface complex between the carbonyl groups attached to C-2 and C-3' atoms of AGUs and surface iron atom hematite. A comparison of the selective flocculation performance with adsorption results established that flocculation occurs by the classical bridging mechanism. Application of starch as a selective flocculant has been reported[56].

Guar Gum

Guar gum, which structurally comprises of a straight chain of D-mannose with a D-galactose side chain on approximately every alternate mannose unit, has a molecular weight of the order of 220,000. As a result of its wide range properties, guar gum is the most extensively

used gum, both in food and industrial applications. It is nonionic and hence an effective flocculant over a wide range of pH and ionic strengths. Flocculation[57,58] studies of allophanic clay system with xanthan gum and several of its hydrolytic intermediates have been reported. In the mining industry guar gum is used as a flocculant or flotation agent, foam stabilizer, filtration and water treating agent. In the textile industry, it is used as a sizing agent and as a thickener for dyestuffs. The biggest consumer of guar gum is the paper industry where it facilitates wet-end processing and improves the properties of the product. However, one disadvantage of guar gum is its relatively rapid biological decomposition in aqueous solutions, which, of course, can be controlled by addition of chelating agents and grafting with polyacrylamide chains[59].

Chitin Derivatives and Chitosan

Chitin is water-insoluble high molecular weight polymer of 2-acetamido-2-deoxy-D-glucopyranosyl units linked through $\beta(1\rightarrow4)$ D-bonds. This may be converted to chitosan by partial or complete deacetylation. In the protonated form, this cationic polyelectrolyte is water soluble[60] with a number of potential commercial uses including flocculation, viscosification, drug delivery etc. Graft copolymers of chitosan[61] with acrylethyl triethylammonium bromide have been tested for flocculation studies in kaolin suspension with respect to sedimentation rate, residual turbidity etc. Hydroxyethyl chitin and other water-soluble derivatives are useful wet-end additives in paper-making and flocculants for anionic waste streams. Use of carboxymethyl chitin[62] in the treatment of printing and dyeing waste water has been reported. Salts of chitosan[63] based on maleic acid, acetic acid and HCl have been shown to be good flocculating agents.

Sodium Carboxymethyl Cellulose

This water soluble gum is produced from alkali cellulose (alkali salt of poly β-D-glucose) and monochloroacetic acid with degree of substitution in the range of 0.4-1.5. Unlike many flocculants derived from natural products, it is relatively resistant both to biological and hydrolytic degradation.

1.5.4. Graft copolymers

Graft copolymerization has been successfully used to alter significantly the soloution properties of many polymers like starch, cellulose, synthetic polysaccharides etc. by grafting suitable acrylic polymers onto them. The viscosity, gelling characteristics, solution rheology e.g. degree of pseudoplasticity, ion compatibility etc. can be drastically altered through graft copolymerization reaction. Enhanced functionality can also be imparted to substrates which will allow them to be more effective in flocculation, dispersion and other applications such as retention aids in paper, dry strength additives etc. Polyelectrolyte side chains can be introduced onto suitable substrates by either grafting an ion-containing monomer or a suitable monomer which can then be transformed to an electrolyte by a simple chemical reaction. An example of the latter is where methylmethacrylate or acrylonitrile can be grafted onto starch and then

transformed by alkaline hydrolysis to acrylic acid or methacrylic acid grafts. Vinyl pyridine or dimethyl aminoethyl methacrylate can be grafted and then subsequently quaternized.

Anionic/Nonionic Graft Copolymers

Most of the prior work on graft copolymerization has been with starch and cellulosics using either styrene, acrylonitrile-acrylamide or acrylic acid as the grafting monomer employing the ceric ion or radiation method. The alkaline hydrolysis of starch-g-polyacrylamide produces a mixture of carboxylic acid and carboxamide groups, but these are little effective in flocculation. Acrylic acid/methyl cellulose graft copolymers have been used as clay binders in foundry sands. Water soluble graft copolymers with exceptionally high molecular weight grafted side chains using acrylamide and acrylic acid have been prepared using ionizing radiation as the grafting mechanism. These materials are excellent flocculating agents.

