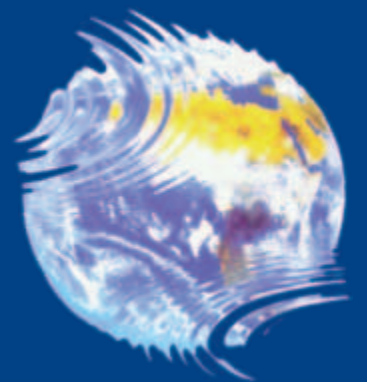


Water Soluble Polymers



Water soluble polymers cover a wide range of highly varied families of products of natural or synthetic origin, and have numerous uses.

Among these families, synthetic polymers, and more particularly coagulants and flocculants, are used mainly for facilitating the separation of materials in suspension in aqueous media. They also help to dewater sludge from various separation processes.

The separation of solids in a liquid medium takes place rapidly when the density of the particles is markedly different from that of the liquid medium. Either the particles settle out or they float on top of the liquid.

Difficulties occur when the particle size allows it to remain in suspension in the liquid medium. In this case, the use of coagulants and flocculants allows separation to be carried out.

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6 *Basic principles of colloid science*

In liquid media and more particularly aqueous media, organic or inorganic materials are present in dissolved or solid form.

These two forms are distinguished by the size of the particles.

Dissolved compounds are:

- *Inorganic compounds, ions and/or organic compounds of low molecular weight with a particle size of at most 10^{-3} μm ;*
- *Soluble organic compounds of high molecular weight, such as proteins or polymers, with a slightly larger particle size of between 10^{-3} and 10^{-2} μm .*

Solid compounds are:

- *Colloids with a particle size of between about 10^{-2} and 1 μm ;*
- *Materials in suspension with a particle size of more than 1 μm .*

III-1 Colloidal suspensions

Colloidal particles, invisible to the naked eye, undergo high-speed Brownian motion - the speed is between 0.004 m/s in the case of the largest particles and 100 m/s in the case of the smallest. These particles also have a very high specific surface area (inversely proportional to the particle diameter). They are therefore more sensitive to surface phenomena than to gravitational forces. Thus, the largest colloid particles will have a natural settling time over a depth of 1 m of water of about two years.

Colloidal particles can therefore form suspensions which are very stable over time.

The stability of a colloid suspension depends on the equilibrium between two types of opposing forces involved. These are Van der Waals'-type force - the universal attractive force between atoms and molecules, - and an electrostatic interaction force.

These two forces act differently depending on the intrinsic nature of the colloids, which are either hydrophilic, i.e. water molecules are adsorbed onto their surface, or, conversely, hydrophobic.

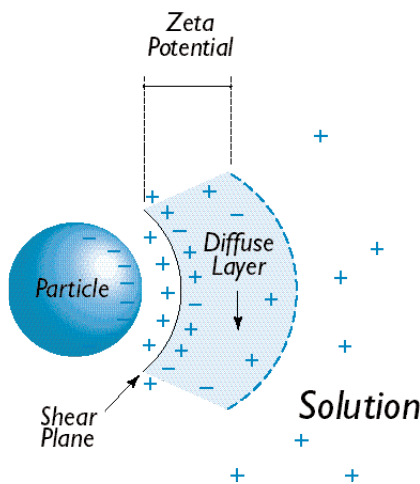
III-1-1 Hydrophobic colloids

Colloids of a hydrophobic nature (for example, clays) form stable suspensions because their surface charge is the same and they repel each other. These charges may come from selective adsorption of an ion onto the surface or from the surface itself (crystal lattice defects).

The surface of the electrically charged particle is at a different potential from the solvent medium. Electrostatic equilibrium between the surface of the particle and the solvent medium is achieved by means of two transitional layers.

The first layer is fixed and remains attached to the surface of the particle. The second layer, separated from the first by a shear plane, is more diffuse.

Figure 1 – Equilibrium layers of a colloidal particle



The potential difference between the shear plane and the solution is called the zeta potential. This potential difference is about 10 to 200 mV. When it is reduced to zero or close to zero (the isoelectric point), the particles tend to agglomerate under the influence of the Van der Waals' forces and the colloidal suspension becomes destabilized.

III -1- 2 Hydrophilic colloids

Colloids of a hydrophilic nature (generally organic substances) owe their stability to the layers of water molecules bonded to the surface of the particle. The bonds are of a chemical nature and the electrostatic charges play only a secondary role. The layers of water molecules prevent any agglomeration between particles. In this case, there is no real interface between the particle and the solvent medium.

The charges have an influence on the solubility of hydrophilic colloids. The importance of the role of the charges depends on the degree of ionization of the particle's functional groups. The degree of ionization itself depends on the pH of the medium. In general, the solubility is a minimum around the isoelectric point, which corresponds to a pH of between 4.0 and 6.5.

Hydrophilic colloidal suspensions therefore are akin to an actual solution of very large molecules or of aggregates of small molecules, with a very high affinity for the solvent.

In some cases, hydrophilic colloids can be adsorbed onto the surface of hydrophobic colloids, such as clays for example, and thus impart a hydrophilic nature to the hydrophobic particle. Such colloidal suspensions are then very difficult to destabilize.

III-2 Measurement of the colloid concentration

There are no direct measurements of the colloid concentration.

The colloidal particles can be directly observed with a microscope. They are visible indirectly by light reflection or the Tyndall effect, which is why colloidal solutions are turbid.

The turbidity may be quantified by nephelometry, a relative measurement expressed in NTU (Nephelometric Turbidity Unit) with respect to a calibration solution of formazine in water which has zero turbidity (French Standard NFT 90.053).

8 *Coagulation and flocculation*

The conventional methods of solid-liquid separation, such as filtration, sedimentation, centrifugation and flotation, cannot be used directly on stabilized suspensions. The particles are too fine and remain separated from each other. Coagulation and flocculation destabilize these suspensions and allow solid-liquid separation.

Two mechanisms are mainly involved, namely charge neutralization and adsorption.

IV-1 Charge neutralization

In aqueous media, hydrophobic colloidal particles are generally negatively charged. The increase in the cation content of the solution reduces the zeta potential and therefore the thickness of the double layer which surrounds the colloidal particle.

When the electrical protection of the particles has been removed or sufficiently reduced, the moving particles can collide with each other due to the momentum of Brownian motion, the movement of the fluid in which they are contained and the relative movement of the particles by sedimentation.

The Van der Waals' forces and the surface adsorption phenomena then become dominant again. Since the particle can bond together, the suspension is destabilized.

This charge neutralization mechanism is reversible. There is a limiting cation concentration which allows destabilization to occur. Above this critical concentration, if cations continue to be added, a new ionic imbalance between the particle and the solution may be created, leading to the formation of a new double layer and to the restabilization of the suspension.

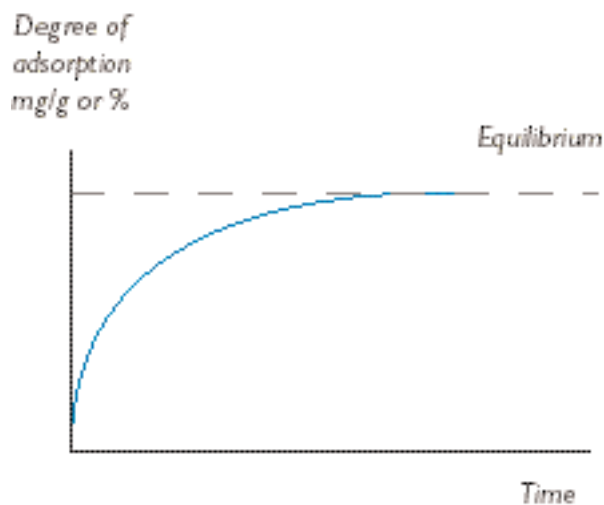
The charge neutralization efficiency of an electrolyte increases with its valency (the Schulze and Hardy rule). This explains the predominant use of bivalent or trivalent electrolytes for destabilizing colloidal suspensions.

IV-2 Adsorption

Adsorption is a surface mechanism which allows two contacting particles to be bonded to each other by Van der Waals' forces or hydrogen bonds.

Measuring the amount of polymer adsorbed by a colloidal suspension as a function of time allows a characteristic curve, called a Langmuir isotherm, to be plotted:

Figure 2 – Adsorption isotherm



The characteristic curve is called an isotherm since the adsorption is strongly dependent on the temperature and any measurement must be carried out at constant temperature.

Adsorption is an irreversible mechanism which takes place in two steps. Firstly, after a few seconds, most of the reaction has taken place. After a relatively long second step, a balance is achieved, which is limited by the number of sites available on the surface of the particle. When all the available sites are occupied, no further molecule can be attached to the surface of the particle.

Adsorption is a complex mechanism involving a large number of parameters relating to:

The coagulant:

- structure of the molecular chain
- ionic charge density
- molecular weight

The colloids:

- number of available sites
- surface charges
- specific surface area
- particle concentration

The aqueous medium:

- pH
- conductivity
- presence of other substances
- turbulence
- shear rate temperature
- mixing of the products

The complexity of this system explains the difficulties still encountered at the present time in understanding and modelling this phenomenon. The experimental approach remains indispensable.

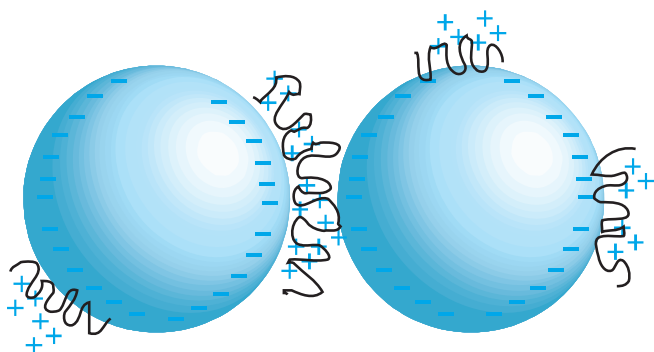
IV-3 Suspension destabilization by coagulation

Coagulation is the destabilization of a colloidal suspension using products with a high ionic charge density. Two types of mechanisms may occur.

In a first type, the cations are added to the colloidal suspension in an amount just equal to neutralize the negative charges. Coagulation occurs directly by charge neutralization. This type of coagulation is extensively used in the treatment of potable water with iron or aluminium cations.

A second type of coagulation is achieved using polymers of Low Molecular Weight (LMW = 20,000 to 1 million) with a high cationic charge. When this type of polymer is in contact with anionic particles, its chains may be entirely adsorbed onto part of the surface of the colloidal particles thus forming regions of a cationic nature.

Figure 3 – Coagulation using a LMW polymer



This adsorption of oppositely charged ions reduces the surface potential and the protection of the particles. Having become true dipoles, these particles are attracted to each other and collide with each other. The Van der Waals' forces then come into play, binding the two particles and destabilizing the suspension.

Coagulation by this type of mechanism generally has higher degrees of aggregation than those of the simple electrical neutralization mechanism.

IV-4 Suspension destabilization by flocculation

Flocculation is the destabilization of a hydrophobic colloidal suspension by bonding between colloidal particles using long polymer chains.

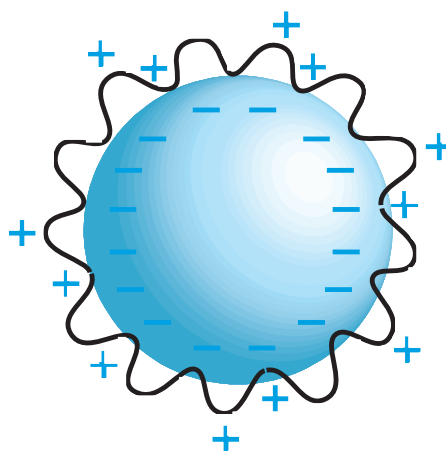
This requires the use of polymers with a high molecular weight (greater than 1 million) and takes place in two main steps: floc initiation and floc growth.

IV-4-1 Initiation of flocs

To initiate flocs, the polymers essentially act via a mechanism of irreversible adsorption of the colloids along their molecular chain. The effect of this mechanism depends on the concentration of polymer, the concentration of particles and the particle size.

If an excess of polymer covers the surface of the particle, the particle will once again be isolated and the suspension will restabilize.

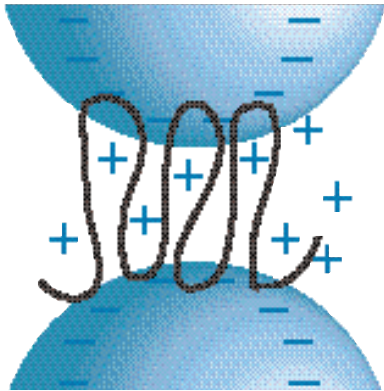
Figure 4 – Isolation of a particle by a polymer



In the case of a suspension containing particles which have a wide particle-size distribution or several particle size distributions, the suspension may be restabilized for different polymer concentrations corresponding to the different particle-size distributions. Thus, good results may be achieved using a given polymer for one particle size, but not for another. As a general rule, when this phenomenon occurs, relatively good flocculation is observed but the solution remains very cloudy.

If the polymer concentration is such that adsorption sites remain free on the particles, the same polymer chain may be able to be adsorbed onto two different particles:

Figure 5 – Bridging between two particles



In this mechanism, the polymer allows part of its molecular chain to uncoil in the solution beyond the particle's double layer. The free end of the molecular chain is in turn adsorbed onto the surface of a second particle, which thus creates bridging between the two particles.

In general, it is found that the optimum polymer concentration must be such that more than half the adsorption sites remain available on the particles.

