FLOCCULATING AGENTS

1. Introduction

Flocculation is defined as the process by which fine particles, suspended in a liquid medium, form stable aggregates called flocs. The degree of flocculation can be defined mathematically as the number of particles in a system before flocculation divided by the number of particles (flocs) after flocculation. Flocculation makes the suspension nonhomogeneous on a macroscopic scale. A complete or partial separation of the solid from the liquid phase can then be made by using a number of different mechanical devices. Flocculating agents are chemical additives, which, at relatively low levels compared to the weight of the solid phase, increase the degree of flocculation of a suspension. They act on a molecular level on the surfaces of the particles to reduce repulsive forces and increase attractive forces. In most cases, the liquid medium is water (or an aqueous solution), which has a unique physical chemistry, unlike most other liquids. Sometimes flocculating agents are classified as either coagulants (eg, alum) or flocculants (eg, polyacrylamides) depending on the mechanism of floc formation, the type of floc that forms or the nature of the interparticle forces. Both terms appear in the literature. In actual use, however, agents that have been classified as belonging to different types are often used in combination with each other, as part of an overall process. For this reason, the term flocculating agent and flocculation will be used in all cases. Another important concept in discussing flocculating agents is that they are only part of an overall process, in which hydrodynamic and mechanical forces such as shear have a major effect.

2. Applications

The principal use of flocculating agents is to aid in making solid–liquid separations, which, for the most part, can be divided into two types: settling and filtration. In the first case, floc formation increases the settling rate of the suspended solids, by increasing the size of the suspended particles. The settling rate of a suspension can be approximated as the terminal velocity of an individual particle in a viscous medium. This rate is roughly proportional to the square of the radius of the particle (using a spherical model as an approximation). In the case of filtration, flocculation has several effects. First of all, it prevents fine particles from either passing through the filter or clogging the filter. Although the filter cake is somewhat compressible, it is the strength of the flocs that keeps the interstial spaces open to allow the liquid to pass through. The flocculated material also has a certain cohesivness. This prevents it from being squeezed out the sides in a belt filter, eg. It also promotes release of cake from the filter. Permeability and cohesiveness of the flocculated material are also desirable when a centrifuge is used to make a solid–liquid separation.

The principal uses of flocculating agents are

1. Removing small amounts of suspended inorganic or organic particles from surface water prior to its use as drinking water or industrial process water. This is often called raw water clarification and can involve both inorganic and organic flocculating agents. Some of the inorganic flocculating agents used for this purpose also remove dissolved organic matter that gives the untreated water an undesirable color or taste. Clarification can also remove pathogenic organisms.
2. Concentrating the organic solids in municipal, agricultural, and industrial wastewater to produce a sludge with a minimum volume and water content for incineration or other means of disposal, and a clarified (very low suspended solids) water that can be discharged or recycled. This operation is often called dewatering (qv). Some of the inorganic flocculating agents used for this purpose also remove some undesirable dissolved ions such as phosphate and sulfide.
3. Removing suspended inorganic material from waste streams generated in the beneficiation of ores or nonmetallic minerals, to form a concentrated slurry that can be used for reclamation of mined out areas or other uses and a clarified water that can be discharged or recycled.
4. Separating the solid–liquid phases in leaching operations, where a valuable material is contained in the liquid phase, so its recovery is to be maximized. One major application is in the Bayer process, where polymeric flocculants are used to flocculate the insoluble residue from the digestion of bauxite.
5. Other industrial solid–liquid separations such as juice clarification in the sugar industry (1) and treatment of water used in oil and gas drilling (2) and biotechnology (3,4). In a few cases, minerals can be separated from other minerals by selective flocculation (5,6).

There are other applications for flocculating agents, in which a solid–liquid separation is not the objective:

6. Polymeric flocculants are used to bind fine cellulose fibers and solid inorganic additives to long cellulose fibers as the paper pulp is being formed into sheets on a paper machine (see 1). These materials are classified as “retention aids”.

7. Polymeric flocculants are used as an additive to irrigation water to control the loss of soil in the run off. In this application, flocculation of the surface layer of fine soil particles prevents their suspension in the flowing water. Flocculation also stabilizes the soil structure and makes it more permeable to irrigation water (7). Flocculants can be used to reduce erosion of exposed soil by rainwater at construction sites.

The environmental legislation in the United States and elsewhere, such as the Clean Water Act and the Safe Drinking Water Act, and the 1998 European Drinking Water Directive, have focused considerable attention and a large research effort on flocculation in the first three application areas. In recent years, this concern has spread to other areas of the world. As new legislation takes effect, the requirements for flocculating agents to meet these regulations change. In particular with drinking water treatment, any residual chemical species from the treatment may exceed a new standard or guideline.

The fourth application is primarily in the area of extractive metallurgy. Research has been driven primarily by the economic incentive to improve the process. In the Bayer process, eg, increasing the underflow density in the thickeners, leads to increased recovery of alumina and decreased loss of caustic. It is also desirable to decrease the amount of fine material in the thickener overflow, which has to be removed by filtration.

The fifth application area is relatively small, but growing. These materials must meet additional requirements if they are used in food processing, because any material used for that purpose is considered a food additive, by law in many countries.

The sixth application is specific to the paper industry. They are similar in chemistry and mechanism to the flocculants used for other applications and are included here for that reason. Note that highly cross-linked insoluble polymers are sometimes used as retention aids. Strictly speaking, these polymers are not flocculating agents. Research in this area is driven by the goal of improving the quality of the paper and the economics of its production.

3. Chemical Composition

Flocculants can be classified as inorganic or organic.

3.1. Inorganic Flocculating Agents.

The inorganic flocculating agents are water-soluble salts of divalent or trivalent metals. For all practical purposes these metals are aluminum, iron, and calcium. The principal materials currently in use are described in the following.

Aluminum sulfate (hydrate) [17927-65-0], [57292-32-7] is commonly known as alum [10043-01-3], [10043-67-1] (see ALUMINIUM, SULPHATE AND ALUMS). The use of this material has been known for centuries. It is made by the leaching of aluminous ores, such as bauxite or clay, with sulfuric acid. The use of alum has grown 2–3%/year recently (8) despite competition from other inorganics and polymers. It is still used in municipal wastewater treatment, and to some extent in drinking water treatment. The principal disadvantages of alum are that it lowers the pH of the system, which often necessitates addition of base, and it leaves aluminum in the effluent. Some of the aluminum in the effluent is in the form of very fine particles, which can be removed by filtration, using a polymer as a filter aid (9). The use of alum in the paper industry has declined with the growth of alkaline papermaking. Its principal use is in conjunction with rosin size emulsions. In this application, alum is both a flocculating agent as well as a precipitant for the chemically modified rosin (10). Alum is sold both as a solution and as a dry chemical. The former is easier to dispense, but must be kept warm to prevent crystallization. Grades lower in iron are used in papermaking and command a higher price than high iron grades used in waste treatment.

It is now well known that the activity of alum is primarily due to the hydrolysis products formed *in situ*. Their rate of formation and the species formed is controlled by the pH and the presence of other ions. A stable Al13 oligomer has been detected in solutions made with alum (11). The conditions in the waste stream may not be favorable for the formation of polymeric species. For this reason, a number of prepolymerized aluminum compounds have been introduced into the market (12a,b). These have the advantages of working over a wider pH range, working well in cold water and leaving less residual aluminum in the water.

