

POLYMERIC FLOCCULANTS FOR WASTEWATER AND INDUSTRIAL EFFLUENT TREATMENT

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ABSTRACT

The fact that water is the most important material used by mankind defines the importance of water purification. Wastewater and industrial effluent treatment require removal of suspended solids for purification and possible re-usage. The removal can be accomplished by gravitation (very slow), by coagulation (dependent on electric charge situation) and by flocculation (not dependent on electric charges and the fastest). Inorganic flocculants are used in very large quantities, they leave large amounts of sludge and are strongly affected by pH changes. We describe the mechanism of flocculation by polymers in ppm concentrations by strong solvation of the liquid by the flocculant, thus pushing the solid particles outside the solvated domains. The solid particles aggregate in much smaller regions than available to them. Polymeric flocculants cause formation of large cohesive aggregates (flocs) and are inert to pH changes. Both natural and synthetic polymers are used as flocculants. Natural polymers are biodegradable, are effective at large dosages and are shear stable. Synthetic polymers are highly effective flocculants at small dosages and have high tailorability but poor shear stability. Concern for environmental and ecological issues warrants the use of biodegradable flocculants. Natural polysaccharides such as starch, guar gum, alginate, glycogen or dextran can be used. Chemical modification of these polysaccharides to improve their flocculation efficacy is possible, including grafting polyacrylamide branches on polysaccharide backbones and insertion of cationic moieties on the backbones. We discuss flocculants based on polysaccharides more in detail since they provide both shear stability and biodegradability. Since flocculants exist as polymers in solution, their standard characterization is in terms of the radius of gyration; that radius is related to the flocculation efficacy. Drag reduction (DR) is also related to flocculation since the same polymeric agents cause both. DR is briefly described and the common mechanism of both phenomena is explained. Possibilities of using recycled industrial water after flocculation as agricultural water are pointed out. Such usage results in less contamination of the environment and also in saving fresh water.

1. INTRODUCTION

Materials play a major role also in lowering pollution and contamination of the environment. For this reason there are intensive research activities in the areas of lowering toxicity of industrial waste, lowering toxicity of exhausts, confinement of contamination and recycling of materials of many kinds – including water. So far standard instruction in Materials Science and Engineering (MSE) largely ignores these activities. A course on Environmental Protection taught at the Poznan University of Technology by Paukszta and Garbarczyk¹ is an exception. Other exceptions are those metallurgical and ceramic engineering curricula which include mineral processing so that flocculation is at least mentioned². The present article represents a further step to remedy this situation.

Effluent disposal is a major problem around the world. Growing along with the population growth, industries create environmental problems and health hazards for the population. Hence, environmental concerns and progressing depletion of raw material resources behoove scientists and engineers to develop materials from renewable agricultural and plant resources to lower the extent of pollution of the environment.

The world population is increasing – while availability of potable water is decreasing. Water is essential for the survival of human beings – not to mention modern industry. Although the earth consists of 75% of water, water for drinking, sanitation, agricultural and industrial processes is not easily available. According to the United Nations Organization Report of 2005, 1.2 billion people lack access to adequate amounts of clean water and 2.6 billion people lack proper sanitation. This situation got only worse since 2005 and necessitates recycling of municipal wastewater and industrial effluents on a massive scale. To meet the requirements of potable, industrial and agricultural water, we have to treat the wastewater, particularly the municipal sewage sludges and slimes and industrial effluents.

Water is used, among other applications, in mineral processing, such as in bringing metal ores in the form of water slurries from their original location below the Earth surface to the surface and also in subsequent transport. Movement of coal from its deposits in coal mines and the subsequent surface transport similarly requires the use of water. It is for such reasons that the problem of potable water is related to that of industrial water. Clearly less use of industrial water - or recycling some of it - will increase the supply of potable water.

The effluents are highly undesirable and unsafe to use. Wastewater contains solid particles with a wide variety of shapes, sizes, densities and composition. Specific properties of these particles affect their behavior in liquid phases - and thus the removal capabilities. Many chemical and microbiological contaminants found in wastewater are adsorbed on or incorporated in the solid particles. Thus, essential for purification and recycling of both wastewater and industrial effluents is the removal of solid particles.