The length of the completely uncoiled polymer chains is about $1\ \mu\text{m}$, possibly as much as a few tens of μm in the case of the longest chains. These lengths should be compared with the dimensions of the particles, which are about $1\ \mu\text{m}$.

Inter-particle bridging can occur with nonionic, cationic or anionic polymers. In these mechanisms, the charge neutralization phenomena have a secondary influence. This explains why flocculation reactions can occur with polymers carrying charges of the same sign as the colloidal suspension.

The charges may have an influence which promotes better uncoiling of the polymer chains due to the effect of electrostatic repulsion. The shape of the polymer chain may also be a key factor in this process.

The ionicity of the solution may also influence chain uncoiling by limiting or eliminating the repulsion effect. This phenomenon is known as the counterion effect or salt effect.

For a given polymer, bridging mainly depends on two parameters: the number of sites available for adsorption on the surface of the particle and the rate of collision of the particles.

IV-4-2 Kinetics of floc development

Depending on the mechanisms described above, development of the flocs takes place in several sequential steps:

- Dispersion of the polymer in the medium
- Diffusion of the polymer towards the solid-liquid interface
- Adsorption of the polymer onto the surface of a particle
Collision of particles carrying an adsorbed flocculant with another particle
- Adsorption of the flocculant onto a second particle in order to form a bridge and a microfloc
- Growth of the microflocs by successive collisions and adsorptions
- Breaking of the flocs formed, by shear.

Each step takes place according to its own kinetics and the final result, in terms of the floc, depends on the relative rates of the various steps. Thus, for example, if the adsorption phase is much more rapid than the growth phase, there will be many small flocs whereas, if the growth rate is higher, the flocs will be larger and fewer in number.

In general, adsorption reactions are extremely rapid. The limiting step in the development of flocs is mainly due to the frequency of collision between particles and collisions with flocs already formed.

IV-4 -3 Consistency of flocs

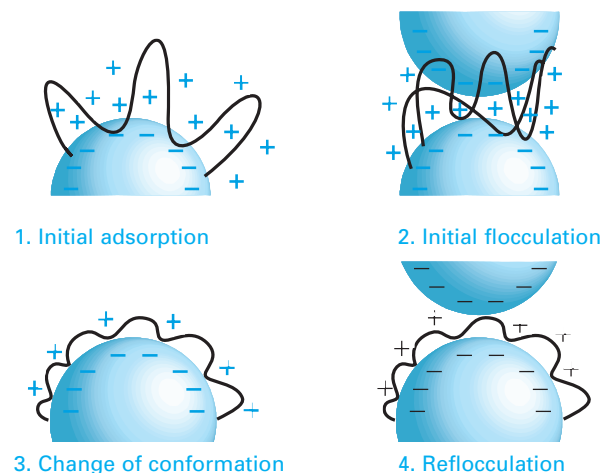
Flocs can be of two types consistencies, namely “soft”, which are reversible, and “hard”, which are irreversible.

When a floc provides good retention of fine particles for low shear rates in a quiescent zone, as the shear rate increases the retention of the fine particles decreases. On returning to the initial shear conditions, if the floc resumes its initial structure, it is called a soft floc. Soft flocs are generally obtained with polymers of low molecular weight.

A hard floc, is stronger, maintains good retention of fine particles over wider turbulence and increased shear. However, when it is subjected to high turbulence for an excessive length of time, the retention of fine particles decreases. The floc then becomes soft.

The assumed reasons for this phenomenon stem from the configuration of the polymer chains on the surface of the particle. A hard floc is composed of particles connected by bridging via molecular chains which uncoil in the space around the particle:

Figure 6 – Hard floc by double flocculation



After shear, the molecular chains, due to the influence of the ionic forces, have a tendency to cover more of the surface of the particle, giving, by bridging, a floc of soft consistency.

IV-5 Other suspension destabilization systems

Three other systems are also encountered - still employing the two basic mechanisms, namely charge neutralization and adsorption.

IV -5-1 “Encapsulation” systems

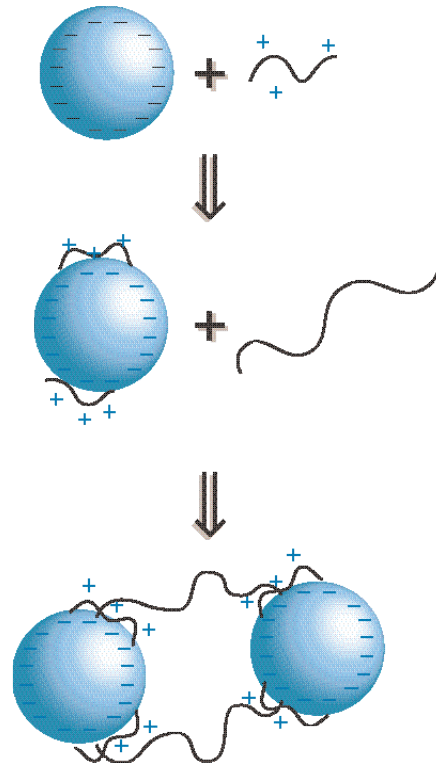
The bridging system described above is based on the primary interaction between a polymer chain and the particle in order to initiate flocculation. As regards encapsulation mechanisms, these occur when two or more polymer chains react first of all with each other due to the influence of electrostatic interactions or of hydrogen bonds. This reaction produces a network of crosslinked polymer chains which mechanically trap the particle. In this mechanism, which is not very well understood, the electrostatic interactions between the particles and the polymer do not play an important role.

IV-5-2 Two-polymer-component coagulation systems

The sequential addition of two polymers of opposite charge allows very good coagulation to be achieved. In practice, a cationic polymer of low or moderate molecular weight is firstly introduced into the solution, followed by an anionic polymer of high molecular weight.

The low-molecular-weight cationic polymer is adsorbed onto the particle to form cationic regions onto which the high-molecular-weight anionic polymer may be fixed. The anionic molecular chain tends to uncoil in the solution due to the effect of charges of the same type carried by the particle. Eventually the chain is adsorbed onto other particles via bridging.

Figure 7 – Two-component coagulation



It is important for a slight excess of cationic polymer to remain in solution when the anionic polymer is added. If it does not, the polymers can react with each other in the liquid phase and form a gel.

IV-5-3 Microparticulate systems

Microparticulate systems generally involve a cationic polymer and fine inorganic anionic particles (bentonite, silica, etc.).

They allow small, very strong, flocs to be obtained which do not retain water.

IV-6 Efficiency of flocculation and coagulation

The efficiency of coagulation and flocculation is essentially measured by the size of the flocs and their characteristics, the amount of flocculated or coagulated matter in suspension and the turbidity of the supernatant liquid.

These various parameters depend on the specific characteristics of the flocs, and also on the separation processes used. In order to measure the efficiency of flocculation, it is therefore necessary to carry out tests according to the separation process employed.

Table I gives the main characteristics of flocs for various separation processes:

Table I

Separation	Characteristics of the flocs
Filtration	Porous, strong, permeable
Sedimentation	Dense, strong, large, uniform shape, minimal porosity
Centrifuging	Strong, dense, large
Flotation	Low density, strong uniform size, large

IV-7 Parameters having an influence on the efficiency of flocculation and coagulation

The efficiency of coagulation and flocculation depends on many parameters relating to the particles, the polymers used and the solution to be treated.

To date, many studies have appeared on the subject, particularly aiming to provide simplified models which allow extrapolation.

Without attempting to give all the parameters that influence the efficiency of coagulation and flocculation, the following are the main ones.

IV-7.1 Influence of the particles

Usually, flocculation occurs for individual particles smaller than 50 μm . Large particles (greater than 100 μm) generally do not flocculate since the collision rates are too low. It is difficult for the polymers to become fixed to their surfaces during collision and the rate of breakage of the flocs formed is very high.

However, flocculation of large particles can take place using suitable polymers with a very high molecular weight.

Depending on their nature and their concentration, the flocculation of suspended matter is:

- Either diffuse, in which all the flocs are separated and of different size. The large flocs settle rapidly, leaving the finer flocs and microflocs in suspension, these being unable to settle and often leave a settling tank via its overflow. The flocculation times are long-between about 1 and 15 minutes;
- Or homogeneous, in which the flocs are of similar size and settle at the same rate, leaving a clear interstitial water.

In the case of clays for example, the flocculation is diffuse for a concentration of less than about 2 g/l and homogeneous type for a concentration of about 2 to 5 g/l.

Above a certain concentration, flocculant-suspension mixing no longer occurs and no floc appears.

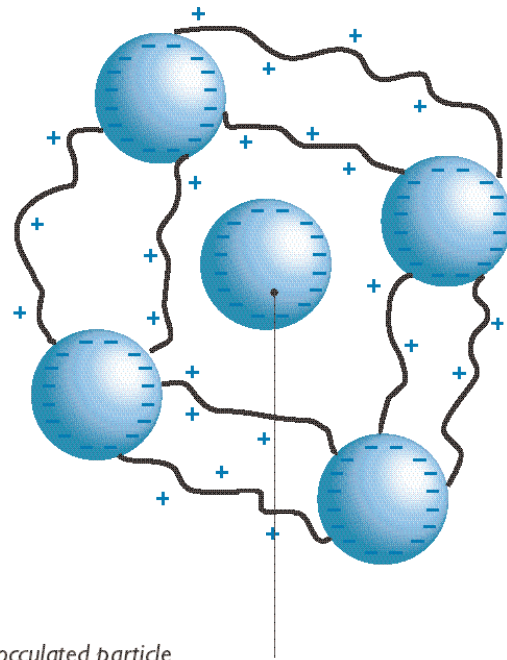
The particle concentration in the suspension has an effect on the nature of the phenomena involved. In general it is found that at low particle concentrations the dominant phenomena involve charge neutralization, whereas, for higher concentrations, the phenomena of adsorption and bridging are dominant. Moreover, the flocs formed with a high particle concentration are stronger and contain a higher concentration of suspended matter.

IV-7- 2 Influence of the polymers

The nature of the polymer is the main element in flocculation. In this case, three main characteristics are involved the molecular weight, the concentration and the ionic charge.

In general, the efficiency of the polymer is greater the longer its molecular chain, the chain length depending on the molecular weight and on the spatial configuration of the molecule. The longer the chain, the greater is the possibility of creating bridging and the smaller the amount of polymer used for the same result. In addition, high-molecular-weight polymers can have a secondary effect: the filter effect, in which an unflocculated particle becomes trapped in the floc mesh. The structure of the chain (linear, branched or crosslinked) also plays an important role.

Figure 8 – Filter effect



Unflocculated particle

However, the molecular chains must not be too long as their efficiency is limited by problems of diffusion in the solution and of steric hindrance. Furthermore, increasing the chain length has the effect of increasing the viscosity of the solution and the time required to dissolve the polymer.

These polymer diffusion and dissolution problems also depend on the necessary dosage to be used (the amount of polymer per tonne of dry matter). The appearance of the floc allows the right dosage to be determined. For example, on a filter, a matt appearance indicates good flocculation, whereas a shiny appearance indicates that too much polymer has been added.

In practice, for a high or moderate dosage (polymer quantities of between 1 kg and 10 kg per tonne of dry matter for municipal sludge), the size of the floc particles is directly related to the molecular weight of the polymer. The higher the molecular weight, the larger the floc. On the other hand, for low dosages, polymers of moderate molecular weight give better results because of the poor mixing of high-molecular-weight polymers and their tendency to retain unflocculated particles.

The influence of the polymer charge on the flocs is expressed in relation to the ionic demand of the medium. Weaker charges give flexible flocs, having good shear strength, but their filtration properties are not exceptional. On the other hand, a moderate or stronger charge gives better filtration properties, but the flocs obtained are more shear-sensitive.

One particular case consists of flocculation in a high-pressure centrifuge. In this case, the polymer must be present in the free form over the entire amount of sludge to allow both initial flocculation and re-flocculation after the initial flocs have been sheared. In this case, any excess polymer must not produce a sludge redispersion effect.

IV-7-3 Influence of polymer mixing in the solution

The conditions under which the polymer is mixed in the solution are fundamental to achieving good coagulation and flocculation.

Since the adsorption reactions are irreversible and very rapid, the quality of mixing must be high enough to allow rapid diffusion of the polymer in the suspension. Moreover, since the polymers are generally used in concentrated form and in small quantities, they must be distributed uniformly throughout the medium.

An experimental compromise therefore has to be found so that, depending on the points at which the polymer is injected, the quality of mixing is satisfactory without shearing the flocs which are forming. Because, above a certain size, the flocs become very shear-sensitive.

Because of their intrinsic shear strength and the shear rate in the medium, the flocs can break up and become smaller flocs or even individual particles. Over time, an equilibrium is established between the formation and disappearance of the flocs.

The hydrodynamic state of the solution is also important for mixing. Flocculation gives good results in laminar or turbulent-flow. In the latter, smaller flocs result due to shearing. In the interim state, the performance is unpredictable.

IV-7-4 Influence of the pH and the temperature of the solution

We have seen that the pH of the solution has a direct effect on the behaviour of the polymer chains. It can also have other effects:

Adjusting the pH of the solution allows metal hydroxides to be precipitated, and these may directly interfere with flocculation, for example by capturing the colloids.

Hydrolysis, and therefore the ionic charge of the polymer, depends on the pH.

Strongly anionic polymers are very effective in basic medium, but their performance is not as good in acid medium because the carboxylate/carboxylic functional groups do not dissociate in such a medium. Nonionic or moderately cationic polymers are the best performers in acid medium.