Aluminum chloride hydroxide [1327-41-9] also called polyaluminum chloride or PAC, is made by partial hydrolysis of aluminum chloride to form a mixture of polymeric species. The Al13 oligomer has been detected in PAC. It is more expensive than alum on a weight basis, but shows better cost effectiveness in some applications. It is sometimes used with rosin size emuslsions in papermaking instead of alum. It is sold as a solution.

Another commercial product is polyaluminum—silicate—sulfate or PASS (12a,b). It is more effective than other inorganics on a dosage basis, works well in cold water, and leaves less residual aluminum. Analysis of PASS solutions shows the presence of polymeric species.

In recent years, iron salts have been replacing aluminum salts in the treatment of drinking water. Iron compounds (qv) include ferric chloride [7705-08-0], ferric sulfate [10028-22-5], and ferrous sulfate [7720-78-7]. Currently, the most commonly used one is ferric chloride. The use of this chemical is growing at 3–4%/year (13). It is produced from a variety of sources, which include steel pickle liquor, treatment of titanium ore (ilmenite), and reaction of scrap iron with chlorine. It is used in municipal and industrial wastewater where it acts as a flocculating agent. Its use in raw water clarification is increasing. The principal benefit in this application is its abilility to remove dissolved organic matter along with fine particulates, prior to chlorination. This reduces the production of chorinated organics, as mandated by the Disinfectants/Disinfection By-Products Rule (an amendment to the Safe Drinking Water Act, that took effect in 1998). It is sold either as a solution or a solid. As with the aluminum salts, the active agents are the hydrolysis products of the additive. Prehydrolyzed ferric compounds are also available, but are not widely used currently. These include polyferric sulfate and polyphosphorus iron chloride (12a,b).

The principal calcium salt used as a flocculant is calcium hydroxide [1305-62-0] or lime. It has been used in water treatment for centuries (see ALCOHOLS, HIGHER ALIPHATIC, SURVEY AND NATURAL ALCOHOLS MANUFACTURE). Newer polymeric products are more effective, and the use of lime in water and effluent treatment is declining. It is still used as a pH modifier, and to precipitate metals as insoluble hydroxides, which are then flocculated by polymers. Lime is also sometimes used in combination with polymeric flocculants, such as anionic polyacrylamides, because the Ca^{+2} ion promotes adsorption of the anionic polymer on certain minerals, such as kaolinite (14).

In addition to their usefulness in removing suspended solids, iron, calcium, and aluminum compounds have other functions in water treatment. They precipitate phosphate from aqueous solutions, whereas organic flocculants do not. This is an advantage if a low phosphate effluent is desired. Phosphate is a pollutant that leads to the eutrification of lakes and streams. On the other hand, it is a disadvantage if phosphate is required as a nutrient for bacteria used for biological sludge treatment. Iron and aluminum salts also precipitate organic color bodies, and iron salts also remove hydrogen sulfide by forming an insoluble precipitate.

Sodium silicate is usually added to slurries as a dispersant (see DISPERSANTS), however, small amounts of sodium silicate are used as flocculants. The active species are polymeric silicates formed by hydrolysis. Fine precipitated silica or clay is sometimes added to waste streams as a collector of suspended organic material, such as agricultural waste, which does not respond on its own to flocculating agents. The organics attach to the inorganic particles that are then flocculated with a water soluble polymer (15).

3.2. Organic Flocculants. The organic flocculants are all water-soluble natural or synthetic polymers.

Natural Products. The use of natural polymers has been known for a long time; eg, the soluble protein albumin is used for clarifying wine. Since the 1950s the use of natural products as flocculating agents has steadily declined as more effective synthetics have taken their place. The only natural polymers used to a significant degree as flocculants are starch and guar gum.

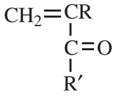
Starch is a polysaccharide found in many plant species. Corn and potatoes are two common sources of industrial starch. The composition of starch varies somewhat in terms of the amount of branching of the polymer chains (16). Its principal use as a flocculant was in the Bayer process for extracting aluminum from bauxite ore. The digestion of bauxite in sodium hydroxide solution produces a suspension of finely divided iron minerals and silicates, called red mud, in a highly alkaline liquor. Starch was used to settle the red mud so that relatively pure alumina can be produced from the clarified liquor. It has been largely replaced by acrylic acid and acrylamide-based (17,18) polymers, although a few plants still add some starch, in addition to synthetic polymers, to reduce the level of residual suspended solids in the liquor. Starch [9005-25-8] can be modified with various reagents to produce semisynthetic polymers with different functional groups. The principal one of these is cationic starch, which is used as a retention aid in paper production as a component of a dual system (19,20) or a microparticle system (21).

Guar gum [9000-30-0], derived from the seed of a legume (22), is used as a flocculant in the filtration of mineral pulps leached with acid or cyanide for the recovery of uranium and gold (23). It is also used as a retention aid, usually in a chemically modified form (20,24). Starch and guar gum are subject to biological degradation in solution, so they are usually sold as dry powders that are dissolved immediately before use. Starch requires heating in most cases to be fully dissolved (16).

If you want to divide the section of 2.2.2 Synthetic polymers, the subsets of this heading are acrylic polymers, polyamines, polyethylene oxide) and allylic polymers. The structural formula for acrylic monomers should be removed from Fig. 1 and inserted in the text.

Synthetic Polymers. These materials are made by free-radical polymerization of unsaturated monomers or by step-growth condensation reactions. Examples of polymers in this class include acrylamide–acrylic polymers and their derivatives, polyamines and their derivatives, poly(ethylene oxide), and allylamine polymers.

Acrylic polymers are made by free-radical polymerization of monomers containing the acrylic structure, where R is $-H$ or $-CH_3$ and R′ is $-NH_2$ or a substituted amide or the alkoxy group of an ester.



$$CH_2{=}\underset{\underset{\displaystyle R'}{|}}{\underset{\displaystyle C{=}O}{\underset{|}{C}}}R$$

Their common structural feature is a backbone of carbon atoms, which is chemically stable under most conditions. The ability to change the charge density, functionality, molecular weight, and degree of branching of this overall class of polymers makes its use applicable to many different substrates and separation processes.