As renewable raw materials, polysaccharides already play an important role as alternatives to fossil raw materials - due to both their generally non-toxic nature and the constantly rising global demand for energy and raw materials. Polysaccharides are large organic molecules that occur in a variety of natural sources. Depending upon the source, the polysaccharides contain various impurities and also exhibit a variety of molecular characteristics. However, by purification, grafting and cationization, useful products can be made – usable as flocculating, drag reducing and viscosity enhancing agents³.

2. METHODS OF REMOVAL OF SOLID PARTICLES SUSPENDED IN LIQUIDS

The simplest process imaginable is by *gravity*. Solid particles have higher densities than water. However, fine particles with diameters on the order of 10 μm will *not* settle out of suspension by gravity alone in an economically reasonable amount of time. We note that particle sizes in

emulsions are still smaller, 0.05 – 5 μm , hence the removal of particles from emulsions (de-emulsification) is even more difficult.

The second process, still widely used, is *coagulation*. Destabilization of colloidal suspensions occurs by neutralizing the electric forces that keep the suspended particles separated⁴. The aggregates formed in the coagulation process are small and loosely bound; their sedimentation velocities are relatively low – although higher than in gravity separation. Given the nature of the process, the results are strongly dependent on pH and its variations.

Flocculation is caused by the addition of minute quantities of chemicals known as flocculants. Both inorganic and organic flocculants are in use. Among the inorganic flocculants, salts of multivalent metals like aluminum and iron are applied most often - at high concentrations⁴. Inorganic flocculants are used in very large quantities, they leave large amounts of sludge and are strongly affected by pH changes. Organic flocculants are typically polymeric in nature; by contrast to inorganic ones, they are effective already in ppm concentrations. Both synthetic and natural water-soluble polymers are used as flocculants.

In contrast to the process of coagulation, electric charge manipulation is *not* the dominant mechanism of action in flocculation. In fact, flocculation is possible without significant changes in the particle surface charges. As a consequence, flocculation is not strongly affected by pH in a given medium, or by pH variations. Moreover, flocculation is much more effective than coagulation since the so-called flocs are larger and more strongly bound than the aggregates obtained by coagulation. Thus, among the possible options, flocculation is the method of choice.

3. MECHANISMS OF FLOCCULATION

Polymeric flocculants act by *extensive solvation*⁵. Here lies, first of all, an explanation

how ppm concentrations of a flocculating agent are sufficient. In Figure 1 we show a schematic illustrating how one chain pervades a large volume of the liquid.

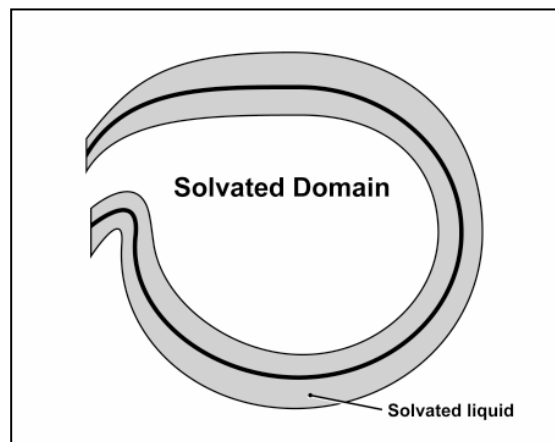


Figure 1. A section of a macromolecular chain in forming of a domain pervaded by a chain in the system of liquid + suspended solid particles. Liquid molecules are either solvated by the chain (shaded area) or else are located inside a domain. Size of the domain is related to the polymer radius of gyration -- as discussed in the text. When a flocculant is applied and such domains then formed, the solid particulate matter remains outside of the domains.

A measure of the pervaded volume is the radius of gyration R_G . The radius is the root-mean-square distance of the collection of atoms from their common center of gravity:

$$R_G^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i} \quad (1)$$

Here m_i is the mass of the i -th atom while r_i is the vector from the center of gravity to that atom; the summations run over all atoms. As discussed by Lucas and her colleagues⁷ and also by Gedde⁸, there are several methods of experimental determination of R_G , including light scattering and viscometry.