The temperature of the solution directly influences the kinetics of the reactions involved and the activity of the colloids. Thus, lowering the temperature reduces flocculation.

IV-7-5 Influence of the organic nature of the suspension

A final important factor regarding the suspension is its organic nature. In general, the more organic the nature of the suspension the greater the cationicity of the polymer. Conversely, anionic polymers are more effective in inorganic solutions.

IV-8 Advantages of synthetic coagulants

Well known for their higher unit cost than inorganic substances, organic polymers prove, in many cases, to be more economical to use than inorganic substances because of their following specific advantages:

- The amounts needed are generally 10 times lower than those of inorganic substances;
- They do not increase the amounts of solid matter to be removed and therefore help to minimize the cost of treating the residual sludge;
- The flocs obtained using organic polymers have a higher shear strength than those formed using inorganic substances, inter-particle bridging resulting from stronger elastic bonding;
- The flocs obtained using inorganic coagulants are not very compressible. They therefore take up more space on a filter medium and rapidly increase the head loss;
- Organic polymers are less sensitive to pH variations and can therefore be used for treating a greater variety of water types;
- Organic polymers help to reduce the amount of trivalent salts dissolved in the water (in particular, there is a fear of aluminium because of Alzheimer's disease);
- Synthetic polymers can be used together with inorganic substances, the organic polymers mechanically reinforcing the structure formed by the inorganic substance.

18 Water soluble polymers

V-1 Coagulants

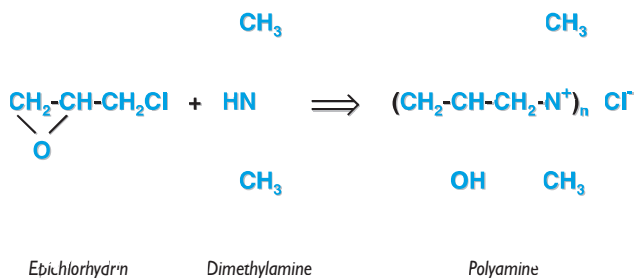
The two main characteristics of a coagulant are:

- a very high cationic charge, to neutralize the negative charges of the colloids
- a relatively low molecular weight, to allow rapid diffusion in the medium and around the particles.

Three large families of products are used, namely quaternary polyamines, polyDADMAC and dicyandiamide resins.

V-1-1 Quaternary polyamines

The condensation reaction of epichlorhydrin with a primary or secondary amine, usually dimethylamine, produces a polymer of moderate molecular weight in which all the nitrogen atoms are in quaternized form:



Controlling the addition of monomer into the reactor allows the molecular weight to be varied.

The addition of polyamines allows the branching and total length of the chain to be controlled.

Polyamines differ from other polymers because the cationic charge is on the main chain.

Such polymers have the following characteristics:

- Molecular weight between 10,000 and 1,000,000
- Liquid form with 40 to 50% concentration
- Cationic site on the main chain
- Viscosity at 50% of between 40 and 20,000 centipoise
- Chlorine stability
- Compatibility with inorganic coagulants
- Good storage stability
- Use with or without pre-dilution.

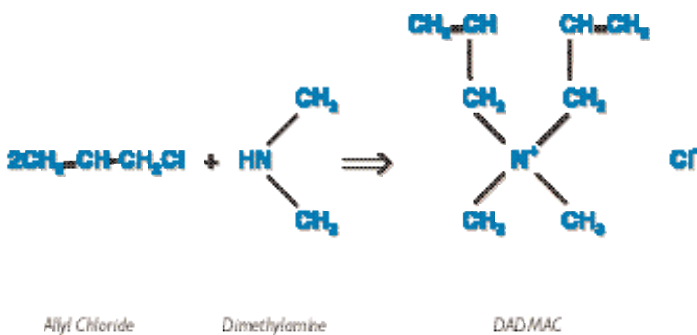
Polyamines are organic coagulants which may completely or partially replace the inorganic coagulants (aluminium sulphate, aluminium perchloride, ferric chloride, etc.).

These substances are approved for potable water in the United States, South America, Great Britain, Russia and Korea.

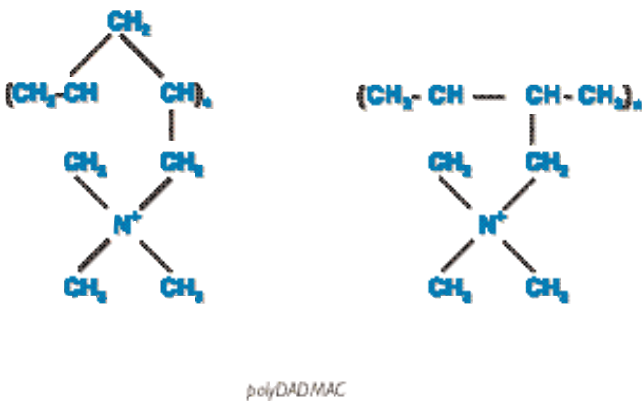
Polyamines are also used in the manufacture of paper, drilling muds, latex coagulation, etc.

V- 1-2 PolyDADMAC

Diallyldimethyl ammonium chloride (DADMAC) is obtained by the reaction of allyl chloride with dimethylamine. Polymerization of DADMAC, limited by the reactivity of the allyl radical, produces a water-soluble cyclic polymer of low to medium molecular weight:



By polymerization via a cyclization mechanism, the following two structures are obtained:



PolyDADMACs have the following main characteristics:

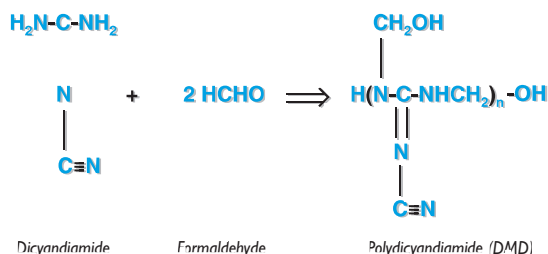
- Molecular weight: 10,000 to 1,000,000
- Liquid or bead form at 20% to 100% concentration
- Cationic sites on a side chain
- Viscosity of the liquids at 40%: between 1000 and 20,000 centipoise
- Chlorine stability
- Compatibility in terms of mixing with inorganic coagulants
- Good storage stability
- Use with or without pre-dilution
- pH stability.

The main applications of PolyDADMAC are:

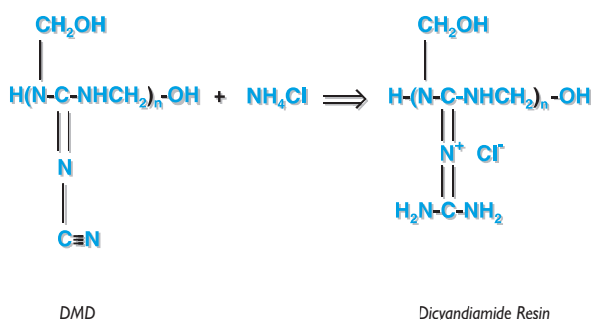
- Coagulants for potable water with the same regulatory situation as for polyamines. In addition, polyDADMAC is at the present time the only polymer approved for potable water in China;
- Coagulants for process water;
- Conditioning agents for cosmetics;
- Neutralizing agents for harmful anionic colloidal substances;
- Copolymers with acrylamide for water treatment and for temporary wet strength in paper;
- Agents for treating the ultrafines recirculating in the white water in papermaking.

V-1-3 Dicyandiamide resins

Dicyandiamide resins are obtained by condensation of dicyandiamide with formaldehyde:



followed by quaternization with ammonium chloride:



The main characteristics of dicyandiamide resins are:

- Molecular weight: 3000 to 150,000
- Cationic sites on a side chain
- Liquid at 40 to 60% concentration
- Viscosity of the liquids: 50 to 300 centipoise
- Very high cationicity.

Their main applications are in water treatment, as dye fixers for textile printing and in paper.

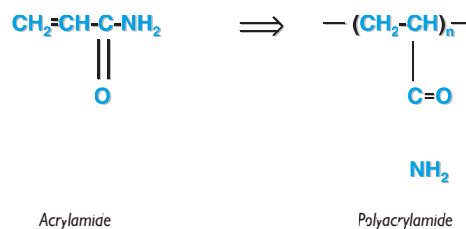
V-2 Flocculants

Flocculants are hydrophilic polymers having a molecular weight varying from 1 to 30 million, i.e. a degree of polymerization of between 14,000 and 420,000 monomer units. Their water solubility comes from sufficiently strong solvation of the polar groups (either ionic or nonionic) that they contain, so that the various segments of a chain are dissociated.

Usually based on acrylamide, they have, by homopolymerization, a nonionic nature and may have, by copolymerization, a cationic or anionic nature, with a degree of ionicity varying between 0% and 100%.

V-2-1 Nonionic flocculants

Nonionic flocculants are acrylamide homopolymers:



These polymers are called nonionic, even though slight hydrolysis of the amide groups gives them an anionic nature (with an anionicity of less than 1%). Nonionic polymers containing less than 1% of anionic groups may be obtained under special polymerization conditions.

Their main characteristics are:

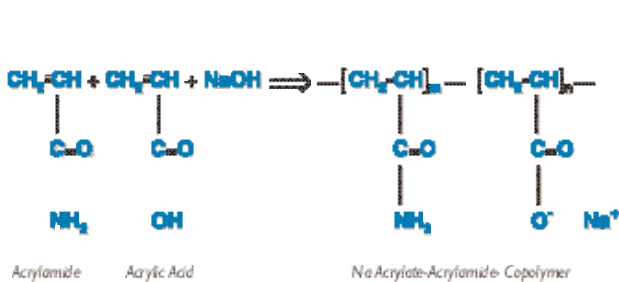
- Molecular weight: between 1.5 and 15 million
- Viscosity at 5 g/l: between 8 and 200 cps.

They are used for the treatment of potable water, the treatment of waste process water, the treatment of municipal sewage and the treatment of ores.

V- 2-2 Anionic flocculants

Anionic flocculants are obtained either by hydrolysis of the amide groups on a polyacrylamide chain or by copolymerization of the polyacrylamide with a carboxylic or sulphonic acid salt.

The most commonly used is acrylic acid:



The anionicity of these copolymers can vary between 0% and 100% depending on the ratio of the monomers involved.

The main characteristics of the copolymers are:

- Molecular weight: 3 to 30 million
- Viscosity at 5 g/l: between 200 and 2800 cps.

The main applications are given in Chapter IX and X. They relate to water treatment and mining industry. They are also used as thickeners in the petroleum, textile, cosmetic and other industries.

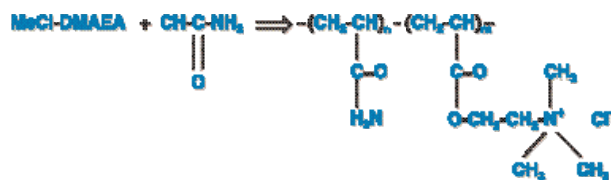
V-2-3 Cationic flocculants

Cationic flocculants are mainly derived from the copolymerization of acrylamide with dimethylaminoethyl acrylate (DMAEA) in quaternized form.

A first reaction of DMAEA with methyl chloride allows it to be converted into a quaternary ammonium salt in the form of chloromethylated DMAEA (DMAEA-MeCl):



The copolymerization of DMAEA-MeCl with acrylamide produces the cationic polymer:



The cationic charge of the copolymer is determined by the ratio of each monomer and may vary between 0 and 100%.

The ester group of the copolymer is very sensitive to the pH above a pH of 6:



Hydrolysis of the polymer reduces its efficiency by creating amphoteric polymers and then anionic polymers. It is therefore essential to prepare these polymers at a pH of about 5.5, even though the flocculation is carried out at a higher pH. However, during flocculation, the floc may be converted by chemical modification of the polymer when the contact times are long, for example during settling.

The main characteristics of the products obtained are: Molecular weight: 3 to 10 million, Viscosity at 5 g/l: 100 to 1700 cps

Their main applications are given in Chapters IX and X.

V-3 Amphoteric polymers

Amphoteric polymers exhibit both cationic and anionic behaviour, for example acrylamide-acrylic acid-DMAEA-MeCl or DADMAC-acrylic acid.

The strength and the relative number of sites of opposite ionic nature may vary.

V-4 Other polymers

There are many other forms of polymers and the imagination of chemists is unlimited. However, despite remarkable properties, the industrial use of these products is often limited by their cost or by the performance of a single product compared with a wide range of polyacrylamides. Among products that have found an industrial outlet, mention may be made of:

Polyethyleneimines:

the polymerization of ethyleneimine:

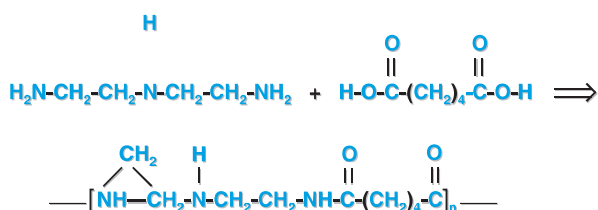


produces a highly cationic polymer of low molecular weight, especially used as a drainage aid in papermaking.

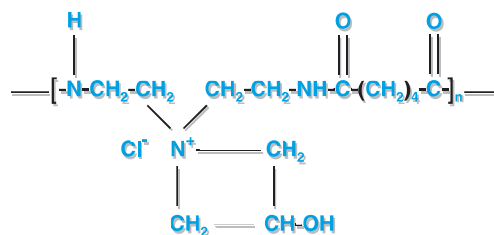
Polyamide-amines:

the condensation of adipic acid with diethylenetriamine and with epichlorhydrin produces a low-molecular-weight copolymer in which all the amine groups are quaternized by the epichlorhydrin. The manufacturing process takes place in two steps:

-condensation of diethylenetriamine with adipic acid:



- followed by condensation with epichlorhydrin in order to give tertiary amine groups and to cause branching and crosslinking:



The solubility is maintained by controlling the degree of branching between the epoxy groups on one polymer chain and the secondary amine on another chain.