Acrylic Monomer. The principal monomer is acrylamide [79-06-1], where R = H and R′ = NH_2, made by the hydrolysis of acrylonitrile. The homopolymer [9003-05-8] of acrylamide, which in theory has no electrical charge, has some

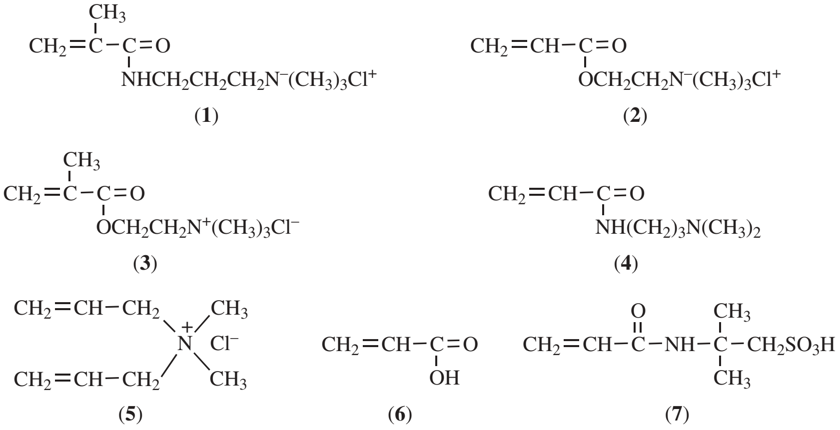


Fig. 1. Functional monomers used in acrylamide copolymers. Methacrylamidopropyltrimethylammonium chloride [51410-72-1] (**1**), acryloyloxyethyltrimethylammonium chloride [44992-01-0] (**2**), methacryloyloxyethyltrimethylammonium chloride [50339-78-1] (**3**), *N,N*-dimethylaminoethyl methacrylate [2867-47-2] (**4**), diallyldimethylammonium chloride [7398-69-8] (**5**), acrylic acid (and its salts) [79-10-7] (**6**), and 2-acrylamido-2-methylpropanesulfonic acid (and its salts) [15214-89-8]) (**7**).

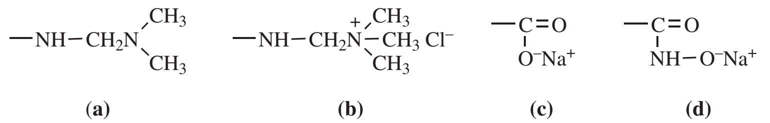


Fig. 2. Functional groups on modified polyacrylamides: (**a**) formed by reaction with dimethylamine and formaldehyde (Mannich reaction); (**b**), quaternized Mannich amine; (**c**), carboxylate formed by acid or base-catalyzed, and (**d**) hydroxamate formed by transamination with hydroxylamine.

use as a flocculant; however, the majority of acrylamide-based flocculants are copolymers with acrylic monomers containing charged functional groups, (25–27) such as those shown in Figure 1, or polymers containing functional groups formed by modification of acrylamide homopolymers or copolymers (Fig. 2).

There are two main advantages of acrylamide–acrylic-based flocculants that have allowed them to dominate the market for polymeric flocculants in many application areas. The first is that these polymers can be made on a commercial scale with molecular weights up to 10–15 million, which is much higher than any natural product. These high molecular weight polymers give rapid formation of large flocs, which settle rapidly. The second is that their electrical charge in solution and the charge density can be varied over a wide range by copolymerizing acrylamide with a variety of functional monomers or by chemical modification.

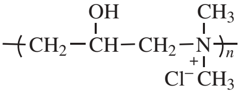
The high molecular weight of these polymers makes their solutions very viscous, which presents a problem on an industrial scale with regard to shipping, handling, and dissolving. The two principal forms in which these polymers are sold, dry powders and inverse emulsions (25–27), represent two different solutions to this problem. The dry powder form can be made by two different routes. In the first, a concentrated monomer solution is polymerized, producing a gel that is cut up, granulated or extruded, and dried in a fluidized-bed drier to produce a free-flowing powder. In the second method, the concentrated monomer solution is suspended as droplets in an immiscible organic liquid. After polymerization, the polymer is in the form of spherical beads containing polymer and water. The beads can be removed and dried to give a dry powder made up of spherical particles. Drying of nonionic polyacrylamides may introduce a slight anionic charge because of hydrolysis.

The inverse emulsion form is made by emulsifying an aqueous monomer solution in a light hydrocarbon oil to form an oil-continuous emulsion stabilized by a surfactant system (25), which is polymerized to form an emulsion of aqueous polymer particle ranging in size from 1.0 to $\sim$ 10 μm dispersed in oil. By addition of appropriate surfactants, the emulsion is made self-inverting, which means that when it is added to water with agitation, the oil is emulsified and the polymer goes into solution in a few minutes. Alternatively, a surfactant can be added to the water before addition of the inverse polymer emulsion (see EMULSIONS).

Certain acrylamide polymers can also be made as dispersions that have two aqueous phases. The discontinuous aqueous phase consists of swollen polymer. The continuous aqueous phase contains dissolved salts, which reduce the solubility of the polymer, and a stabilizer, which in most cases is a polymeric surfactant (28–30).

If high molecular weight polymers, either in the form of dry powder or an inverse emulsion are not properly mixed with water, large lumps of polymer form that do not dissolve. This not only wastes material, but can also cause downstream problems. This is especially true for paper where visible defects may be formed. Specialized equipment for dissolving both dry polymers and inverse emulsions on a continuous basis is available (31,32). As a rule, to insure maximum effectiveness of the polymer solution, dry powders should be made up as dilute as possible, because the rate of dissolution decreases as the viscosity of the solution increases. In contrast, inverse emulsions should be broken at as high a concentration as possible, to have a sufficient concentration of inverting surfactant or breaker. In this case, the upper limit on the polymer concentration is determined by the viscosity of the solution. High shear in the first few seconds of inversion is critical. Inverting emulsions in a batch tank with poor agitation, especially if the liquid in the tank already contains some polymer, is not recommended. Some care must be taken with regard to water quality when dissolving polyacrylamides. Anionic polymers can degrade rapidly in the presence of ferrous ion sometimes present in well water (33). Some cationic polymers can lose charge by hydrolysis at high pH (34).

Polyamines are condensation polymers containing nitrogen; they are made by a variety of synthetic routes. Most of the commercial polyamines are made by reaction of epichlorohydrin with amines such as methylamine [25988-97-0] or dimethylamine [39660-17-8] (35,36). Branching can be increased by adding small amounts of diamines such as ethylenediamine [42751-79-1]. A typical structure of this type of polyamine is structure (**8**).



$$\left(\mathrm{CH_2-\overset{OH}{\overset{|}{C}}H-CH_2-\underset{Cl^-\,CH_3}{\overset{CH_3}{\overset{|}{N^+}}}}\right)_n$$

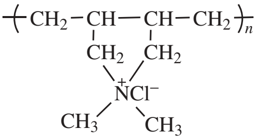
(**8**)

Polyamines can also be made by reaction of ethylene dichloride with amines (35). Products of this type are sometimes formed as by-products in the manufacture of amines. A third type of polyamine is polyethyleneimine [9002-98-6], which can be made by several routes; the most frequently used method is the polymerization of aziridine [151-56-4] (35). The process can be adjusted to vary the amount of branching (see IMINES, CYCLIC). Polyamines are considerably lower in molecular weight compared to acrylamide polymers, and therefore their solution viscosities are much lower. They are sold commercially as viscous solutions containing 1–20% polymer, and also any by-product salts from the polymerization reaction. The charge on polyamines depends on the pH of the medium. They can be quaternized to make their charge independent of pH (35,36).