With large solvent volumes pervaded by the macromolecular chains, solid particulates are *pushed outside* the solvated domains such as shown in Figure 1. This is the main mechanism of action of the flocculating agents. The solid particles aggregate in much smaller regions now available to them. Clearly higher molar mass of the polymer results in larger or more solvated

domains. We shall return to this issue in a quantitative way later in this review when looking at suspensions containing specific solids and flocculants used to treat them.

It has been found that polymeric flocculants are also drag reduction (DR) agents^{9, 10}. The DR phenomenon is used to advantage in oil pipeline conduits, oil well operations, flood water disposal, fire fighting, field irrigation, transport of suspensions and slurries, sewer systems, water heating and cooling systems, airplane tank filling, marine systems. Most airplane passengers do not realize that filling their plane fuel tank would take much more time without the use of DR agents. The importance of drag reducers in saving human life during a fire can hardly be overstated.

We do have a joint explanation of flocculation and DR. The large volumes pervaded by polymeric chains cause DR. In turbulent flow the solvated domains such as seen in Figure 1 resist the eddies of turbulence and - not much affected - move along the flow. The only difference is in the shape; the domains in flow are oval rather than static approximately spherical ones. It has been demonstrated that solvation numbers obtained from ultrasound velocities are related to the DR efficacy; the larger the solvation number, the stronger is a given DR agent⁶. Thus, a domain flows as a unit, with some perturbation to its shape caused by the turbulence along the way. Here we see the reason for DR: individual solvent molecules solvated by polymer chains are not 'attacked' individually by eddies of the turbulence. When such an attack occurs, the solvent molecules defend themselves *collectively*. The solvent molecules inside the domains (see again Figure 1) are protected even more than those which by solvation are attached to macromolecular chains outside.

We now return to flocculation. Given the practical importance of this phenomenon, various explanations have been advanced before the mechanism described in Ref. 5 was formulated. Two such explanations still mentioned on occasion are surface charge neutralization and bridging. We shall consider them in turn.

The surface charge explanation is in terms of contamination of solid particles in solution by electrostatic adsorption of ions on their surfaces. We see why this cannot be a general mechanism of flocculation. There are suspensions in which flocculation occurs while the electrostatic forces are unimportant. Needless to say, in the presence of ions we can have flocculation enhanced by electrostatic adsorption of ions. The adsorption can cause repulsion between solid particles, attraction of counter ions into the vicinity of the particles, and thus formation of an electrical double layer - a phenomenon known for a century or so.

Since it was clear for a long time that the electrostatic mechanism cannot be operational in a number of systems in which flocculation occurs, as far back as 1952 a *bridging mechanism* model of flocculation was developed by Ruehrwein and Ward¹¹. One assumes that a single polymer chain forms a bridge between two or more particles. The basics of this model have been subsequently refined, but the main points are unchanged; the loops and tails of the adsorbed polymer chain on one particle protrude into solution and get attached to a second solid particle. The first problem with this model is that it cannot explain how ppm concentrations of a polymer are sufficient to cause flocculation. Second, what would be the force pushing a macromolecular chain to get adsorbed on a second particle? But assume for the sake of argument that such force exists, that anchoring of a macromolecular chain on two distinct suspension particles occurs somehow, conceivably as a consequence of simple Brownian dynamics motions. Then a 'bridge' would result in doubling the mass of the suspension particle, not more. The fact that flocs are much larger and heavier than just twice the size of particles before flocculation cannot be explained by the bridge formation. Thus, we are left with the solvation model described in the beginning of this Section as the only one explaining the totality of observed phenomena.

4. CLASSES OF ORGANIC FLOCCULANT

The organic flocculants fall into two categories, namely natural and synthetic. The polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen etc. are among the natural polymers used in flocculation. Synthetic flocculants are broadly divided as anionic, cationic and non-ionic categories. Polyacrylamide (PAM) and poly(ethylene oxide) (PEO) are non-ionic. The majority of the cationic groups of polyelectrolytes are derived by introducing quaternary ammonium groups onto the polymer backbone, although polymers containing sulfonium and phosphonium groups are used to a limited extent. The most commonly used cationic polyelectrolytes are poly(diallyl dimethyl ammonium chloride) (polyDADMAC). In the anionic group of polyelectrolytes, mainly two types of polymers are used; one type is polymers containing carboxyl functional groups and the other containing sulfonic acid groups. A representative of the former is poly(acrylic acid) and its derivatives, of the latter poly(styrene sulfonic acid) (PSSA).