The polyamide-amines are used in papermaking as a dry-strength additive.

Polyamine-based polymers:

These are condensates of halogenated compounds (dichloroethane, epichlorhydrin, etc.) with polyamines. They cover an entire family of polymers, some of which have been studied in flocculation applications.

Polyethylene oxides (PEO):

These have a very high molecular weight (2 to 8 millions) and although they do not have an electric charge, they are non-ionic in nature because of a free electron pair on the oxygen atom. These products are particularly specific to the flocculation of silica. They are also used for the flotation of ores and the reduction of head losses, and they are used in paper as a retention agent in newsprint production and as a formation agent for "tissue" paper.

Sulphonated compounds:

- The sodium polystyrene sulphonate or sodium polyvinyl-sulphonate type, which are highly anionic polymers of low molecular weight;
- Copolymers of acrylic acid with, in particular, 2-acrylamido-2-methylpropanesulphonic acid (AMPSA).

Polyacrylate-type dispersants:

The dispersants are sodium polyacrylates of low molecular weight.

V-5 Products in solution

For uses in coagulation, for example for dispersion, the polymers must have a low or even very low molecular weight. Only the technique of solution polymerization allows this type of polymer to be obtained in a simple manner.

The main solution products are:

- The Mannich reaction product, in which polyacrylamide is made to react with formaldehyde and a secondary amine, such as dimethylamine. This reaction may be followed by quaternization and gives a polymer which is used as a flocculant;
- The product of the reaction with glyoxal, the main application which is in papermaking as a wet-strength agent;
- The product of Hoffman degradation with hypochlorite, which gives an acrylamide-vinylamine copolymer used in the treatment of sludge and for wet or dry strength in paper.

V-6 Branched polymers

These polymers are formed by introducing small amounts of multifunctional monomers into the polymerization of monofunctional monomers.

They have the advantage of forming more stable flocs without the risk of the suspension restabilizing. These properties derive from the characteristics of these polymers. Being less deformable, they are unable to cover all the active sites of the same particle. Several polymer molecules can therefore be adsorbed onto the same particle. This allows more structured, and therefore more stable, flocs to be formed, although they are small.

V-7 Thickening agents

A final family of polymers relates to synthetic thickeners.

These products derive from acrylic copolymers, generally of high molecular weight, with a small number of branches (acrylic acid, maleic acid, acrylamide, etc.). They carry carboxylic functional groups at the end of the chain which, in the presence of water, are easily hydrated, so as to develop a thickening action. In the swollen state, the volume of these so-called short thickeners is one hundred times greater.

In an acid medium, the polymer has a slight tendency to be ionized and has few electric charges along the chain, which remains flexible and tends to coil up on itself. During alkanization, the chain carries negatively charged groups which repel each other. The molecular chain extends and becomes rigid, causing the thickening action in water.

These products are sensitive to electrolytes, causing a drop in viscosity.

24 *Physical forms of polymers*

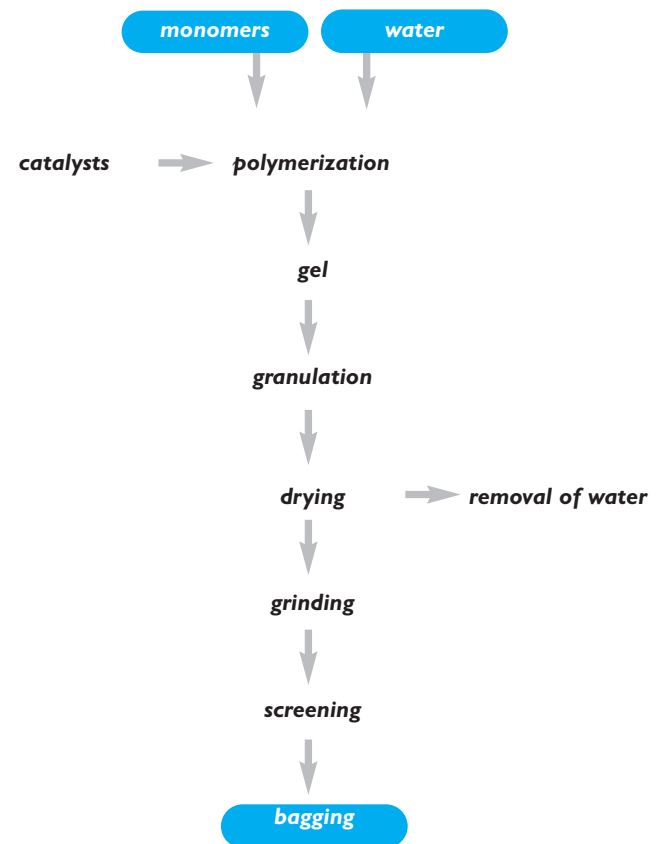
The main physical forms of polymers are powders, emulsions, beads and liquid solutions.

Manufactured from the same monomers, these products are distinguished by their manufacturing processes.

VI-1 Powders

Powders are obtained by the gel polymerisation, a basic production process. The process is as follows:

Figure 9 – Gel process



The monomers are polymerized in liquid form. Next, the gel obtained is ground and then dried. The quality obtained by this process, particularly with regard to solubility, is exceptionally good and the molecular weight is very high.

The powders thus obtained have a particle size of 0 to 1mm and may be dissolved in 30 to 240 minutes depending on the type and the molecular weight.

It is essential that these polymers be dispersed in water without any agglomerates (fisheyes) using various types of dispersing equipment in the form of vane-type, pump-type, pneumatic transfer-type ejectors, or similar equipment.

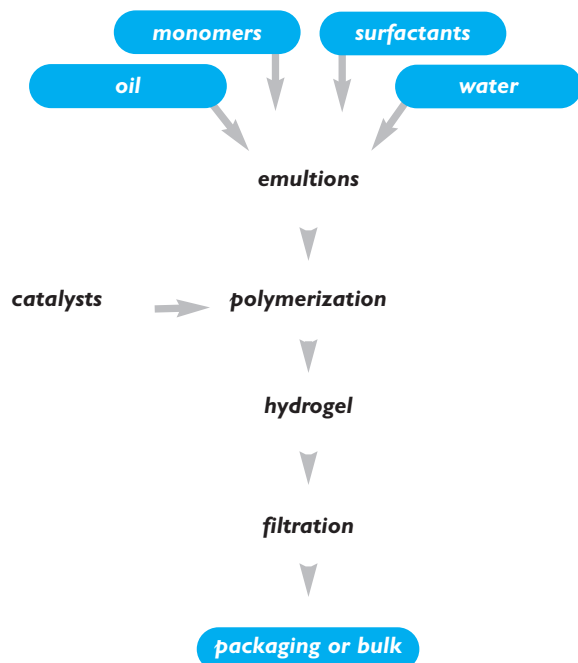


VI-2 Emulsions

Emulsions are suspensions of polymer hydrogels in a oil. They generally contain 25 to 50% of active material. The hydrogel-a hydrated polymer - is in the form of microspheres with an average diameter of 1 μm . These microspheres are dispersed in the oil and protected from agglomeration by surfactants.

The manufacturing process normally does not include drying and therefore allows high-molecular-weight polymers with a high solubility to be obtained. The process is as follows:

Figure 10 – Emulsion process



26 Physical forms of polymers

By varying the amount of surfactant it is possible to create semi-microemulsions (0.2 μm in size) or micro emulsions (less than 0.1 μm in size and transparent) having properties similar to emulsions.

The emulsions are formed using hydrophobic surfactants (Hydrophilic Lipophilic Balance, $\text{HLB} \leq 6$) creating reverse (water-in-oil) emulsions which are insoluble in water.

It is necessary, after polymerization or in some cases during polymerization, to add a hydrophilic surfactant to them to allow the emulsion to undergo “inversion” on contact with water and allow the hydrogel particles to dissolve.

Depending on the mechanical dissolution conditions, the dissolving time may vary from a few seconds to a few minutes. It is important to observe an optimum concentration in solution, corresponding to approximately 5 g/l of active material.

It is recommended that these emulsions be stored under dry conditions at a temperature of between 0 and 35°C and that a StockEMULTM-type storage tank, allowing easier metering, be used.



An alternative process consists in distilling the emulsions in order to remove the water. Thus, the following characteristics are achieved:

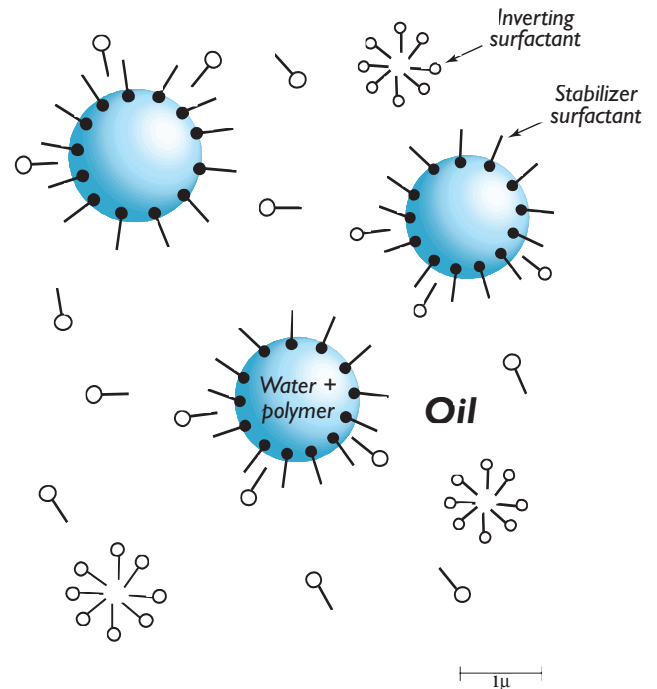
A high concentration, thereby reducing the packaging and transport costs

Good stability over time (lifetime: 12 months)

High fluidity, easy to handle

But a higher cost and a slight loss of efficiency because of the heating during distillation.

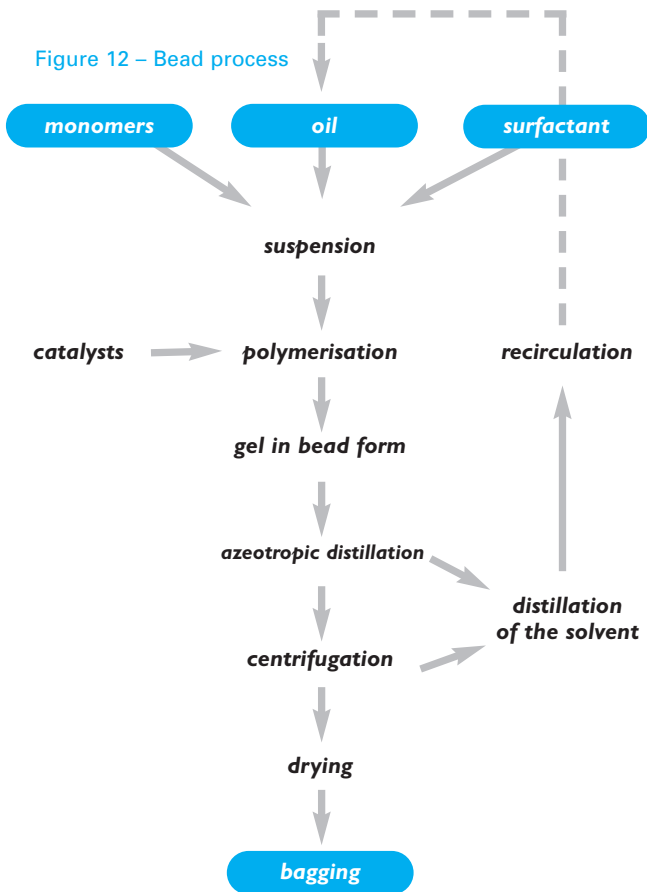
Figure 11 – Emulsion of polyacrylamide



VI-3 Polyacrylamides in bead form

Another method used for synthesizing polymers is the production of beads. The process is as follows:

Figure 12 – Bead process



The beads have essentially the following advantages:

- More rapid dissolution time (order of magnitude 30 minutes) because their particle size is less than 300 μm ;
- Better flow, but, like the powder products, requiring the use of dispersion equipment;
- No dust.

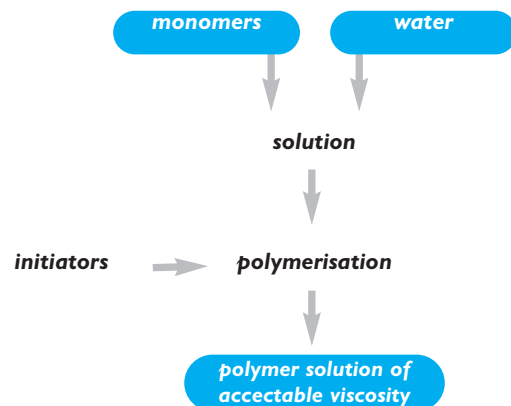
The molecular weights achieved are lower than those obtained using the solution, emulsion or powder process. Very low molecular weight polymers can thus be produced for specific applications (textile, oil drilling...)

VI-4 Products in solution

For use as a coagulant or dispersant, it is necessary for the molecular weights to be low or even very low.