Poly(ethylene oxide) [25372-68-3] is made by condensation of ethylene oxide with a basic catalyst. In order to achieve a very high molecular weight, water and other compounds that can act as chain terminators must be rigorously excluded. Polymers up to a molecular weight of 8 million are available commercially in the form of dry powders (37). These must be dissolved carefully using similar techniques to those used for dry polyacrylamides. Poly(ethylene oxide) precipitates from water solutions just below the boiling point (see POLYETHERS, ETHYLENE

OXIDE POLYMERS). The principal use of these polymers is principally as retention aids in paper. Poly(ethylene oxide) has been shown to be an effective flocculant for phosphate slimes, coal refuse, and other substrates (38), however, it is not used commercially, probably because of its high cost.

Allylic polymers are made by free-radical polymerization of diallyl compounds, most frequently diallyldimethylammonium chloride (DADMAC) [7398-69-8] forming a chain containing a five-membered ring (**9**) poly(DADMAC) [26062-79-3] (39).



(**9**)

This monomer can also be copolymerized with acrylamide. Because of the high chain-transfer rate of allylic radicals, the molecular weights tend to be lower than for acrylic polymers. These polymers are sold either as a viscous solution or a dry powder made by suspension polymerization.

3.3. Mechanism of Flocculation. In order to form flocs, the individual particles in a suspension must collide. The effect of the flocculating agent is to bind the particles together after collision. Flocculation can be classified as either orthokinetic or perikinetic. In orthokinetic flocculation, particle motion results from turbulence in the suspension. For all practical purposes, this is the main type of flocculation. In many industrial applications, flocculation is a continuous process and the turbulence is created by the liquid flow. In other applications, mechanical agitators are used in large vessels. At very close distances, polar materials are attracted by dipole-induced dipole interactions commonly called van der Waals forces (40). In most aqueous suspensions, ionization of surface groups gives the particle an overall negative charge. The charged particles in suspension are surrounded by a group of positive ions referred to as the double layer. When particles approach each other, the resulting electrostatic repulsion of the double layers prevents the particle from joining to form a floc. In this situation, the action of convection currents and Brownian motion is sufficient to keep very fine particles in suspension. Increasing the ionic strength of the liquid medium reduces the repulsion until the particles start to aggregate. This ionic strength is called the critical flocculation concentration. The thickness of the double layer can be reduced by deliberately adding higher charged ions to the system. This allows the particles to become closer and be attracted by the van der Waals forces. This mechanism is called double-layer compression or charge neutralization and is often cited as the mechanism for the inorganic flocculating agents. It is the explanation for the empirically derived Schulze-Hardy rule that the critical flocculation concentration of positive ions for a particular system decreases proportionally with the sixth power of the charge (41). As predicted by this rule, trivalent ions, such as Al^{+3} and Fe^{+3} cause flocculation at low concentration. However, application of this rule is somewhat of an oversimplification since individual Fe^{+3} and Al^{+3} ions do not exist in aqueous solutions under most conditions of pH and concentration. When aluminum and ferric salts are added to water under certain conditions of pH and temperature they can hydrolyze to form insoluble precipitates that coat and entrain suspended particles as well as adsorb dissolved organic material. This mechanism is called sweep flocculation (11). It is used primarily in very low solids systems such as raw water clarification (11). In some systems, such as lake and river waters, the suspended inorganic particles may be coated by biological polymers, termed humic substances, which prevent flocculation by either steric or electrostatic mechanisms. Iron and aluminum salts can neutralize the charge on these polymers, and therefore promote flocculation. Therefore, in actual practice, the activity of inorganic flocculating agents is the result of a number of different mechaisms going on simultaneously (11). Time is an important factor in this process, because the formation of polymeric species from aluminum and ferric salts is much faster than hydroxide precipitation.

The mechanisms of organic polymeric flocculating agents are in most cases different from the inorganics. The first of these mechanisms is referred to as the charge patch or electrostatic mechanism (42). It is the predominant mechanism for highly charged polymers, in particular cationic polymers, such as poly(DADMAC) and polyamines, whose coil diameters in solution are much smaller than the particles in the substrate. These polymers adsorbed on a negative particle surface in a flat conformation. That is to say, most of the charged groups are close to the surface of the particle, as illustrated in Figure 3. This promotes flocculation by first reducing the overall negative charge on the particle thus reducing interparticle repulsion. This effect is called charge neutralization and is associated with reduced zeta potential, In addition, the areas of polymer adsorption can actually have a net positive charge because of the high charge density of the polymer. The positive regions are also attracted to negative regions

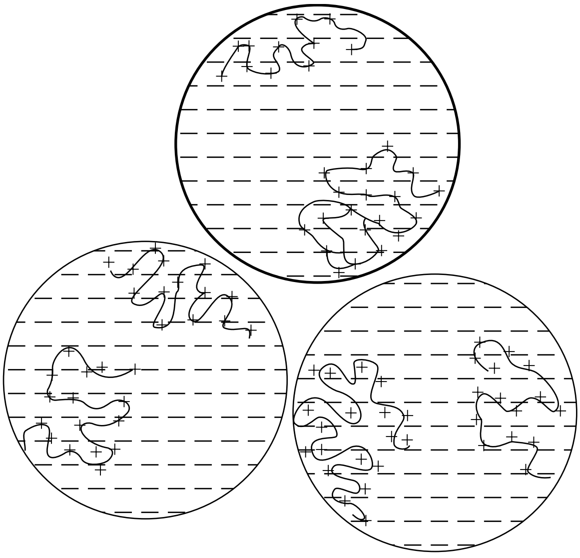


Fig. 3. Adsorbed cationic polymer-forming charge patch on particle surface (43).

on other particles. This is called heterocoagulation. To some extent, prepolymerized inorganic flocculating agents might also act by charge patch neutralization.

The mechanism of high molecular weight polymeric flocculating agents is called bridging. Some individual segments of a very high molecular weight polymer, usually a high molecular weight anionic polyacrylamide, adsorb on a surface. As shown in Figure 4**a**, large segments of the polymer extend into the liquid phase where other segments are adsorbed on other particles, effectively linking the particles together with polymer bridges. Note that this bridging is essentially a nonequilibrium process that occurs only in a limited time period after the polymer is adsorbed. If the polymer particle system is subjected to shear, the bridges tend to be broken and the polymer molecules adsorb to the surface of a single particle (42). In contrast to the first two mechanisms, bridging is strongly affected by molecular weight and the ionic content of the solution. Only large molecules can bridge between particles. Low molecular weight anionic polymers actually act as dispersants in the same systems. The coil diameter in solution can be somewhat smaller than the average particle size of the substrate (44). This type of flocculation is strongly affected by hydrodynamic forces and mixing because the polymer adsorbtion kinetics are on the same time scale as the mixing and are essentially irreversible. If, eg, a highly concentrated polymer is added to a suspension, most of the polymer will adsorb on a few of the particles and the rest of the particles will not form flocs. If the polymer is diluted, but added all at once to the slurry, large flocs will form immediately and start to settle, removing most of the solids and polymer, but leaving some material behind, resulting in a bimodal particle size distribution (45). Some turbulence is needed to cause collisions, but shear forces also tend to break up the flocs. Flocs formed by bridging with high molecular weight polymers tend to be large and settle rapidly, because the gravitational force that in the case of a small floc is roughly proportional to the cube of the diameter, increases more than the viscous drag, which is proportional to the square of the diameter. There is a limit to this increase in settling rate increase with size. Large flocs formed by polymer bridging exhibit what is called a fractal geometry (46), which means that the density of the floc decreases with size. This causes the settling rate to eventually level off, with increased polymer dose. In many cases, compaction of the flocculated bed in