Singh et al[64-68]. have reported the synthesis and applications of graft copolymers of polyacrylamide onto natural polymer like CMC[64], guar gum[67], xanthan gum[65], starch[64] and amylose[66]. The drag reducing properties as well as the shear stability of the graft copolymers were studied. It was found that grafting of polyacrylamide, which is highly prone to shear degradation onto polysaccharide backbones not only results in efficient drag reducing agents, but also makes the graft copolymers reasonably shear resistant[67]. Further, variation in the number and length of polyacrylamide chains were affected by varying the synthetic parameters. It was observed that in a series of graft copolymers with a particular polysaccharide, the one with fewer but longer[67] polyacrylamide chains performed the best.The study of the flocculation behaviour of the graft copolymers showed the same trend. Among the graft copolymers with various polysaccharides, starch-g-polyacrylamide was the best in performance[68]. In another study, Karmakar[68] studied the flocculation and rheological studies of starch-g-polyacrylamide and amylose-g-polyacrylamide. Starch-g-polyacrylamide was found to be the better in performance.When the performance of amylopectin-g-polyacrylamide was investigated by Rath and Singh it was found to performs better than any other graft copolymers and various commercial flocculants. This behaviour was explained by Singh model which is based on easy approachability of dangling polyacrylamide branches on rigid amylopectin to contaminants in the industrial effluents. Since in amylopectin-g-polyacrylamide the polyacrylamide branches are grafted on backbone as well as on amylopectin branches, this provides better approachability of grafted polyacrylamide branches to contaminants.

Cationic graft copolymers

Various quaternary ammonium monomers have been graft copolymerized onto starch in attempts to prepare improved flocculants and pigment retention aids useful in paper making. Of particular interest is the work of Fanta et al.[69] on the graft copolymerization of 2-hydroxy-3-methyacryloyloxypropyl trimethylammonium chloride onto starch and its evaluation as flocculating agents. Fanta et al[70]. also investigated the graft copolymers of starch with mixtures of acrylamide and the nitric acid salt of dimethylaminoethyl mehacrylate and

evaluated their flocculation performance. Jones and Jordan[71] investigated the graft and terpolymers of starch with 2-hydroxy-3-methacryloyloxypropyl trimethyl ammonium chloride and acrylamide for use as silica depressants in the flotation-beneficiation of silaceous ores. Hoover and Sinkovitz[72] developed some new cationic graft copolymers made by the graft copolymerization of diallyldimethylammonium chloride or 2-hydroxy-3-methacryloyloxypropyl trimethylammonium chloride and acrylamide onto dextran substrate and their use as additives for improving the dry strength of paper. Larsson and Wall[73] have synthesised cationic amylopectin using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (QUAB) as the monomer and studied its flocculation performance in colloidal silica suspension.

Because of the unlimited opportunity for structure variation and opportunities for providing multiple functionality, the technology of graft copolymerization is receiving significant attention by current researchers. Out of these efforts mny valuable commercial products are expected to materialize in the near future.

1.6 Polymers vs Inorganic Flocculants

Polymeric flocculants offer some distinct advantages over inorganic flocculants. The flocs are larger and stronger and are more rapidly formed. The salt concentration is not increased and much less sludge is generated. The dosage requirement is quite low (typically 1% on a dry weight basis) whereas that of inorganic flocculants may be as high as 20%. The inorganic flocculants frequently require pH adjustment, which is not necessary with polymeric flocculants. Futher, the polymeric flocculants are more convenient and easier to use. However, inorganic flocculants are inexpensive and often used for economic reasons.

1.7 Natural vs Synthetic Flocculants

A comparison of the natural and synthetic polymers may be as follows. Principal advantages of natural polymers are that they are non-toxic and readily available from renewable natural resources. Unfortunately, their efficiency is low, thus requiring a high dosage that varies with origin of natural polymers. The biggest advantage of natural polymers is their biodegradability. But this very advantage becomes a drawback in reducing its storage life and tells upon their efficiency as a result of molecular breakdown. The synthetic polymers on the other hand are highly efficient with product consistency and uniformity, and biological as well as chemical stability. These can be tailored in terms of functional groups, structure and molecular weight to suit to a particular application. However their disadvantages are that they are mostly non-biodegradable, highly expensive and may be toxic[74,75] (it may be noted that the synthetic polymers are not toxic but the associated monomers may be toxic).

1.8 Flocculation : The Test Methods

The principal purpose of a flocculation test[76] procedure is to establish the optimal

conditions for floc formation, but the nature of test may be greatly influenced by the process considerations. If the aim of flocculation process is to clarify turbid water, then the optimum conditions might be judged in terms of minimum supernatant turbidity after sedimentation of flocs. On the other hand, if solids recovery is the main purpose, settling rate could be the chosen parameter. In case of sludge dewatering, flocculants are used to increase filterability, so that filter cake permeability or specific resistance to filtration is considered as the desired parameter.