These products are obtained by solution polymerization of the monomers, followed by a post reaction with specific reagents. Since solution polymers are highly viscous, it is not possible to obtain high concentrations.

Figure 13 – Solution process



The main parameters normally used to characterize polymers are:

• **The nature of the monomers and of the polymers:**

- polyacrylamides
- polyacrylates
- acrylamide-dimethylaminoethyl acrylate copolymers
- polyamines
- polyethyleneimines
- polyamidoamines
- polyethylene oxide

• **The molecular weight:**

- low molecular weight (LMW): 1 to 3 millions
- medium molecular weight: 3 to 6 millions
- standard molecular weight: 6 to 10 millions
- high molecular weight: 10 to 15 millions
- very high molecular weight: greater than 15 millions

• **The molecular distribution:**

- low polydispersity
- high polydispersity

• **The nature of the charges:**

- nonionic
- anionic
- cationic
- amphoteric

• **The charge density:**

- low: 1 to 10 %
- medium: 10 to 40 %
- high: 40 to 80 %
- very high: 80 to 100 %

• **The charge distribution:**

- random polymers
- block polymers

• **The viscosity, which depends on the charge and the molecular weight**

• **The physical form:**

- emulsion
- solution
- powder
- beads

• **The stability:**

- storage stability
- temperature stability
- pH stability
- gel stability
- moisture stability

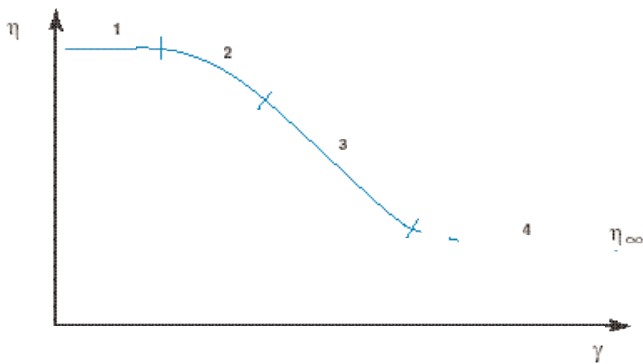
VII-1 Viscosity

The viscosity η is the coefficient of proportionality between the applied shear stress σ and the shear rate $\dot{\gamma}$:

$$\eta = \sigma / \dot{\gamma}$$

The viscosity of a solution of a given polymer generally depends on the shear applied:

Figure 14 – Variation of viscosity vs shear rate



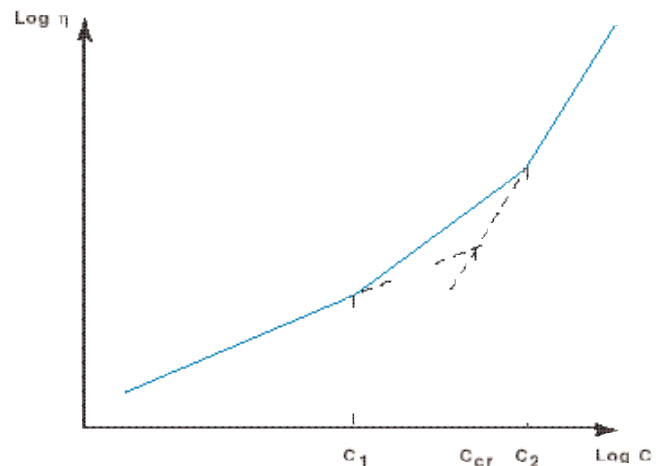
Four regions may be distinguished:

- 1 - Constant-viscosity region in which the behaviour of the solution is Newtonian. This region is associated with low shear rates and/or low concentrations.
- 2 - Transition region, which corresponds to the polymer molecules undergoing deformation due to the effect of the increasing shear rate.
- 3 - Region in which the viscosity decreases as the shear rate increases. The greater the shear, the more the molecular chains orient in the flow direction. The behaviour of the solution is pseudo plastic.
- 4 - Transition region, which corresponds to high degrees of shear.

The viscosity also depends on the polymer concentration in the solution.

When the variation in the viscosity of a solution is plotted as a function of the concentration on a log-log plot, three regions may generally be distinguished:

Figure 15 – Variation of viscosity of a polymer solution vs concentration



At low concentration, the polymer molecules individually retract on themselves like a ball of string separated by solvent molecules. When the concentration increases, the balls move closer together. Above a concentration C_1 , the balls start to come into contact with each other. Increasing the concentration further, the balls start to interpenetrate and to contact up to the concentration C_2 . The concentration C_{cr} - the critical concentration - defines the point at which all the balls are in contact with each other and have just started interpenetration.

It is important to determine these limiting concentrations if it is desired to measure the behaviour of the individual macromolecules and in particular to measure the molecular mass of the polymer. In this case, the viscosity measurements have to be carried out at concentrations of less than C_c .

The critical shear rate depends on the molecular weight of the polymer. This critical rate decreases as the molecular weight increases.

VII-2 Measurement of the molecular mass

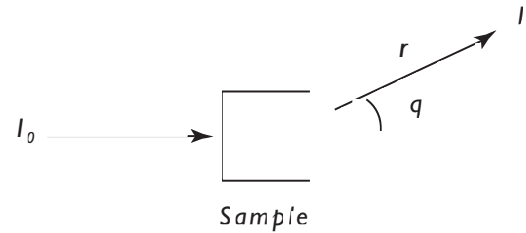
The molecular mass can be measured by a direct method, namely light scattering or an indirect method, namely intrinsic viscosity.

VII-2-1 Light scattering method

If macromolecules in dilute solution are illuminated with a laser, the light is scattered in space.

If I_0 is the intensity of the incident light, the intensity of the scattered light I , for a given solution, is a unique function of the distance r and the angle q :

Figure 16



For an ideal solution, the difference in intensity of the scattered light between the polymer solution and the solvent is proportional to the molecular mass of the polymer. The following equation can be applied:

$$\frac{I_{\text{solution}} - I_{\text{solvent}}}{I} = K \frac{(1 + \cos^2 \theta)}{r^2} C M_w$$

where K is a constant

C is the concentration of the polymer in g/l

M_w is the molecular mass in g/mol

The constant K can be more precisely defined by the following equation:

$$K = \frac{2 \pi^2 n_0^2}{\lambda_0^4 N} \left(\frac{dn}{dc} \right)^2$$

where $n_0 = 1.33$ (refractive index of the solvent)

$\lambda_0 = 632.8 \text{ nm}$ (wavelength of the laser)

$N_a = 6.023 \times 10^{23}$ (Avogadro's number)

$\frac{dn}{dc} = 0.15$ (refractive index increment of the polymer in the solvent and at the wavelength of the laser)

For real solutions, the anisotropy and fluctuations in the scattered intensity have to be taken into account.

VII-2-2 Intrinsic viscosity method

In order to determine the molecular masses of polymers, an indirect method is used which consists in calculating the molecular mass from the Mark-Houwink equation:

$$h = k M^a$$

where h is the intrinsic viscosity, M is the average molecular mass and k and a are two constants which depend on the polymer-solvent pair and the temperature.

For polyacrylamides, the constants usually have the following values for capillary viscometry measurements:

$$K = 3.73 \times 10^{-4} \text{ and } a = 0.66$$

The intrinsic viscosity is the extrapolation, to zero concentration, of the reduced viscosity which is defined by the equation:

$$\eta_{red} = \frac{h - h_0}{h_0 C}$$

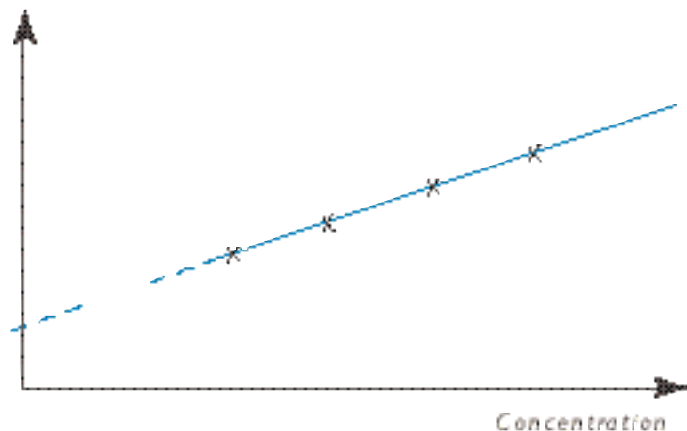
where h is the viscosity of the polymer solution

h_0 is the viscosity of the solvent at the same temperature

C is the polymer concentration in the solution

In order to determine the intrinsic viscosity, the reduced viscosity at various concentrations is usually measured by means of a capillary viscometer. The intrinsic viscosity is obtained by extrapolation to zero concentration.

Figure 17 – Determination of the intrinsic viscosity



VII-3 Stability

In general, polymers are stable over periods of several months. However, in solution, chemical, mechanical or bacteriological degradation may occur, sometimes rapidly.

VII-3-1 Chemical and biochemical stability

The chemical degradation of polymers can be distinguished by processes such as hydrolysis and molecular attack by foreign bodies.

With regard to hydrolytic degradation, the stability of polyacrylamides depends on the pH according to their ionic nature:

nonionic: stable from pH 1 to pH 12

anionic: stable from pH 4 to pH 12

cationic: stable from pH 4 to pH 6

Polyamines and polyDADMAC are stable from pH 1 to pH 14.

The external factors affecting the degradation of water-soluble polymers are:

- free radicals which cause chain scission and rapid reduction in the molecular weight. Products resulting in redox systems are the most detrimental, such as the oxygen/ferrous ion pair often encountered in underground water;
- aerobic and anaerobic bacteria which, by forming precipitates, rapidly reduce the efficiency of the products;
- divalent and trivalent ions which precipitate the polymers and polymers of opposite charge;
- UV radiation, which degrades the polymer chain by forming free radicals. It is recommended for the solutions to be kept away from light.

The following table gives the stability times for polymer solutions prepared in demineralized water:

Table 2

Stability (5 g/l):	anionic:	8 days
	cationic:	24 hours
Stability (1 g/l):	anionic:	2 days
	cationic:	4 hours

VII-3-2 Mechanical stability

From a mechanical standpoint, as we have already mentioned, long polymer chains can be broken by high shear stress. The longer the molecular chain the more shear sensitive is a polymer.

Under service conditions, the equipment - centrifuges, pumps, stirrers and nozzles - may be sources of significant shear degradation.

VII-4 Ionicity

The degree of ionicity of a polymer, expressed in mol% is normally measured using a colloidal method.

The anionic charges are measured by the reaction of a cationic colloid, such as methyl glycol chitosan, which reacts stoichiometrically with the anionic charges. In practice, a known excess of cationic polymer is added to a known mass of anionic polymer. Next, the excess is back-titrated with potassium polyvinyl sulphate (an anionic polymer) in the presence of toluidine blue. The color turns violet when the point of equivalence is obtained.

The cationic charges are measured directly using potassium polyvinyl sulphate in the presence of toluidine blue.

The precipitation of polymers of opposite charge significantly modifies the titration time and the precision of the measurement.

VII-5 Residual polymer content

In some cases - process studies (in mining) or characterization of the effluents - it is necessary to determine the residual polymer content in the water.

When the type of polymer is known, the colloidal method is used to determine its concentration when this is of the order of 100 ppm.

For concentrations of the order of 1 ppm, compared flocculation methods are normally used.

Below 1 ppm, only state-of-the-art analytical methods allow the content to be determined.

VII-6 Toxicity

In general, the polymers referred to in this report are of no danger to human health. Moreover, some of them play an important role in very strictly regulated industries relating directly to human food: potable water, paper in contact with food, treatment of sugar, etc., these products also being used in applications sensitive to environmental protection issues. At the present time, many studies have been carried out and published for the purpose of determining whether these products have any impact.

In particular, the effects of ageing on the aquatic toxicity of cationic polyacrylamides, which are among the polymers most widely used, have been studied. It has thus been demonstrated that very rapid hydrolysis of the chain removes the cationic charges and therefore the effect on aquatic organisms.

With regard to anionic polyacrylamides, it has also been demonstrated that there is no systemic toxicity towards aquatic organisms or micro-organisms. The only deleterious effects, observed in laboratory tests, have been at concentrations that are always greater than 100 mg/l and are probably due to the high viscosity obtained in the test medium.

Finally, polyacrylamides are very UV-sensitive. Photolysis results in the degradation of the polymer chain and the formation of much smaller molecules which can be biologically degraded. Polyacrylamides therefore neither persist nor accumulate in the environment.

34 *Laboratory tests and industrial trials*

The complexity of the coagulation and flocculation systems means that a polymer cannot be selected for a given application without experimental testing. The testing is generally carried out in two stages:

- **laboratory tests for selecting the type of product and more particularly the optimum ionicity**
- **industrial trials for confirming the product selection and for determining its amount and its molecular weight.**

VIII-1 Principles

Laboratory simulation of actual operational conditions is not possible. In particular, the shear conditions (in mixers, pipework, separation equipment, filters, centrifuges, etc.), which are key factors in choosing the molecular weight, are difficult to reproduce in the laboratory.

Only cumulative experience and rigorous test methods allow the optimum solution to be determined. However, there may be some cases in which the laboratory results are not confirmed in industrial trials.

There are two main reasons for this:

- **Non-representativeness of the specimen used in the laboratory.**

If the characteristics of the effluents vary over time, a representative average specimen must be used.

If the composition of the specimen changes over time, the tests must be carried out as rapidly as possible on site, or the change must be limited by refrigerating the specimens or treating them with a bactericide.