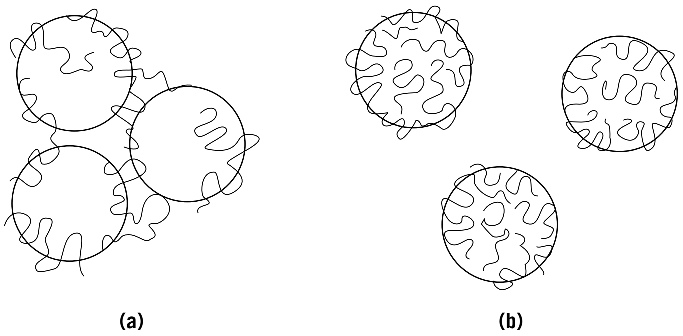


Fig. 4. (**a**) Polymer bridging between particles; and (**b**), particle stabilization by adsorbed polymer (43).

a thickener is important, and this may eventually decrease with higher flocculant dose. In some cases, continued shearing of the flocs may cause a restructuring and an increase in floc density (47). The overall process in a continous system is rather complex as illustrated by Bagster (48) Figure 5 and is greatly affected by fluid mechanical factors.

Cationic polymers can also bridge between particles, if the molecular weight is high enough. Bridging is cited as the mechanism for cationic retention aids

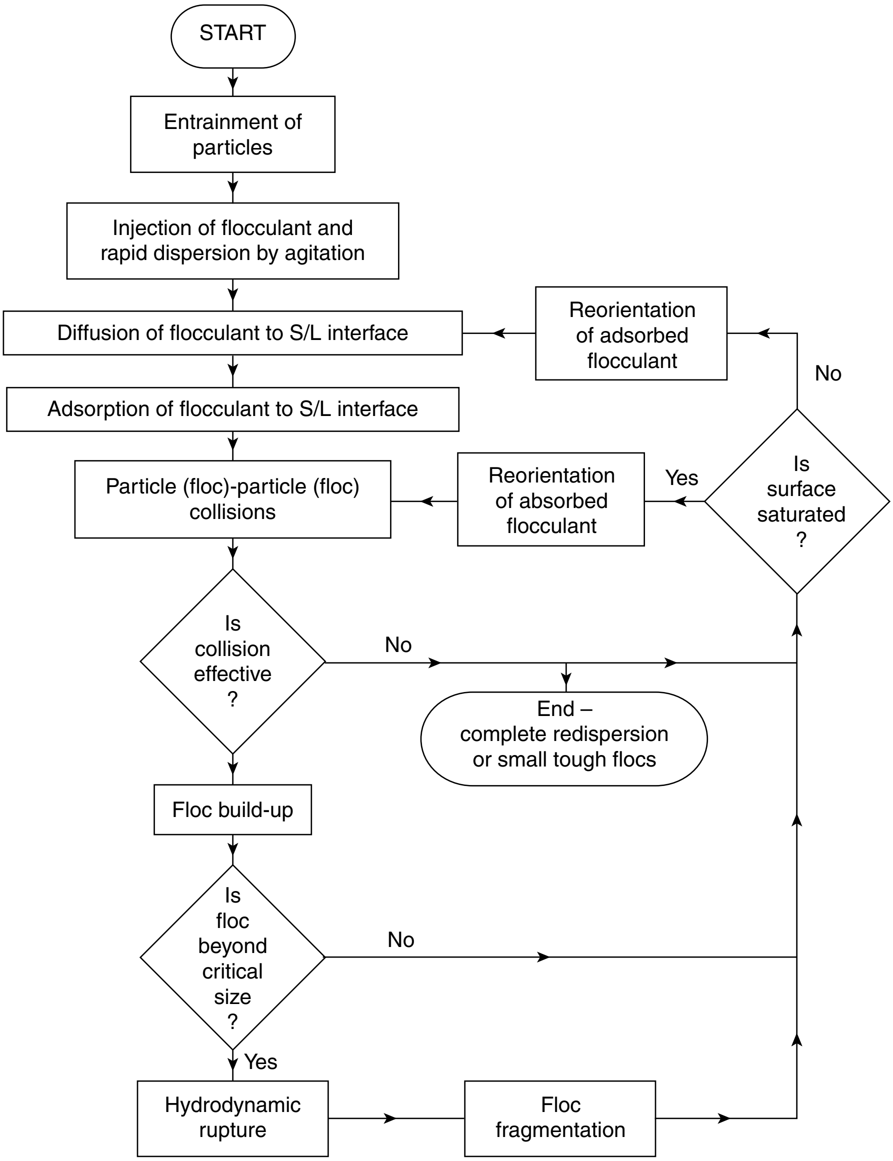


Fig. 5. Reaction flow chart for flocculation process (48).

(49). If the substrate has a high negative charge, the cationic polymer tends to adsorb in a flatter conformation than an anionic polymer, with fewer loops extending out to bridge with other particles.

In many applications, negatively charged polymers are used to flocculate particles with a negative surface charge. In this case, the cations present in the aqueous phase have a major effect because the partial adsorption of the anionic polymer on a negatively charged particle is promoted by the presence of divalent and trivalent ions (50). For example, the presence of calcium ions has a significant beneficial effect on flocculation by anionic polyacrylamides (41). Cation bridging has been proposed as the major bonding mechanism for anionic polymers to the surface of clay minerals (14). The charge density of the polymer is also critical. As the negative charge on the polymer increases, the mutual repulsion of negatively charged groups along the chain causes the molecule to have a more extended conformation and larger coil diameter that favors bridging, rather than adsorption, on a single particle. The higher charge, however, works against adsorption on negatively charged particles. Increasing the ionic strength of the medium promotes adsorption; however, the ions shield the negatively charged groups along the chain, which favors a less extended conformation. For this reason, for each combination of aqueous and solid phases there is an optimal charge on the polymer, which gives the maximum amount of bridging (51). This effect was first reported in 1954 (52). This principle is well illustrated in the Bayer process, where the residue from bauxite leaching is alternately flocculated and repulped in solutions with decreasing ionic content. As the ionic content goes down, the optimal charge, in terms of settling rate, of the anionic polymer used as a flocculant decreases (53). Differences in the composition of the aqueous phase of suspensions of similar minerals can have a large effect of flocculant performance.

In most applications, the flocs formed by these mechanisms are composed of chemically similar particles. However, in the case of retention aids the substrate is a heterogeneous mixture of cellulose fibers and inorganic fillers and pigments such as TiO_2, $CaCO_3$, and clay. The flocculant must have the ability to hold all of these together. The process may be complicated by the fact that some of this material, ie, clay, may have been treated with dispersants that can block some of the available adsorption sites on their surface (54). In some cases, however, having a heterogeneous substrate may promote flocculation, if the different components such as titanium oxide pigment and paper fibers have opposite electrical charge at the same pH. This is another example of heterocoagulation.

Combinations of cationic and anionic polymers are often used in mineral processing applications. The cationic polymer is usually added first to neutralize the charge on the particles and form charge patches. Alum or ferric salts can also be used for this purpose. These cationic sites can serve as adsorption sites for higher molecular weight anionic flocculants.