It seems reasonable to assume that optimum flocculation condition determined on the basis of different tests should coincide, especially if thorough mixing of additives could be achieved rapidly. However, there is very little evidence on this point in practical systems. In fact where flocculation is carried out for some specific purpose such as colour or phosphate removal, then it is the best to monitor the removal directly. Ideally, a flocculation test procedure should simulate the operation of a full-scale unit and be capable of predicting plant performance on the basis of laboratory trials. But due to various reasons, such prediction is difficult to achieve and a more realistic aim is to establish optimal chemical conditions in laboratory trials, which correspond closely to those giving optimum plant performance. The actual performance of the plant, in terms of clarification, settling rate or other parameters, may not be the same as that found in the laboratory test under the same chemical conditions, but it is possible to establish an empirical relationship, which can be used for predictive purposes. Usually, measurement of three parameters, namely sedimentation rate, settled volume and supernatant turbidity give information on the state of aggregation of a suspension.

Sedimentation (at fairly high solids concentration) can most conveniently be measured in the zone settling region, where the movement of the boundary layer can be followed with time. Settled volume of flocs is sometimes used in laboratory evaluation of polymeric flocculants, but is not usually employed in routine tests.

Measurement of supernatant turbidity is frequently employed as an indicator of flocculation performance. Ideally, a well-flocculated suspension should settle leaving no suspended solids in the supernatant liquid and hence a very low turbidity. Turbidity measurements are based on transmitted light or light scattering, the latter being more effective. For very low turbidities, some other measures of solids content like Silting Density Index (SDI) may be more appropriate. The supernatant turbidity, although a directly relevant parameter in applications like water clarification, some difficulties may arise in interpreting the results. For instance, the result may be greatly influenced by a residual haze, which may represent an extremely small proportion of the original solids. Incomplete mixing of the flocculant may result in local overdosing and restabilization of a small number of particles, giving rise to a persistent haze in the supernatant liquid. This effect is likely to occur with polymeric flocculants.

The Jar Test

       One of the most common pieces of bench test apparatus found in water treatment laboratories to identify potential coagulation-flocculation conditions in liquid suspensions is

the jar test[76,77] apparatus. The test is used to confirm the preferred chemicals and also to identify the best concentrations. The batch-test consists of using six identical jars containing the same volume and concentration of feed, which are charged simultaneously with six different doses of a potentially effective flocculant. The six jars can be stirred simultaneously at known speeds. The treated feed samples are mixed rapidly and then slowly and then allowed to settle. These three stages correspond respectively to the fundamental processes of dispersing the flocculant onto the particle surface, gently sweeping the colloidal particles together to form large flocs, and allowing the flocks to settle. These three stages are also an approximation of the sequences based on the large-scale plants of rapid mix, coagulation-flocculation and settling basins. At the end of the settling period, test samples are drawn from the jars and turbidity of supernatant liquid is measured. A plot of turbidity against flocculant dose gives an indication of the optimum dosage (i.e. the minimum amount required to give acceptable clarification). The criteria thus obtained from a bench jar test are the quality of resultant floc and the clarity of the supernatant liquid after settling. The design of the full-scale plant process is then done based on the bench-scale selection of chemicals and their concentrations.

Unfortunately, the jar test suffers from a number of disadvantages, despite its widespread application. It is a batch test, which can be very time-consuming. A thorough exploration of optimum flocculation conditions for raw water can easily take a few days. Such an extensive series of trials would require very large volume of sample which may be inconvenient if testing is to be carried out remote from the raw water source. Finally, the results obtained from a series of jar tests might not correspond to the results obtained on a full-scale plant. Many new methods[78] have been developed to substitute the conventional jar test including techniques[79,80] for characterization of floc structure.

1.9. Factors Affecting the Flocculation

1.9.1. Effects of polymer molecular weight and charge density

The effects of polymer molecular weight on flocculation[81-83] is best described in terms of bridging and electrostatic patch mechanisms. For systems in which bridging predominates irrespective of charge, an increase in molecular weight improves flocculation. At higher molecular weight, as the polymer gets adsorbed, it can extend further away from the particle surface and is slower to reach equilibrium. This, in turn, increases particle radius and collision number and hence flocculation rate. Although anionic charge on polymer can impede adsorption onto a negative surface, it serves to promote extension of polymer chain through mutual charge repulsion, enhancing its approachability. It has been observed that beyond an optimum molecular weight, flocculation efficiency decreases which is attributed to steric repulsion between polymer molecules. On the other hand, molecular weight effects are less well defined in systems where the electrostatic patch mechanism is rate controlling. Optimum flocculant concentration has been found to be independent of molecular weight but

dependent on ionic strength. Adachi *et al.*[84] observed the rate of initial flocculation of a polystyrene latex to be remarkably enhanced by the addition of polyelectrolytes, but the extent of this enhancement decreased with an increase in ionic strength. Equally important is the configuration of the solvated polymer, particularly in bridging flocculation. Molecular effects are more apparent when the polymer has a rod-like character.