Finally, difficulties may occur in the case of different raw materials (dissolving water or post-dilution water, for example).

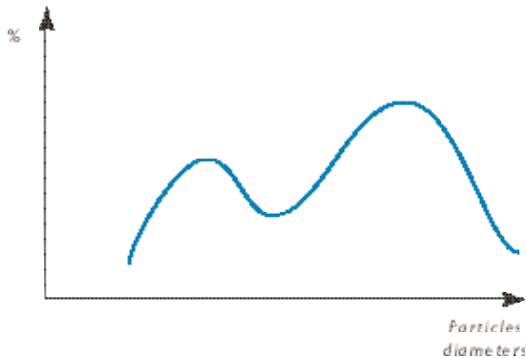
- **Difficulty of mixing under industrial conditions.**

If the polymer is mixed in the solution too soon or too late compared with flocculation, differently sized flocs are obtained in industrial trials from those obtained in the laboratory. In this case, various options may be considered:

- changing the polymer concentration,
- changing the point of introduction of the polymer,
- introducing the polymer at several points
- or possibly changing the polymer.

Of course, laboratory error cannot be excluded. This can occur for example when the specimen studied is heterogeneous, in terms of particle size or ionic charge, in particular as a function of the specific surface area of the particles.

Figure 18 – Particle size distribution



The heterogeneity of the suspension (particle size, organic matter, etc.) may mean that polymers of different cationicities are selected in the laboratory. The product giving the best clarification or floc strength then has to be selected.

However, when there is such heterogeneity, it may prove difficult to select the polymer. In particular, a 0 to 30% excess of polymer compared with the laboratory conditions may be necessary for industrial equipment. It is therefore absolutely necessary to carry out trials which take into account this excess, and its effects on ionic redispersion.

The flocculation step, which consists in bringing the polymer solution into contact with the suspension to be treated, proves in practice to be very tricky. It depends on the existing equipment and it is often necessary to adapt the quality, quantity and dilution of the flocculant to the equipment.

As a general rule:

- In the case of settling of a dilute suspension (diffuse flocculation), the mixing takes place in a low-speed flocculator. The contact time is inversely proportional to the concentration of the suspended matter. This contact time may vary between 10 seconds and 15 minutes. In recirculation or sludge-blanket plants, flocculation is much more rapid. In this case, the flocculant is premixed with the water to be treated, just before mixing it with the sludge;
- In the case of a belt filter, the sludge and the flocculant are introduced into a variable-speed mixer. Optimization is achieved by varying the speed;
- In the case of a centrifuge, a central injection pipe allows mixing inside the centrifuge. The dissolution and dilution concentrations are key factors in determining the level of performance obtained.

VIII-2 Main laboratory tests for process-water and municipal water treatment applications

The laboratory tests are comparative tests making it possible to classify the efficiency of the various products tested one with respect to another.

The main tests used include:

- Standard jar-test method: determination of the degree of clarification.



- A method in which a suspension of average concentration (1 g/l of dry matter) is stirred.

- A method in which the samples are turned upside down (DIN 23007 Standard using 6 samples) for suspensions giving homogeneous-type flocculation, either directly or after the formation of a sludge bed.



- Flotation tests in which water saturated with air at a pressure of 7 bar is injected.

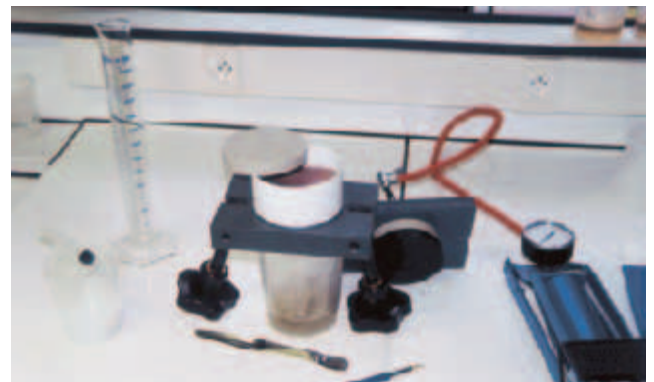
- Vacuum filtration tests: Büchner filtration and submerged-cell method.

- Tests on the dehydration of sludge by draining, while recording the filtration rate.



- Measurement of the diffusion rate on a porous substrate (CST).

- Measurement of the dryness limit under pressure.



- Measurement of the zeta potential.

- Measurement of the SCD (Streaming Current Detection).

These methods are more or less standardized, but often have to be adapted to the practical conditions under which the flocculants are used.

VIII-3 Use of the polymers

VIII-3-1 Polymers in powder form and in bead form

The use of powders firstly requires that they are properly dissolved in order to avoid forming lumps. The dissolving time can vary from 30 minutes to 4 hours, depending on the products.

These times also depend on several parameters:

- The dissolution concentration:
the more concentrated the solution, the shorter the dissolving time, if the mixing conditions are satisfactory;
- The water temperature:
35 to 40°C maximum, provided that the polymer is stable. Below 5°C, very slow dissolution is observed;
- The nature of the product, particularly the ionic charge and the particle size.

In order to ensure that the polymers are properly dissolved, it is essential to comply with the following steps:

- Effective dispersion at the highest possible concentration compatible with the equipment used (3 to 10 g/l). This high concentration makes it possible both to reduce the size of the equipment and to increase the solubility of the polymer. There are many types of dispersion equipment: pneumatic mixers, pumps, wetting blades, ejectors, etc.
- Dissolution with stirring at the dispersion concentration for the minimum time recommended for the polymer;
- Transfer to a storage tank, which is stirred to prevent agglomerated or poorly dissolved particles from settling;
- Dosing and diluting to the final use concentration via a static mixer.

To prevent the polymers from degrading, it is recommended to use positive-displacement pumps (of the Moineau-, gear- or lobe-type) and non-centrifugal pumps, as well as stirrers whose peripheral velocity is less than 8 m/s.

It is also essential to check that the dissolving water does not contain elements prejudicial to the stability of the polymers (hardness, ferrous cations, etc.).

Specific equipment is available on the market that are efficient and properly prepare polymer solutions.

VIII- -2 Polymer emulsions

Emulsions are usually most effective when the dissolving operation is carried out continuously. This is particularly important when they are used in centrifuges.

Specific equipment is available on the market for both adapting the dissolution concentration and for injecting the emulsion.

Special precautions have to be taken when storing the emulsions. The "Emulsion handbook" instructions recommend the storage conditions and the materials that can be used

VIII-3-3 Polymer solutions

Depending on their nature, the polymer solutions are either diluted in line or metered directly. For rapid mixing, it is recommended to limit the viscosity of the dilute solution to 10 cps.

38 *General applications*

The main applications of the polymers are in water treatment, coagulation,

flocculation and sludge treatment.

Many other polymer properties are particularly useful in specific applications:

- *Textile thickeners*
- *Cosmetic thickeners*
- *Hair conditioners*
- *Pharmaceutical adjuvants*
- *Friction reducers, etc.*

In the case of water treatment, two types of polymer may be considered, although their actions are often common:

- **Organic coagulants**, e.g. polyamines, polyDADMAC, etc., are used for treating water with low suspended solids content and they replace (completely or partly) the inorganic coagulants (e.g. aluminium sulphate, aluminium polychloride and ferric chloride). Commercial polymers are used at a concentration of 1 to 10 ppm.

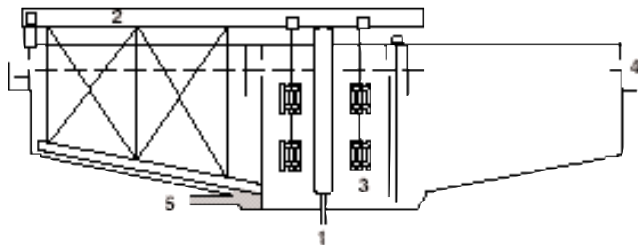
- **Organic flocculants**, especially polyacrylamides and polyethylene oxides, are used for settling at concentrations of 0.1 to 10 ppm and for sludge treatment at 0.5 to 15 kg per tonne.

IX-1 Separation processes using flocculation

IX-1-1 Settling

Conventional flocculation takes place in one pass, in stirred or static tanks with baffles. Several types of equipment are available. Figure 19 shows an example of a flocculator/settling tank.

Figure 19 – Flocculator/settling tank



1. Raw water inlet
2. Rotating scraper bridge
3. Flocculation zone
4. Clarified water
5. Sludge extraction

Increasing the mass of sludge fosters contact between flocs and microflocs and therefore improves the efficiency of the flocculation. This principle is used in sludge-contact flocculation processes using either sludge recirculation or a sludge bed. These processes are more specific for the treatment of potable water.

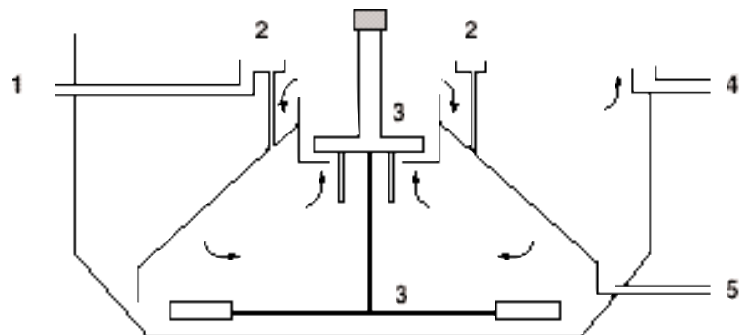
In recirculation systems, the concentrated sludge, taken from the bottom of the settling tank, is sent back into the tank in order to maintain the optimum concentration.

In sludge-bed systems, the velocity of the upflowing water slows down the rate of settling of the downflowing sludge and, above a certain sludge concentration, a sludge bed is formed which has a degree of cohesion.

These contact-enhancing systems have many advantages:

- Removal of all fines by adsorption on the flocs
- Formation of homogeneous flocs
- Reduction in the flocculation and settling times
- Homogeneous-type settling velocity.

Fig. 20: Settling tank with sludge recirculation



1. Raw water inlet
2. Raw water distribution chute
3. Sludge recirculation turbine
4. Clarified water outlet
5. Sludge extraction

IX-1-2 Centrifuging

Centrifuging uses the action of the centrifugal force to separate particles from a solid-liquid mixture into two separate phases - the sediment, which is the collection of the solid particles, and the centrate, which generally consists of a well-clarified liquid phase. The acceleration generated by the rotating machines ie centrifuges, allows very rapid separation due to the centrifugal forces which vary from 800 to 4000g, depending on the size of the machine. The most widespread application is the separation of the solid matter in highly concentrated suspensions for treating the residual sludge.

Industrial machines used for this application are continuous solid-bowl centrifuges.

This type of centrifuge has a horizontal bowl of cylindrical-conical shape, rotating at high speed. Inside the bowl, a helical feed screw rotates, about the same axis, at a slightly lower speed. The shape of the screw matches perfectly the internal surface of the bowl, while maintaining a clearance between the bowl and the screw.

The suspension is fed into the centrifuge, along the axis, using a manifold and is then propelled by the centrifugal force into the annular space between the bowl and the body of the screw.

Settling takes place mainly in the cylindrical part. The relative velocity of the screw with respect to the bowl allows the settled product to advance inside the bowl towards the conical part, from where the thickened sludge is extracted.

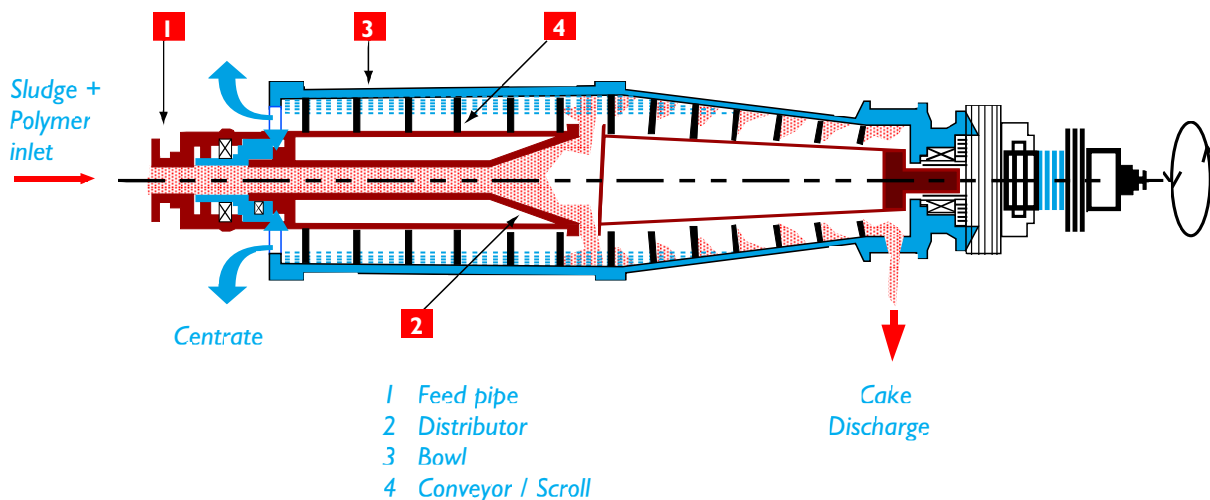
The clarified liquid is removed at the other end, by flowing over an adjustable sill which maintains a ring of liquid over a cylindrical surface.

When the solid has been removed from the ring of liquid, the residual part of the cone allows final draining of the sludge.

Continuous centrifuging has many advantages:

- Strictly continuous operation;
- Faster separation;
- Screw transfer of the thickened sludge, preventing any risk of blockage;
- Production of a homogeneous sediment with a high solids content, thanks to the use of polymers.