3.4. Flocculant Performance and Selection.

There is no comprehensive quantitative theory for predicting flocculation behavior that can be used for flocculant selection. This must ultimately be determined experimentally. There are three variables that affect the results obtained in any particular process that uses flocculation. These are the type of flocculant, type of substrate, and type of mechanical treatment of the flocculated substrate. The size and physical properties of the flocs that form, rather than the degree of flocculation, are the key elements in determining the practical effectiveness of a flocculant in any specific application. The effect of mechanical treatment can be viewed in terms of the type of force applied to the flocs. In thickeners and settling basins, the flocs are acted on by gravity and by the weight of material added on top of them. In vacuum filters, the flocs are subjected to atmospheric pressure. In belt presses and plate-and-frame filters, the flocs are subjected to mechanical pressure and in centrifuges they are subject to centrifugal forces. In a flowing system, such as a continuous paper machine, they are subjected to shear and elongational forces on the same scale as the particle size. In addition to the type of force that is applied to the flocs, the kinetics of floc formation also plays an important role in the results obtained in their application.

The effect of mechanical treatment on floc behavior is illustrated in Figure 6. In this work (55), identical slurries were treated with varying doses of the same polymer. At each dosage, it can be assumed that the same type of floc formed at the same rate. However, the dosage response was completely different depending on which parameter of the flocculated slurry was measured. Thus the term optimal flocculation cannot be applied to any flocculant–substrate combination if the solid–liquid separation process or process parameter is not specified.

There are some general principles that can serve as guidelines for initial screening in terms of both flocculant chemistry and molecular weight. In general, the large flocs formed by high molecular weight polymers tend to settle faster than smaller ones. Although floc density has an effect on the settling rate, it is overshadowed by the effect of size. For most substrates, high molecular weight

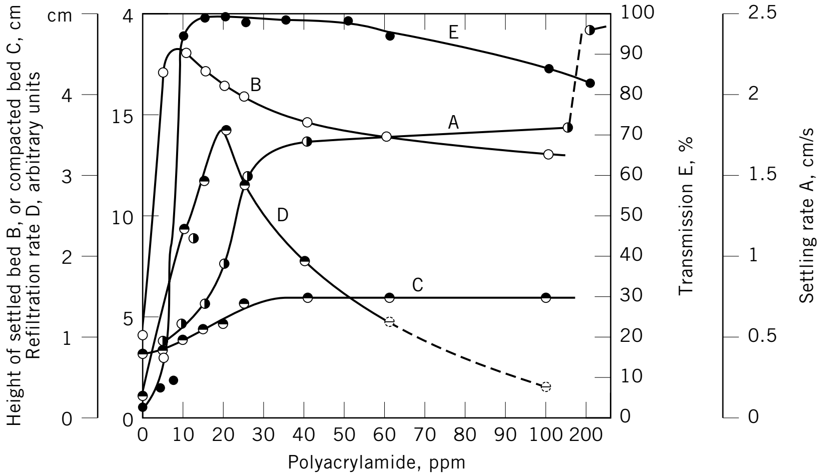


Fig. 6. Effect of polymer dosage on different observed properties of flocculated slurry (55). Comparison of five parameters in a flocculation system (8% fluorite suspension + polyacrylamide Cyanamer P 250). (**A**) Rate of settling of floc boundary, in cm/s; (**B**) height of settled bed, cm; (**C**) height of consolidated filter-cake, cm; (**D**) refiltration rate, arbitrary units; and (**E**) clarification, % optical transmission of 1 cm of supernatant liquid after 3-min settling time.

polymeric flocculants give the largest flocs, when the charge density is optimized for the particular system. In one case, the settling rate was found to be proportional to the sixth power of the polymer molecular weight (56). The rate of floc formation and the initial settling rate are very high with these high molecular weight flocculants. This may remove the flocculant adsorbed on the flocs from the system so fast that some unflocculated material is left in suspension. If this occurs in a thickener, solids may appear in the overflow, which may have an adverse effect on the process. This can often be prevented by adding the polymer in two stages. The initial dose gives small flocs that form and settle slowly, and therefore give a more complete removal of solids. The second dose forms larger flocs that give the desired high settling rate. Alternatively, a lower molecular weight polymer of the same or opposite charge can be added first to form the small flocs, which are then flocculated with a higher molecular weight polymer. Dilution of the flocculant and mixing conditions are important variables in flocculant performance (57) and the effect of these variables should be determined in any flocculant testing program.

In the case of thickeners, the process of compaction of the flocculated material is important. The flocs settle to the bottom and gradually coalesce under the weight of the material on top of them. As the bed of flocculated material compacts, water is released. Usually, the bed is slowly stirred with a rotating rake to release trapped water. The concentrated slurry, called the underflow, is pumped out the bottom. Compaction can often be promoted by mixing coarse material with the substrate because it creates channels for the upward flow of water as it falls through the bed of flocculated material. The amount of compaction is critical in terms of calculating the size of the thickener needed for a particular operation. The process of compaction has been extensively reviewed in the literature (58,59).

For most substrates, the operating dosage of flocculant necessary to give the settling rate necessary to operate a thickener is well below the maximum amount that can be adsorbed on the substrate. As more and more polymer is added above this operating dosage, the flocs can become larger and somewhat sticky. The bed of flocculated material then becomes very viscous. The rake mechanism may become overloaded and the flocculated material may not flow into the underflow pump. The dosage response and the sensitivity to overdosing may affect the selection of flocculating agent.

For filter belt presses and centrifuges, resistance to shear and mechanical pressure is the most important parameter. In general, flocs produced by charge patch neutralization are stronger than those produced by inorganic salts alone. If these flocs are broken, the cationic polymer remains strongly bound to the surface and the flocs can re-form. Very strong flocs can be made with high molecular weight polymers that bridge between particles. However, these may not re-form if broken because the bridging segments have been broken. The residual polymer fragments on the surface may even act as a dispersant by covering the particle surface, as shown in Figure 4**b**.

For vacuum filters, both the rate of filtration and the dryness of the cake may be important. The filter cake can be modeled as a porous solid, and the best flocculants are the ones that can keep the pores open. The large, low density flocs produced by high molecular weight polymers often collapse and cause blinding of the filter. Low molecular weight synthetic polymers and natural products that give small but rigid flocs are often found to be the best.

Retention aid polymers are used in a very high shear environment, so floc strength and the ability for flocs to re-form after being sheared (60) is important. The optimum floc size is a compromise. Larger flocs give better free drainage, but tend to produce an uneven sheet due to air breakthrough in the suction portions of the paper machine (49). In some cases, the type of floc needed for retention can be seen as similar to that needed for vacuum filtration. The substrate materials are the inorganic fillers and fine fibers, whereas the filter is the mat of long fibers formed on the paper machine. Floc size can be controlled by both the type of flocculant and the addition point.

General guidelines concerning the initial selection of flocculant chemistry are (*1*) suspensions of organic materials, such as municipal waste, are usually treated with a cationic flocculant, either inorganic or organic; and (*2*) suspensions of inorganic materials such as clay are usually treated with an anionic polymer or a combination of an anionic polymer with a cationic flocculating agent. There are also some special cases where particular flocculants are applied.