1.9.2. Conformation of polyelectrolyte in solution

It was observed[85] that, in the flocculation of clays by two high molecular weight polyacrylamides of different degrees of hydrolysis, the high molecular weight, 30% hydrolyzed polymer performed best. The flocculation diminished beyond an optimum concentration, which can be explained by bridging mechanism. The higher molecular weight polymers can adsorb in configurations with loops of greater length extending from particle surface, increasing collision probability. Particles bridged by 30% hydrolyzed polymer perform best because the charge not only affects the particle-polymer interaction but also causes an extension of the solvated polymer chain. At 30% hydrolysis, a balance is reached between the effects of like charge repulsive forces of the polymer and the particle surface and polymer surface configuration as it is influenced by the presence of the charged acrylate groups. The concentration effects are due to the need for vacant surface sites on which a bridging polymer can adsorb. In a similar study Yu et al.[86] have established that polymer conformational[87] changes have a beneficial effect on the flocculation of alumina.

1.9.3. Effects of dosing and mixing conditions

The degree of flocculation achieved can be markedly affected by dosing and mixing[88-90] conditions. It has been found[91] that for high solids concentrations and relatively low polymer doses, flocculation occurs rapidly, but the flocs are not stable and can be broken at moderate stirring rates. By reducing the rate of stirring shortly after polymer dosing, floc size (and settling rate) can be held at plateau levels, without subsequent decline, which, however, is difficult to achieve in practice because of the precise control required. It has been suggested that[92-93] optimum flocculation occurs when half the area of solid is covered with polyelectrolytes. At higher concentration the degree of flocculation decreases, and the particles may be completely covered by the absorbed polymer layer. Thus overdosing can be a serious mistake in that it may create a well established suspension that is extremely difficult to separate. But, in principle, a substantial degree of flocculation can be obtained with much lower polymer dosage than is usually required. Hydrodynamic factors[94,95] arising from mechanical agitation play a significant role in flocculant adsorption. Vigorous agitation of flocculating suspension causes floc breakage and the exposure of fresh surfaces to polymer adsorption thereby increasing adsorption capacity. At the same time, however, increased agitation leads to the production of smaller flocs, indicating that enhanced adsorption does not compensate for increased floc breakage. In fact the general rule seems that, provided adsorption does occur, the actual amount adsorbed varies inversely with the extent of flocculation.

1.9.4. Solution properties

Ionic Strength

The configuration of polyelectrolytes in solution is significantly affected by ionic strength and this effects flocculation. This is indicated by the increased viscosity of a polyelectrolyte solution as ionic strength decreases. Similar charges on the polymer chain tend to expand the chain as a result of mutual charge repulsion. As ionic strength increases, these charged sites are shielded and allow the polymer to fold and assume a smaller hydrodynamic volume, as indicated by a decrease in solution viscosity. These effects manifest themselves in the flocculation mechanism. In a high solids system to be flocculated by a high molecular weight charged polymer, decreasing ionic strength expands the polymer in solution and enhances bridging by increasing the effective particle radius. In systems where the electrostatic patch mechanism predominates, the effect of ionic strength is less well understood. On the other hand, when charge-neutralization mechanism is operative, ionic strength effects will be realized through double layer compression in systems where flocculant and surface are oppositely charged.

pH Effects

With inorganic flocculants, the effective species can be a solvated metal ion, which affect flocculation through double-layer compression and Schulze-Hardy effects. With increase in pH, these species become charged and the mechanism of action changes. When the colloids are hydrophilic, e.g. humic acids, pH affects protonation. In presence of ionizable acidic or basic groups, colloid surface charge is affected by pH changes. In organic polymer flocculation as well, pH can affect polymer activity and the mechanism.

Effect of Particle Size

The importance of particle size variation with regard to flocculation has been investigated by many researchers[96]. Moudgil et al.[97] have reported that there exists a strong correlation between aggregation of a given size and the molecular weight of the flocculant. They have explained the correlation between particle size and flocculant molecular weight in terms of floc formation forces provided by polymer bridging and floc breaking forces (e.g. turbulence) encountered in an agitated system. In similar report Mishra et al[98] have reported the decreasing settling rate of coal suspensions with decreased particle size. This has been attributed to an increase in surface area that increased the charge neutralization capacity of the coal surface by the flocculant.