Figure 21 – Continuous solid-bowl centrifuge



Two continuous centrifuge systems are used:

- Concurrent systems in which the sludge is introduced at the start of the cylindrical part and the liquid and solid advance in the same direction. Settling thus takes place with less disturbance and over a longer path. These systems have the advantage of being better suited to low-density low-concentration suspensions. However, the machines are more sensitive to abrasion, with a lower hydraulic capacity and a sediment which is less dry.

- Countercurrent systems in which the sludge is fed into the junction between the cone and the cylinder. Separation of the solid matter is therefore very rapid. This system has the advantage of being better suited to dense sludge and of having a larger hydraulic capacity.

For optimum performance, it is paramount to find the best polymer. The floc obtained must be bulky and very strong. It is difficult to interpret the laboratory tests in order to predict the dynamic behaviour of the sludge because of shear forces and turbulence. Industrial trials therefore remain indispensable.

IX-1-3 Belt filters

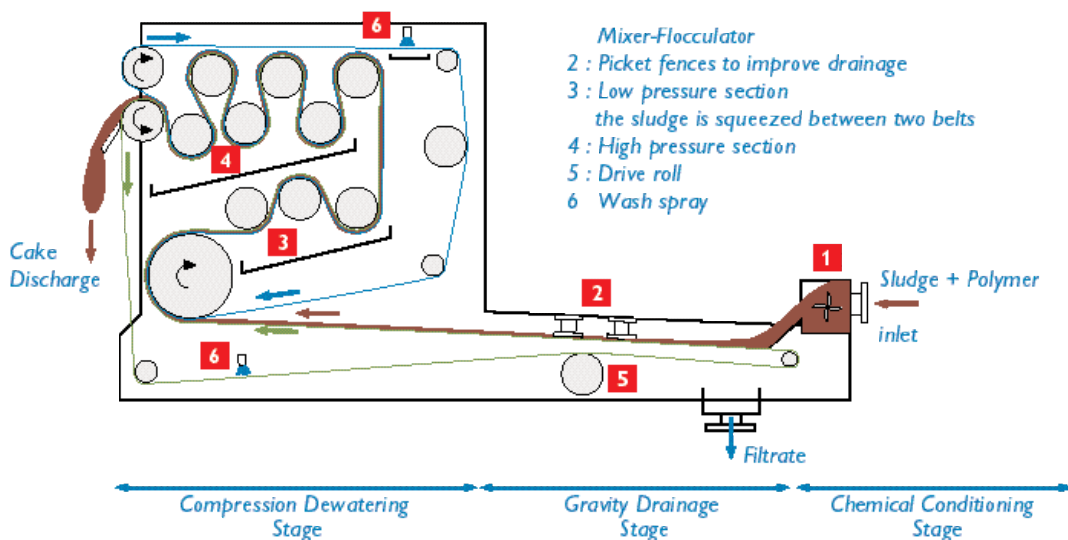
The filtration process comprises the following steps:

- Flocculation in flocculators with a short residence time, or directly in the pipe;
- Draining of the interstitial water over a filter medium;
- Pressing the drained sludge between two filter belts which form a wedge and gradually compress the sludge. The two belts are wrapped around perforated drums and rolls arranged in a staggered configuration.

The efficiency of the dewatering depends on the pressure resulting from the tension in the belts around the rolls. Because of the mechanical strength of the belts and of the rolls, this pressure remains moderate (about 0.3 to 1 bar).

If the pressure is too high, the cohesion of the sludge blanket is destroyed. The sludge is ejected laterally, out of the filtration space, by a creep phenomenon. The pressure causing the creep depends on the physical structure of the sludge.

The efficiency also depends on the pressing time, which itself depends on the active surface area of the wrappings and on the run speed of the belts.



The use of polymers has allowed these machines to be developed specifically for the treatment of residual sludge.

Their main advantages are:

- Very easy operation with visual control of the sludge during dewatering;
- Low operating cost and low investment cost;
- Continuous process with belt washing;
- Simple mechanical machine;
- Production of pelletizable sludge.

IX-2 Potable water

Potable water mainly contains humic substances (humic acid and fulvic acid) which represent 50% to 80% of the COD in surface water generally treated for drinking. These strongly anionic substances may be coagulated by highly cationic organic coagulants.

In primary coagulation, the organic coagulants may be used directly or in combination with metal salts.

The main mechanism of coagulation is charge neutralization. However, a chemical bridging effect can be obtained by varying the molecular weights.

The polymers used are of low or medium molecular weight, with high cationic charge density such as polyDADMAC or polyamines.

After colloidal suspensions have been destabilized by organic or inorganic coagulants, flocculants polymers, at low dosage (0,05 to 0,5 ppm), are frequently used to enhance the performance of clarification process. Because of their very high molecular weight, these flocculants are extremely effective in bridging the micro-flocs formed during coagulation to produce larger macro-flocs.

Flocculants are indispensable in modern treatment plants (lamellar settling tanks, microsand,...).

In the case of soft water, there are some problems with the coagulation performances due to the effect of inorganic coagulants on the pH.

The alkalinity of the water must therefore be increased, using lime for example, in order to obtain better results. Since organic coagulants and flocculants do not have an effect on the pH, they greatly improve this treatment.

The organic coagulants, particularly polyDADMAC, have a significant algicide effect. They allow both flocculation and destruction of microscopic algae, which can thus be incorporated into the microflocs.

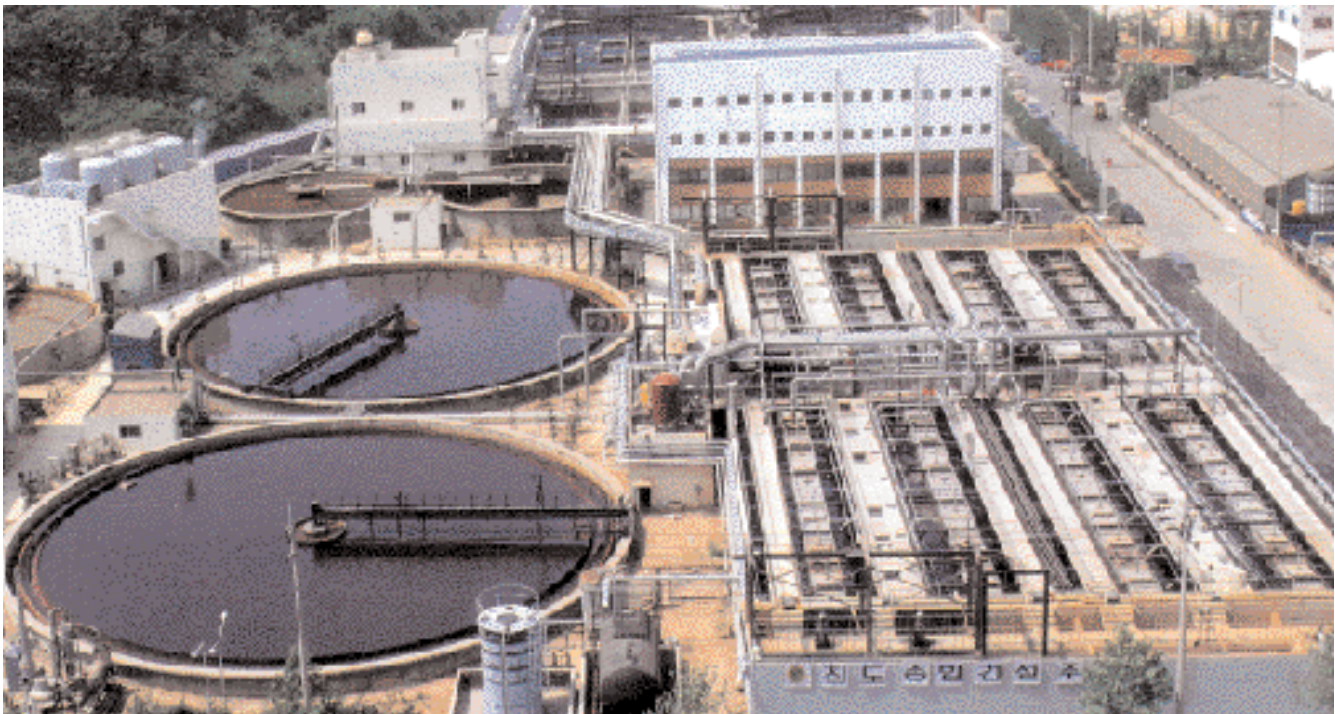
IX-3 Process water (boilers, cooling towers)

Process water used for heat exchange has to undergo specific anti-scale, anti-redeposition or deincrustation treatments. These treatments are carried out with the aid of formulations, and polymers are used at various stages in these treatments:

Low-molecular-weight sodium polyacrylate homopolymers which prevent surface deposition of calcium carbonate, calcium sulphate, barium sulphate, magnesium hydroxide and other low-solubility salts;

Acrylic acid - AMPS copolymers make it possible to stabilize calcium phosphate. These products are very effective dispersants for cooling towers. They keep iron salts in solution and prevent them from being deposited on the walls;

Polyamines and anionic flocculants for the treatment of boiler feedwater, particularly in the nuclear industry.



IX-4 Industrial effluent

There are very many fields of application and the corresponding treatments are:

Biological treatments for water containing organic matter: water treatment using bacteria and sludge dewatering using flocculants;

Physico-chemical treatments using coagulants and flocculants for settling and for sludge dewatering.

The diversity of the applications preclude us giving details about the characteristics of the polymers for each of them. However, it is possible, from experience, to establish a few general rules and these are given in the following table 3:

	Inorganic coagulants	Organic coagulants	Nonionic flocculants	Anionic flocculants	Cationic flocculants	Dicyandiamide resins
Agrifoodstuff						
Sludge treatment					X	
Water treatment	X	X		X	X	X
Dyeing						
Sludge treatment					X	X
Water treatment	X	X		X		
Papermaking						
Sludge treatment	X	X		X	X	
Water treatment	X	X		X	X	X
Chemical industry						
Sludge treatment				X	X	
Water treatment	X	X	X	X	X	X
Effluents with oil		X			X	X
Mechanical industry						
Sludge treatment			X	X	X	
Water treatment		X	X	X		
Effluents with oil		X			X	X
Municipal effluents						
Sludge treatment	X	X		X	X	
Water treatment	X	X	X	X	X	

IX-5 Municipal sewage

Water consumption per person worldwide varies between 4 and 1000 litres per day. The pollution discharged is thus very different depending on lifestyle, eating and hygiene habits, living conditions and climatic conditions.

The treatment of municipal sewage therefore varies according to the qualitative and quantitative nature of the pollutants.

Two types of treatment are used:

1- Biological treatment, which generally comprises four main steps:

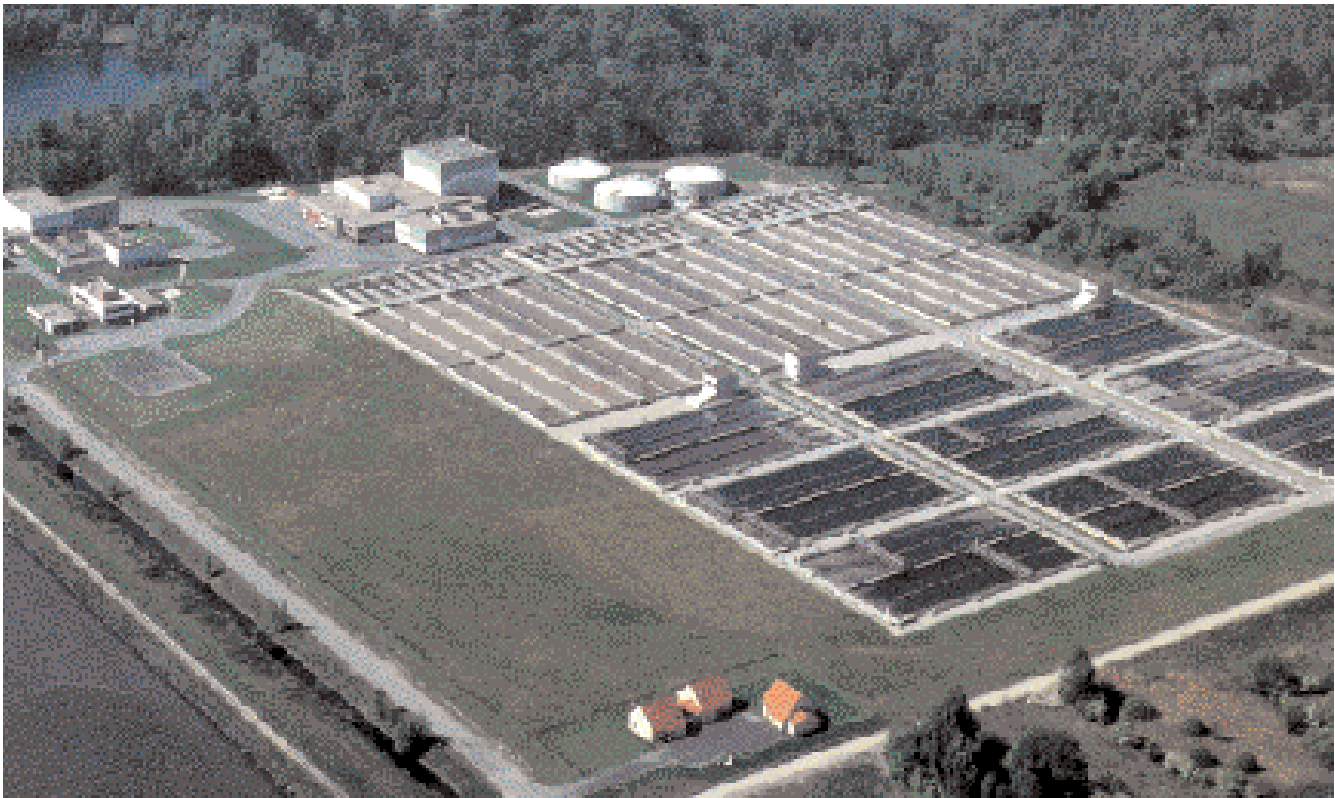
- preliminary treatment for removing the coarsest solid particles by screen cleaning;
- grit and grease removal by aeration;
- primary treatment for removing suspended solids by settling or flotation;

- aeration in order to form biological flocs;
- secondary treatment for settling the biological flocs;
- in some cases, a tertiary treatment is added in order to complete the removal of certain specific pollutants (phosphates).