The extensive use of polymers as flocculants is due to their distinct characteristic attributes^{12, 13}. As already noted, polymers are convenient to use and do not affect the pH of the medium. They are used in ppm quantities - with obvious consequences for the cost of flocculation. The flocs formed are larger, stronger and settle more easily than do the simple coagulation electrolytes. Flocculation efficiency of polymers increases with increasing molecular weight (we shall return to this fact below). Large tonnage use of inorganic compounds produces large amounts of sludge - a problem absent when using polymeric flocculants. Among polymeric flocculants, the synthetic polymers can be tailor made by controlling the molecular weight, molecular weight distribution and chemical structure. Thus, due to tailorability, synthetic polymers can be very efficient flocculants.

However, the synthetic polymers in flow are not shear resistant. Natural polymers - including polysaccharides - are fairly shear stable, bio-

degradable and easily available from reproducible farm or forest resources. The bio-degradability of natural polymers reduces their shelf life and needs to be suitably controlled. Their required dosage is large and their solutions and floc lose stability and strength respectively due to biodegradability. It is thus evident that all the polymers whether natural or synthetic have one or other disadvantages.

In this situation, attempts have been made to combine the best properties of both kinds of polymers by grafting synthetic polymers onto backbones of natural polymers after purification^{2,14-28}. Biodegradability is reduced because of a change in the original regular structure of the natural polymer as well as the increased synthetic polymer content. It is also observed that grafting of shear degradable polymers onto rigid polysaccharide backbone provides fairly shear stable systems.

Cationic polysaccharides can be prepared by a reaction of a polysaccharide with various reagents possessing positively charged groups such as amino, imino, ammonium, sulfonium or phosphonium groups. Cationized polysaccharides are effective flocculants over a wide range of pH. They are non-toxic and their biodegradability can be controlled. They are being used for sustained organic and inorganic matter in wastewater carrying negative charges. They are also used as wet-end additives in paper making - for controlling flocculation, retention and paper strength. Introducing cationic groups onto starch gives good mineral binding properties; this is required for anchoring the mineral to the fibers.

Since we have concluded that synthetic polymers grafted on natural ones provide the best combination of properties, in Figure 2 we show an example how graft polymerization can be initiated. Ceric ions provide here the initiator.

Whether grafting has been successful one can verify by a variety of techniques: Fourier-transform infra-red (FTIR) spectroscopy, elemental analysis (C, H, N analysis), intrinsic viscosity measurement²⁹, thermophysical analysis including determinations of glass and