1.10 Flocculation : The Applications

1.10.1. Water clarification

Flocculants are used for clarification of potable and industrial process water. Their principal function is the removal of suspended solids, which cause turbidity. Flocculants are also used in gravity separation and flotation processes for industrial and municipal water clarification. For wastewater, containing mainly inorganic compounds, anionic flocculants

are preferred whereas for organic compounds, cationic flocculants are most often applied. Polymeric flocculants are employed for wastewater treatment in the metals, chemicals, pulp and paper, food processing, petroleum refining and textile industries.

1.10.2. Paper making

In the process of production of paper from wood and pulp, filler such as clays, titanium dioxide, calcium carbonate etc. are used to provide opacity and whiteness to paper. However, a significant percentage of the fillers added as well as fiber fines may be lost during drainage of the wet paper web. The loss of valuable fillers and fines during drainage is significantly reduced by addition of flocculants, the type of which is dependent on the history of the pulp. Both alum and cationic polymers are used to neutralize the negative paper fibers. Because the alum forms small, easily sheared flocs, it may be used in conjunction with a high or ultrahigh molecular weight cationic or anionic polymer. Starch and cationic starch also function as flocculants when added to fiber slurry to increase the wet strength. An additional benefit of using the flocculants as retention aids in paper industry is that, the residual polymer left in the stream is very effective in clarifying the "white effluent" formed in the process.

1.10.3. Mineral processing

In all mining operations, solids and liquids must be separated which can be facilitated by flocculants in the thickening of froth flotation concentration and clarification steps. In most mineral processing, the suspended fines are impurities arising from crushing and grinding. They are separated as the solid phase rather than the mineral of interest, which remains in solution, coal being an exception. The mining industries requiring flocculants include coal, iron ore, bauxite and uranium etc. The coal industry is the largest user. Both cationic and anionic flocculants[99] are used including some natural polymers. Cationic polymers are of quaternary ammonium type, e.g. poly (DADMAC) or polyamine especially in the recovery of coal. The principal anionic synthetic flocculants are poly (acrylamide-acrylate) copolymers although nonionic polyacrylamide is also utilized. Among natural polymers used are starch, guar gum, animal glue, lignin (sulfonate) etc.

1.10.4. Selective flocculation

One of the applications that have shown considerable promise in the beneficiation of mineral fines is selective flocculation[100-103]. This process involves flocculating particles of one type from a well dispersed suspension of the ore or mixture, followed by separating the flocs by either froth flotation or sedimentation. Selective flocculation, like flotation, takes advantages of the differences in the physico-chemical properties, but unlike flotation, does not depend entirely on the wettability characteristics of the particle surfaces. The selective flocculation involves three steps: dispersing the fine particles, selectively adsorbing the polymer

on the active component (flocculating particles of interest) and forming flocs, and separating the flocs. The major applications of selective flocculation have been in mineral processing, but many potential uses exist in biological and other colloidal systems[102]. These include purification of ceramic powders, separating hazardous solids from chemical wastes and removal of deleterious components from paper pulp[104]. Industrial applicability of this process has so far been limited, e.g. processing of taconite and potash ores, because results obtained by selectively flocculating natural ores or complex synthetic mixtures often do not correlate with the selectivity observed in single component systems. Selective flocculation of desired fraction has become an active area of research in the field of flocculation [105-108] A critical review on iron oxide/quartz separation using starch and polyacrylic acid (PAA) indicates starch to be a more selective reagent[109].The presence of clays, particularly Montmorillonite, is known to have a detrimental effect on the selectivity of separation. To achive the desired selectivity (<10% flocculation of clay), Sodium silicate is to be added. The primary objective of adding sodium silicate is to prevent hetero coagulation. Ravisankar et.al[110] attempted selective flocculation of iron oxide-kaolin mixtures using a modified polyacrylamide flocculant containing hydroxamate functional groups. Flour apatite, the phosphate fertilizer mineral, occurs in nature. In association with silicate and carbonate minerals. During flotation separation of apetite a significant proportion of P_2O_5 values is lost in the form of slimes. Selective flocculation appears to be promising for recovering the fine phosphate values. Pradip et,al.[111,112] have successfully examined the feasibility of selective flocculation of tribasic calcium phosphate using hydrolysed polyacrylamide and polyacrylic acid flocculants.