The flocculants can be used at various steps in the process: primary or secondary settling tanks or thickeners, but their most common use is for sludge dewatering by filtration or centrifuging.

2- Physico-chemical treatment in which the water is treated directly by a coagulant and a flocculant.

The sludge is then dewatered by filtration or centrifugation using a flocculant. This method, which has a slightly lower efficiency than the biological treatment, is often used as an intermediate investment step.



IX-6 Thickening and dewatering of sludge

The use of polymers for promoting sludge dewatering represents one of the most important applications of the polymers.

Table 4 shows the solids contents in sludge coming from water treatment plants:

Sludge treatment	Input concentration (% solids)	Output concentration (% solids)
Static settling	0.03 - 0.2	1 - 5
Continuous thickening with polymer	0.03 - 0.2	3 - 9
Continuous thickening without polymer	0.03 - 0.2	1 - 5
Centrifuging	1 - 5	12 - 30
Filter press	1 - 5	30 - 50
Belt filter	1 - 5	12 - 27

Table 4

Polymers are used for obtaining large dense flocs which facilitate separation from a clear supernatant liquid. Since the flocs are compressible without breaking, filtering and centrifuging are also facilitated. In these cases, the centrifuge centrate and the filtrate have quite high polymer concentrations (5 to 20 ppm) and have to be recycled at the start of the plant. They promote primary settling without affecting the aeration step.

The criteria upon which the polymers are selected are:

- The nature of the sludge, organic/inorganic proportion; cationic polymers are generally used on organic sludge and anionic polymers on inorganic sludge. In the case of very fine, or even colloidal inorganic sludge, coagulants may give the best results
- The pH; cationic polymers in an acid medium (cationic polymers degrade in a basic medium) and anionic polymers in a basic medium
- Dewatering equipment, see floc characteristics (Chapter IX);
- The size and strength of the flocs, depending on the molecular weight of the polymer;
- The sludge concentration.

The nature of the charge depends on the ionicity of the sludge. Sludge coagulated with alum is generally cationic when it is fresh, but becomes anionic on ageing. The polymers used will therefore be of the anionic or cationic type depending on the case. On the other hand, activated sludge is anionic in nature and therefore has to be treated using cationic polymers.

In the case of organic sludge, the organic matter content and the degree of aerobic or anaerobic digestion determine the required cationicity and the amount of polymer.

The organic matter content and the degree of digestion are measured by the pH, the loss on ignition and the total organic carbon content. A well digested sludge normally has a pH of 7 to 8 and a loss on ignition of 30 to 55% by weight, calculated on the dry matter. Poorly digested sludge, fresh sludge and activated sludge have a pH of between 5 and 7 and a loss on ignition of 55 to 80% by weight.

As a general rule:

The more complete the digestion, the lower the cationicity may be;

The higher the proportion of activated sludge, the higher the cationicity must be.

In the case of the usual digested sludge, polymers with a low to medium cationicity give the best results, whereas for fresh, activated and mixed sludge, highly cationic polymers are used. The sludge treatment can also be carried out using partially crosslinked polymers.

48 *Special applications*

X-1 Mining industry



The mining industry consumes a great deal of water:

- Either in ore washing and flotation, in which the gangue (often clays) is separated from the ore to be processed.

In these instances flocculants are used for:

- separating the water from the gangue and recycling the water
- dewatering the sludge obtained (centrifuging, filtration, thickening, etc.)
- separating the water from the suspended one (settling, filtration, centrifuging, etc.)

(there are many ores for which these processes are used: iron, coal, phosphates, diamonds, sand, zinc, uranium, etc.);

- Or in processes for obtaining the metal or metalloid itself. In this case, the ore, which may already have been physically concentrated, is dissolved in an acid, alkaline or specific solution in which the impurities are precipitated using a flocculant. The metal is then recovered in the form of a hydroxide or salt, often by flocculation.

In general, the flocculants used for thickening the flotation concentrates, for the sedimentation of fines and for the treatment of effluent are high-molecular-weight nonionic or anionic polyacrylamides. Nonionic flocculants are specific for acid solutions (leaching solutions) or solutions with a high salt content (potassium solutions).

The main applications are given in the following table 5:

	Suspension	Clarification	Effluents	Clarification after acid treatment	Thickening	Settling Filtration
Aluminium	✓	✓	✓		✓	✓
Calcium Carbonate					✓	
Clay	✓					
Coal						✓
Copper				✓		
Gold		✓				
Lead				✓		
Nickel				✓		
Phosphates			✓			
Sand						✓
Silver		✓				
Titanium Oxide				✓		
Uranium						✓
Zinc				✓		

The mining industry also makes use of polymers for various other applications. In particular:

Pelletization:

this process is used for agglomerating fine wet particles in the form of granules. As the particles are being rotated in pelletizing equipment, the anionic polymers allow consolidation of the granules which form under the effect of the weight of the moving particles;

Dispersion:

polymers are used for keeping clays, calcium carbonate or titanium oxide in suspension, or for grinding them. The products used are low-molecular-weight sodium polyacrylates.

X-2 The paper industry

The paper industry uses polymers in a wide variety of applications: the treatment of debarking water and of green liquor, retention, dewatering, the treatment of stickies, the treatment of ultrafines, the treatment of water and sludge, etc.

The use of polymers allows this industry - the largest consumer of process water - to reduce water consumption, to increase its equipment productivity and to improve the quality of the paper and reduce its impact on the environment.

The main applications and the polymers involved are:

- Retention of fillers (titanium oxide, kaolin, calcium carbonate, etc.) in the paper:
- The polymer is introduced at the headbox of the paper machine in order to flocculate the fibres and fillers. This flocculation allows better retention of the fillers within the sheet. The operation can also be carried out by combining the polymers with microparticulate systems (silica, bentonite, etc.).
- The polymers used are anionic or cationic polyacrylamides, depending on the characteristics of the processes involved.
- Dewatering: polymers are used to increase the speed of board machines and the production rate by improving the dewatering operation at the wet end, and therefore improving the drying operation.
- The recovery of fibres, using moderately or highly charged cationic polymers.
- Increase in the dry strength by adding, for example, low-molecular-weight polymers with a low cationic charge.
- Temporary wet strength increase in the wet web, for example using glyoxalated polyacrylamides.
- The treatment of anionic impurities (pitch) in the paper, using polyDADMAC or polyamines.
- The treatment of factory feedwater, waste water and residual sludge using various polymers described in the corresponding paragraphs.
- Clarification of waste-paper de-inking, with treatment of the water produced using, for example, coagulants followed by a high-molecular-weight flocculant.
- The fixation of dyes on the fibres.
- Finally, the cationization of AKD-type sizing agents.





X-3 The petroleum industry

In the petroleum industry, polymers are used constantly in many applications:

- **Drilling mud in which the polymers have several functions:** viscosity modifier, filtrate reducer, bentonite extender, swelling inhibitor for water-sensitive clays, etc. Depending on their functions, the polymers are chosen from a range of products going from low to medium molecular weights and from moderate to very high anionicities.

- **Enhanced oil recovery (EOR)** in which an aqueous solution, whose viscosity is modified by moderately anionic polymers, is injected in order to displace the oil in situ. The molecular weight of the polymer is determined depending on the permeability of the reservoir and on the viscosity of the oil in situ.

- **Drag reduction**, in which a moderately anionic polymer of high molecular weight is used, because of its cohesion properties, to reduce the frictions and turbulences when injecting water with a high flow rate.

- **Water shut-off**, in which the inflow of water into a well is blocked by injecting a polymer solution which is then gelled by in-situ crosslinking. The water permeability of the reservoir is modified, without affecting the oil permeability, by absorption of the polymer on the rock.

- Finally, polymers are normally used for more conventional applications, **namely oil-water separation by flotation or centrifuging, and water treatment before re-injection or before discharge.**

X-4 The cosmetic industry

The cosmetic industry is one of the most complex and innovative sector. Every day new raw materials and active ingredients for the formulation of cosmetic products are offered.

The various properties of polymers are used in many applications.

X-4-1 Conditioners and film-forming agents for personal care products

In hair care products:

Given their adsorption properties, polymers can deposit a continuous film on the hair surface. They can also be fixed by electrostatic combination.

This film gives the hair a better combability and manageability, a smooth after-feel and shine.

Since hair is anionic in nature, cationic compounds are commonly used as conditioners.

In skin care products:

The film-forming properties of polymers are used in skin care products. They provide a soft and velvety after-feel.



X-4-2 Thickening agents and emulsion stabilizers

Conventionally, emulsions are formulated:

- With surfactants, carefully selected depending on the Hydrophilic Lipophilic Balance (HLB) of the system;
- With a thickening agent in order to structure the external phase, to improve the stability of the emulsion or to increase the viscosity of the product.

Crosslinked and branched acrylic polymers can also be selected for such properties:

- **emulsifier** for the formulation of emulsions without adding emulsifying surfactants. This reduces the irritancy of the formulation and limits re-emulsification of the product after it has been applied;
- **thickener and rheology modifier** to give formulations a pseudoplastic and non-thixotropic nature. During application, the product becomes fluid and so allows uniform spreading.
- **stabilizer** for emulsions and suspensions of solid particles (suncreams);
- **to simplify both the formulation and the manufacture of emulsions**, since it is no longer necessary to calculate the HLB. A wide range of oils can be emulsified;

X-5 The textile industry

The three main applications of polymers in the textile industry are as thickeners, fixing agents and sizing agents.



X-5-1 Synthetic thickeners

Synthetic thickeners are used in the composition of printing pastes and give them a particularly appropriate rheological behaviour. Their high viscosity at low shear prevents any spreading of the paste at rest, thereby allowing very sharp patterns to be obtained. Their low viscosity at higher shear allows the paste to be applied very easily.

In addition, these products have a low solids content. During heat treatment, the alkaline agents are removed and little dry matter remains on the fabric.

Finally, during fixing, the thickener, because of these polyacids, acts as an acid dispenser which helps the film of binder to adhere to the fibre.

X-5-2 Sizing agents

A size gives temporary protection to warp yarns in order to reduce the number of yarn breakages as much as possible. The size improves the elasticity and the abrasion resistance and reduces the hairiness of the yarns which are subjected, during weaving, to high stresses. Given the temporary nature of the size, the products used must be fixed only by weak bonding, without any chemical reaction.

The polymers used are acrylic acid homopolymers or acrylic acid-acrylamide copolymers. They provide the following properties:

- Excellent interstrand cohesion;
- High performance on dry looms;
- No tendency of yarns to stick to the beam;
- No deposition on sizers and looms;
- Easy preparation and desizing.

X-5-3 Fixing agents

Fixing agents prevent reactive and direct dyes from migrating during drying.

The cationic nature of certain polymers makes it possible to block the anionic solubilizing functional groups on dyes and therefore reduces their solubility and affinity for water.

The products used are quaternary ammonium compounds or aliphatic derivatives of polyamines or polyamides (methylolamide, dicyandiamide).

X-6 Agriculture - Soil conditioners

Modern agriculture consumes about 40% of the pumped water used worldwide. With water becoming increasingly scarce, more and more reutilization or saving approaches are being adopted. Organic polymers have many properties allowing the optimum use of agricultural water, especially soil-conditioning polymers.

The first application covers a wide range of polymers in emulsion, powder or block form, suitable for any type of gravity or spray irrigation. Under the action of the polymer, the fine surface particles form aggregates via a true clay flocculation process. This improves the soil porosity, thereby considerably reducing the effects of soil crusting under spray irrigation and erosion under gravity irrigation.

These products are anionic polyacrylamides and their uses have the following advantages:

- Up to 95% reduction in soil loss due to run-off;
- Resistance to compaction, surface erosion and consolidation of soils under irrigation;
- Soil working is easier, especially ploughing, and costs are reduced;
- Environmental protection, by reducing surface run-off of pesticides and fertilizers.
- A second application covers the same range of products for soil stabilization.
- Bare soil is very sensitive to erosion due to the action of wind and rain. In order to improve degraded soil, by covering it with a protective and lasting vegetation, these polymers allow surface soil to be stabilized so that plants can become more easily established.

- By being spread over a surface to be treated, the polymers allow the formation of a synthetic mulch which improves both soil cohesion and permeability. Thus, thanks to superior hydrophilic properties, the soil is more stable on the surface so as to make it easier for seeds to germinate and to ensure that plants take root effectively.



The use of these polymers has the following advantages:

- They are easy to use and can be spread with seeds and fertilizers using hydroseeding equipment;
- They improve soil cohesion and reduce erosion effects;
- A vegetation cover is easy to establish, even on a steep slope;
- They reduce soil improvement costs;
- They resist soil erosion and desertification.