Acidic suspensions such as those produced by acid leaching often respond to natural products such as guar as well as nonionic polyacrylamides and anionic polyacrylamides containing sulfonic acid groups.

Poly(ethylene oxide) forms a unique type of floc with a number of substrates in the mining industry (38) such as phosphate slimes and coal refuse. These large, strong flocs release water readily when subjected to mechanical force. Extensive testing has been done by the U.S. Bureau of Mines to dewater mining wastes by flocculating with PEO and dewatering (qv) with a rotating trommel screen. However, this process has not been widely adopted on a large scale in mineral processing (qv). Poly(ethylene oxide) is also used as a component of dual retention aid systems (61).

Laboratory Flocculant Testing. The objective of laboratory testing of flocculants is to determine which chemical composition and molecular weight will give the best cost performance. The usual method is to simulate on a laboratory scale the formation of flocs and then subject them to the same or similar types of forces as would be encountered in a full-scale dewatering device. For inorganic flocculating agents, the testing may be somewhat complicated because other variables such as the pH have to be included (62). For applications in thickeners and settling basins, the substrate is usually mixed with the flocculant in a graduated cylinder using a plunger or inverting the cylinder. As the flocs form and settle there is usually a sharp boundary between clear liquid and the suspension of flocs. The settling rate is determined from the downward velocity of the interface. Initially this velocity is constant, but as the concentration of flocs increases in the lower portion of the cylinder the rate slows down because of the interaction between the flocs. The compaction of the flocculated material can be measured by measuring the height of the interface over a longer time period (63). A type of continuous flocculant test has been suggested as a replacement for the usual cylinder test. The flocculant and substrate are mixed in a Couette-type flow vessel, in which the shear rate can be varied. The settling rate and residual turbidity are then measured (63). Laboratory-scale thickeners, operated on a continuous basis, are also available to evaluate flocculant performance (64,65).

Small pumps are used to add substrate and flocculant and remove the compacted material. Transparent sides permit direct observation of floc formation. The density of flocculated red muds and other substrates can be measured using a γ-ray densitometer and the results used to evaluate flocculants and to calculate the required thickener size (66). The compressibility of the flocculated cake can also be measured by the direct application of pressure (67).

For evaluation of flocculants for pressure belt filters, both laboratory-scale filters and filter simulators are available (68,69) in many cases from the manufacturers of the full-scale equipment. The former can be run either batchwise or continuously; the simulators require less substrate and are run batchwise. The observed parameters include cake moisture, free drainage, release of the cake from the filter cloth, filter blinding, and retention of the flocculated material during application of pressure. A good correlation with performance of flocculated sludges on a belt filter was claimed for a patented filtration device (44).

Vacuum filters are usually simulated with a Buchner funnel test or filter leaf test (70). The measured parameters are cake weight, cake moisture, and filtration rate. Retention aids are evaluated by a number of different methods (71).

4. Operating Parameters and Control

Flocculating agents differ from other materials used in the chemical process industries in that their effect not only depends on the amount added, but also on the concentration of the solution and the point at which it is added. The process streams to which flocculants are added often vary in composition over relatively short time periods. This presents special problems in process control.

4.1. Dilution.

In many applications, dilution of the flocculant solution before it is mixed with the substrate stream can improve performance (57). The mechanism probably involves getting a more uniform distribution of the polymer molecules. Since the dosage needed to form flocs is usually well below the adsorption maximum, a high local concentration is effectively removed from the system at that point, leaving no flocculant for the rest of the particles. A portion of the clarified overflow can be used for dilution so no extra water is added to the process.

4.2. Addition Point.

The flocculant addition point in a continuous system can also have a significant effect on flocculant performance. The turbulence as the flocculant is mixed in and the flocs travel toward the point where they enter the thickener or filter causes both the formation and breakup of flocs. Usually, there is an optimal addition point or points that have to be determined empirically. In cases where the same polymer is being added at two or more points, the relative amounts added at each point may also affect performance. Thus providing multiple addition points in the design of new installations is recommended. The flocculant addition point is one variable in a computational fluid dynamics model of a thickener (72).

4.3. Automatic Control and Instrumentation.

In some industries, the waste streams can vary in composition over a relatively short time period. When the solids level of a slurry changes, the entire dosage response may change. Automatic systems are available for thickeners that adjust the dosage according to the incoming solids level, overflow turbidity (74,75), and streaming current potential (62,75,76,). Appropriate control software is used, which takes into consideration response times, flow rate, and other factors (62). These systems can improve operation and reduce flocculant usage (77). There are a number of methods for determining the degree of flocculation in a continuous system. (78) Sensors of this type are useful in continuous processes, where a sudden shift in floc size caused by a dosage change could be a serious problem.

5. Analytical Methods

Inorganic flocculants are analyzed by the usual methods for compounds of this type. Residual metal ions in the effluent are measured by spectroscopic techniques such as atomic absorption. Polymeric aluminum species formed in solution have been characterized by ^{27}Al nmr (79).

The detection of organic polymers in solution represents a more difficult problem, especially in industrial water and wastewater. Many methods have been devised for the detection of low levels of acrylamide polymers. (80,81) In theory, charged polymers react with polymers of the opposite charge in solution and such reactions can be used to titrate the concentration of polymer present. There are a number of techniques using this method (81). Methyl quaternized cationic polymers can be detected by nmr (82). Polymers can also be labeled with fluorescent chromophores (83) or radioactive monomers (84). However, the radicals generated by the radiation will cause rapid degradation of high molecular weight polymers. If the molecular weight is high enough, flocculation of a standard slurry of clay or other substrate is a sensitive method for detecting low levels of polyacrylamide (85). Once polymers are adsorbed on a surface, many of these methods cannot be used. One exception is the use of a labeled polymers (83).

The molecular weights and molecular weight distributions of lower molecular weight polymeric flocculants are determined by viscosity measurements, such as the intrinsic viscosity, and by size exclusion chromatography (62). High molecular weight acrylamide-based polymers are characterized by light scattering techniques (62). ^{13}C nmr can be used to determine sequence distribution (86) and the composition of polyacrylamides and their hydrolysis products (62).

6. Health and Safety Factors

There are several routes by which the human population is exposed to flocculating agents and to impurities contained in them. The most direct path is the use of these chemicals to treat public drinking water supplies. A major issue in recent years is a possible link between dietary aluminum and Alzheimer's disease. This stems from the finding of high aluminum levels in the brains of deceased Alzheimer's patients and epidemiological evidence (87) linking the aluminum level in drinking water with the incidence of Alzheimer's disease. In recognition of the possible toxicity of aluminum, limits have been placed on residual aluminum. The maximum permissible aluminum in the 1998 European Drinking Water

Directive is 200 μg/L, with a guide level of 50 μg/L (88). In the United States, the Environmental Protection Agency (EPA) Secondary Maximum Contaminant Level is 50–200 μg/L with state agencies making the final limits (9). The speciation of aluminum in natural waters is quite complex, depending on such variables as pH, temperature, presence of organic compounds (humates), and inorganic ions (fluoride) (89). Some natural waters used as drinking water and not treated with aluminum compounds had levels ~ 50 μg/L (89). The speciation of aluminum in treated water is also complex (9,11). In some cases, the aluminum content was correlated with suspended solids and could be reduced by using a polymeric flocculant followed by filtration. The level of soluble residual aluminum in alum treated water can be reduced by adjusting the pH to minimize the solubility of aluminum. Although their principal advantage is better flocculation with reduced sludge volume, prepolymerized aluminum reagents leave less residual aluminum in the treated (12a,12b), aluminum from drinking water is not the only source of dietary aluminum (90).