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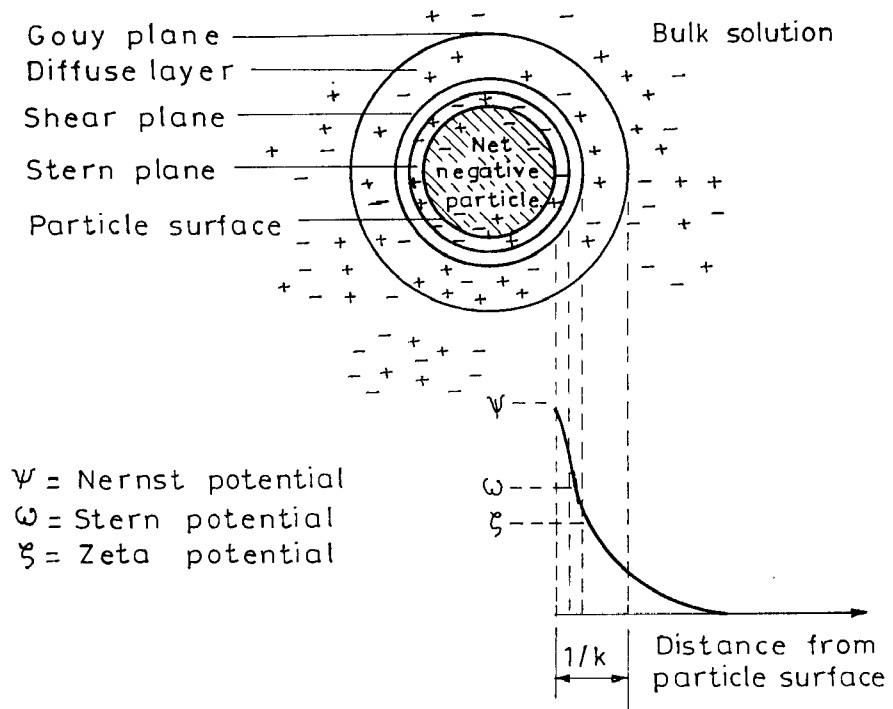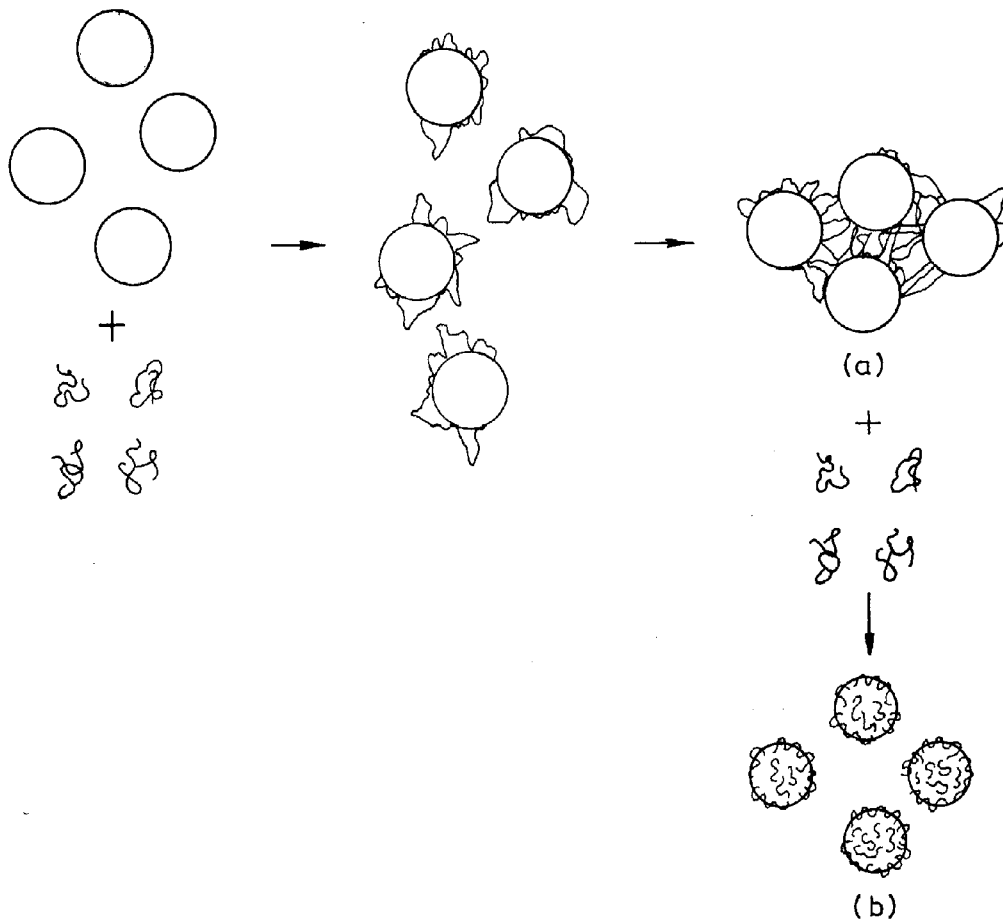
Fig. 1 : Electrical double layer

Fig. 2   Schematic illustration of (a) bridging flocculation
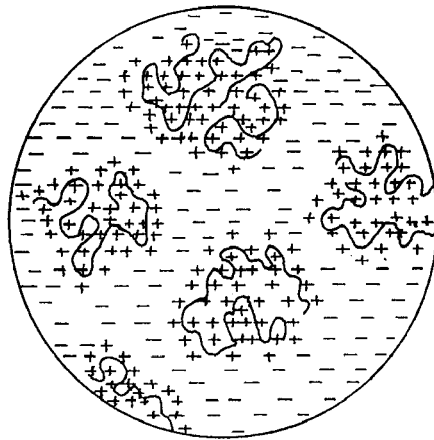and (b) restabilization by adsorbed polymer

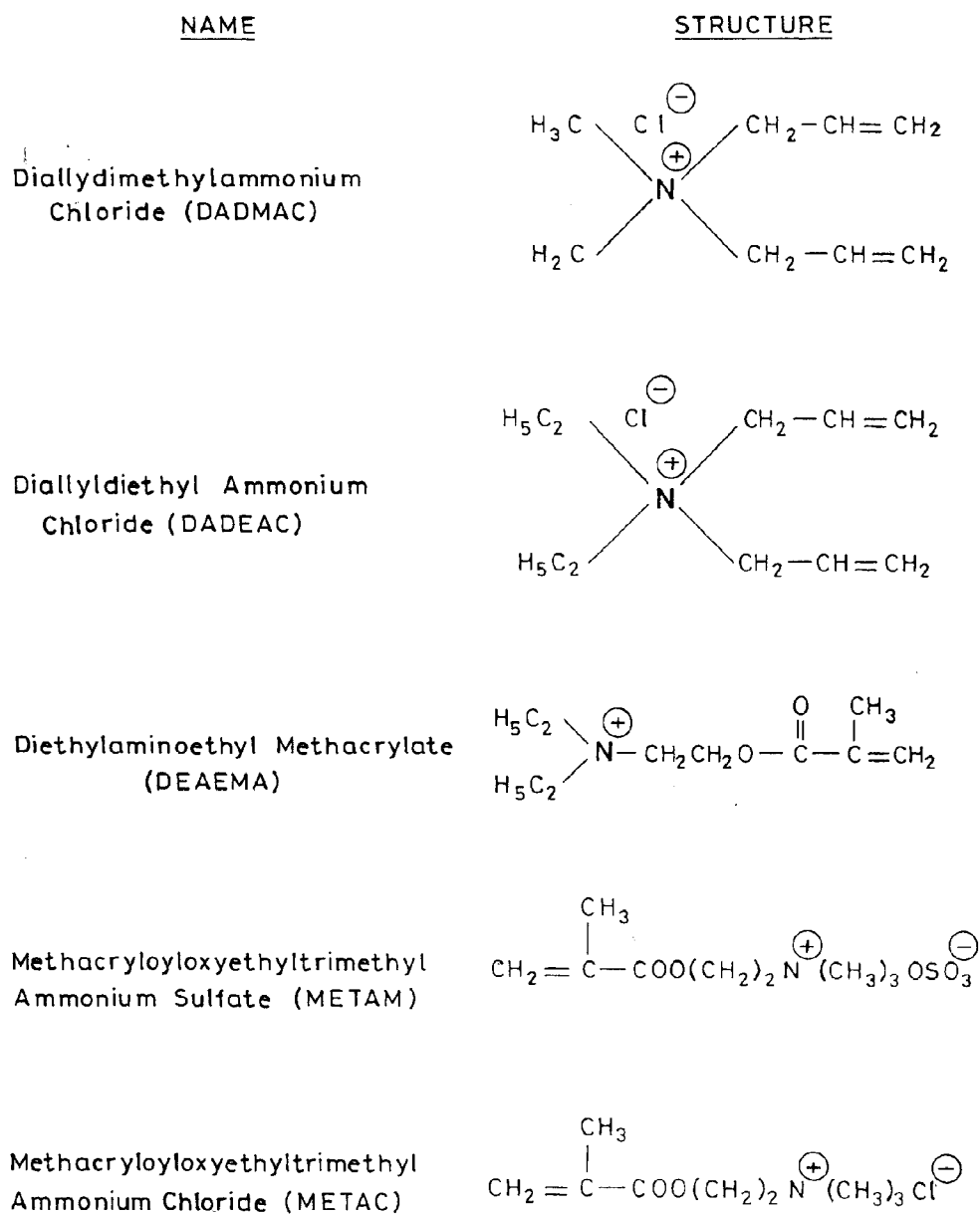**Fig. 3 : Schematic illustration of electrostatic patch mechanism**