Based on animal studies and mutagenicity studies, trace amounts of organic polymers do not appear to present a toxicity problem in drinking water (91). The reaction products with both chlorine and ozone also appear to have low toxicity (92). The principal concern is the presence of unreacted monomer and other toxic and potentially carcinogenic nonpolymeric organic compounds in commercial polymeric flocculants. The principal compounds are acrylamide in acrylamide-based polymers, dimethyldiallyammonium chloride in allylic polymers, and epichlorohydrin and chlorinated propanols in polyamines. In most cases, the concentrations of unreacted monomer and organic contaminants can be kept very low by controlling the manufacturing process. Careful analysis and quality control in production are therefore essential to the safe use of polymeric flocculants. The mandatory standard for acrylamide in the 1998 European Drinking Water Directive is 0.10 and 0.10 μg/L for epichlorohydin (88). Control is by product specification. There has also been concern over the presence of trace metals in by-product inorganic flocculating agents, especially ferric salts that are mainly produced as industrial by-products (93). In the United States, standards for drinking water treatment chemicals have been issued by a consortium of private organizations and the EPA under the direction of National Science Foundation (NSF) Internationsal. The most recent revision is dated Sept. 2003 (94). The limits for acrylamide and epichlorohydrin are 0.5 and 2 μg/L, respectively. A guideline level of 2 mg/L is given for aluminum. Flocculating agents can also come under FDA regulations. Flocculants used in sugar refining are classified as direct food additives and materials used in paper manufacture are classified as indirect food additives, because paper is used in food packaging.

As widely produced industrial chemicals, flocculating agents are subject to the Toxic Substance Control Act. Water soluble polymers have the potential for aquatic toxicity. Anionic polymers show some algicidal effects, probably due to chelation of trace nutrient metals (95). On the other hand, laboratory studies have shown that cationic polymers are toxic to fish because of the interaction of these polymers with gill membranes. This is especially important in the area of municipal and industrial wastewater treatment, where large amounts of cationic polymer are used and there is a possibility of residual flocculating agents in the effluent. Many studies have shown that in natural systems the suspended inorganic matter and humic substances form complexes with the polymer and substantially reduce polymer toxicity. Based on these results, the EPA has added a protocol for testing these polymers for toxicity toward fish in the presence of humic acids (95). This mitigation of toxicity may not apply under certain conditions, such as the presence of high amounts of oligomer and at low pH (95). The addition of anionic polymers to effluent streams containing cationic polymers to reduce their toxicity has been mentioned in the patent literature (96).

7. Economic Aspects

Analyzing market trends for flocculating agents is somewhat difficult, because of the way chemical markets are classified and sales data are reported. When classified in economic terms, most flocculating agents fall into the category of water treatment chemicals. However, not all water treatment chemicals are flocculating agents. Synthetic organic polymers used in water treatment include ion exchange resins, antiscalants as well as polymeric flocculating agents, which are sometimes called "organic coagulants".

However, the "organic coagulants" market may not include other polymeric flocculating agents such as those used in coal and mineral processing and alumina production, or as retention aids, or in soil erosion prevention. In the case of inorganic salts, sales data only reflects which industry products are sold into, rather than the specific function that they are used for.

The U. S. water treating market for specialty chemicals was estimated, in 2002, to be $ 2.8 billion (97), with a worldwide market of $5 billion. Another estimate made in 1998 was $2.95 billion for the U. S. market with a world market of $6.2 billion (8). The same source gave a 1998 U. S. market for organic coagulants and flocculants to be $405 million with a world market of $1.05 billion. However, these figures did not include the paper industry. The estimated growth rate for polymeric flocculants was given as 6.5%, for alum 2–5% and PAC 10–15%. Overall ~ 45% of the aluminum salts are used in paper, with another 45% being used to treat municipal wastewater (97). In 1999, the total U.S. market for polymeric flocculants (including the paper industry) was given as $1.3 billion (98). Table 1 lists the principal manufacturers of polymeric flocculants in the United States Organic polymers were roughly 70% of the total, divided between acrylamide-based polymers at 50% and other polymers at 20%. Inorganics such as alum, PAC, and iron salts made up the remaining 30%. Growth in organic flocculants was estimated to be 6.5%. In another source, the value of the organic flocculants used for waste treatment in the United States (primarily cationic polymers) is estimated to be ~$130 million (62). The growth in polymeric flocculants has been stimulated primarily by requirements to dewater municipal waste to higher cake solids and to reduce suspended solids in drinking water. High molecular weight cationic polyacrylamides produce strong flocs that can be readily dewatered to give a low moisture cake (97). The growth in inorganics has been stimulated mainly by the need to reduce soluble organics in drinking water prior to chlorination and to remove phosphate from municipal wastewater (13). In these two applications, aluminum and iron compounds are not acting primarily as flocculating agents.

Table 1. **U.S. Producers of Organic Polymer Coagulants and Flocculants for Water Management—2001**

Company and headquarters	Polyacrylamides					Quaternary ammonium polymers
	Liquids	Powders	Emulsions	Mannichs	Polyamines	
Ashland Specialty Chemical Company (formerly Ashland Inc.)						
Drew Industrial						
Boonton, N.J.	X		X			X
Baker Petrolite Corporation						
Dallas, TX				X		
St. Louis, Mo.			X		X	X
Buckman Laboratories, Inc.						
Memphis, Tenn.			X	X	X	
Calgon (ONDEO Nalco/Suez)						
Pittsburgh, Pa.	X	X	X	X		
Chemtall, Inc. (S.N.F. Floerger)						
Riceboro, Ga.		X	X			
Ciba Specialty Chemicals Corporation						
Water Treatment Division						
Old Bridge, N.J.						X
Suffolk, Va.		X	X			
Cytec Industries Inc.						
Wayne, N.J.	X	X	X	X	X	X
Noveon, Inc.						
Akron, Ohio	X	X				
BetzDearborn[a] (Process Chemicals and Services Division of Hercules)						
Trevose, Pa.	X			X		X
ONDEO Nalco (Suez)						
Naperville, Il.	X	X	X	X	X	X

Table 1 (*Continued*)

Company and headquarters	Polyacrylamides: Liquids	Powders	Emulsions	Mannichs	Polyamines	Quaternary ammonium polymers
Secodyne Corporation (S.N.F. Floerger) Detroit, Minn.	X			X		
Stockhausen, Inc. (Degussa) Greensboro, N.C.		X	X			
Vulcan Chemicals Vulcan Performance Chemicals Division Columbus, Ga.	X		X		X	

[a] In February 2002, General Electric announced its intention to acquire BetzDearborn from Hercules.

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