NAME   STRUCTURE

Diallydimethylammonium
Chloride (DADMAC)

$$H_3C \diagdown \quad Cl^{\ominus} \quad \diagup CH_2-CH= CH_2$$
$$N^{\oplus}$$
$$H_2C \diagup \qquad \diagdown CH_2-CH=CH_2$$

Diallyldiethyl Ammonium
Chloride (DADEAC)

$$H_5C_2 \diagdown \quad Cl^{\ominus} \quad \diagup CH_2-CH=CH_2$$
$$N^{\oplus}$$
$$H_5C_2 \diagup \qquad \diagdown CH_2-CH=CH_2$$

Diethylaminoethyl Methacrylate
(DEAEMA)

$$H_5C_2 \diagdown \quad \overset{\oplus}{N}-CH_2CH_2O-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$
$$H_5C_2 \diagup$$

Methacryloyloxyethyltrimethyl
Ammonium Sulfate (METAM)

$$CH_2 = \overset{\overset{CH_3}{|}}{C}-COO(CH_2)_2 \overset{\oplus}{N}(CH_3)_3 \ OS\overset{\ominus}{O_3}$$

Methacryloyloxyethyltrimethyl
Ammonium Chloride (METAC)

$$CH_2 = \overset{\overset{CH_3}{|}}{C}-COO(CH_2)_2 \overset{\oplus}{N}(CH_3)_3 \ Cl^{\ominus}$$

Fig. 4 : Cationic monomers (Quaternary ammonium salts)

CH₃ structures shown

Sodium 2—Methacry-
loyloxy Ethyl Sulfon-
ate (SEM)

2-Acrylamido 2-Me-
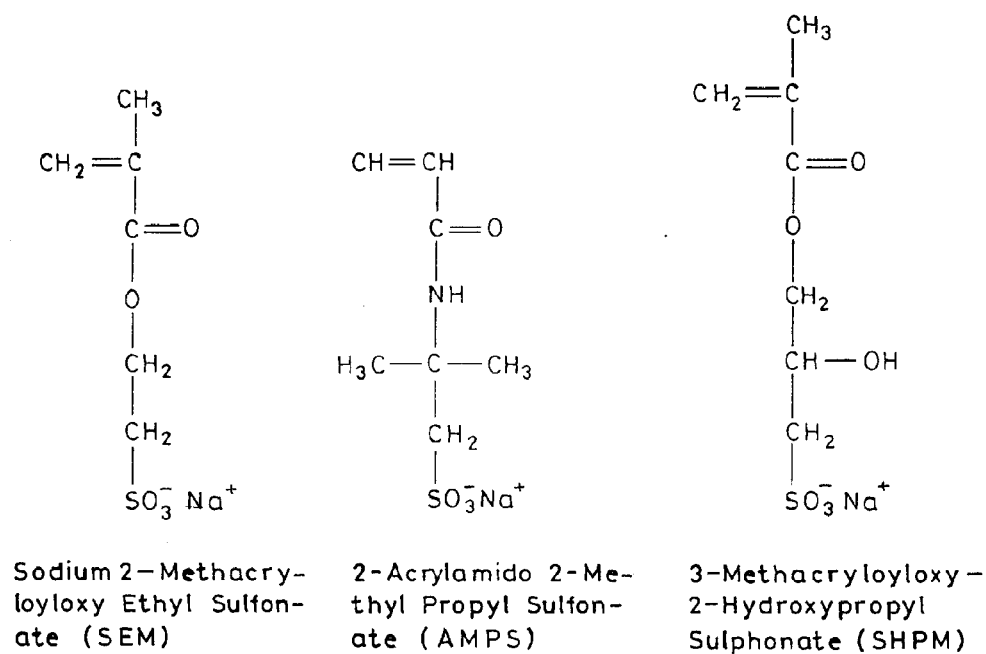thyl Propyl Sulfon-
ate (AMPS)

3-Methacryloyloxy—
2-Hydroxypropyl
Sulphonate (SHPM)

Fig. 5 : Anionic monomers of sulphonic acid salts