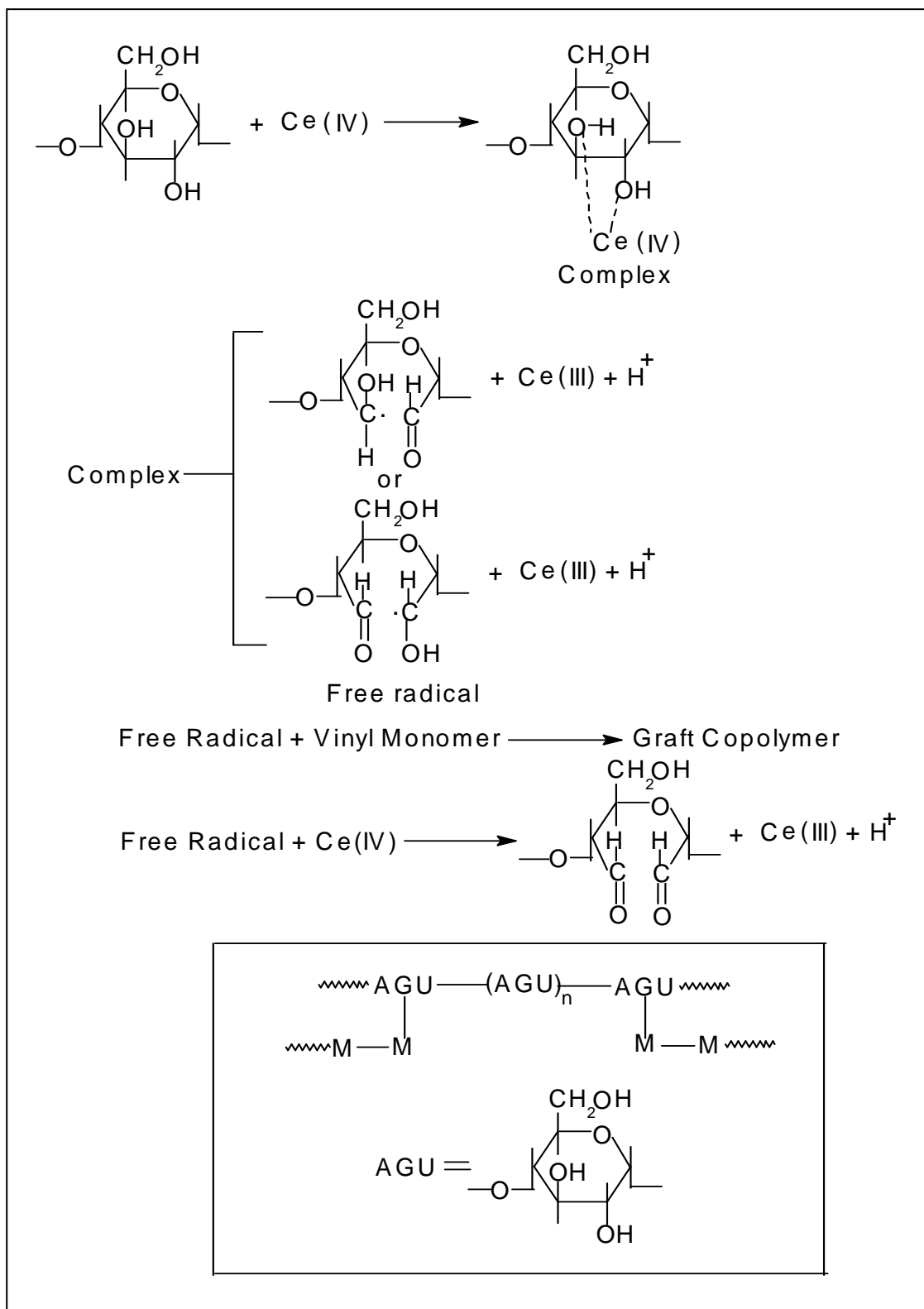


Figure 2. Initiation of graft copolymerization by ceric ions.

melting transitions^{7,8,30-33}, by several techniques for determination of molecular weight and radius of gyration^{7,8} and also by X-ray diffractometry^{7, 34} when crystalline phases are formed.

5. EVALUATION OF FLOCCULATION EFFICACY

When flocculant is introduced into the container, an interface is formed. Above it is the supernatant liquid while below is the suspension containing the contaminants. Under the action of the flocculating agent, that is along with the progress of the flocculation process, that interface descends, until all contaminants are settled at the bottom.

Two methods of flocculation efficacy determination are in use, a so-called jar test and a settling test. In the *jar test* one adds the flocculant in solution form to the suspension. A typical flocculant dose varies from 0.025 ppm to 1 ppm. The system is stirred at a uniform speed, first at a high speed such as 75 rpm for 2 minutes and then at a slow speed such as 25 rpm for 5 minutes. Afterwards, a settling time of 10 min was allowed. At the end of the settling period, the turbidity of the supernatant liquid is measured with a turbidity meter. The lower the turbidity, the better is the flocculant. An example of results so obtained is shown in Figure 3 (the symbols in the insert pertain to different compositions of the flocculant).

Supporters of the settling test claim that their test provides a higher accuracy than the jar test. One reason is that the jar test results show sometimes minima and/or maxima. The nature of the solid suspension may also indicate which test will perform better in a given situation. Where flocs are widely dispersed, it may be necessary to induce a velocity to suspended solids to obtain larger flocs. In this case the jar test is more appropriate. In the *settling test* one typically employs a 100 ml. graduated cylinder and stopwatch. First the suspension sample is placed in the cylinder and then polymeric flocculant solution is added into it. The cylinder

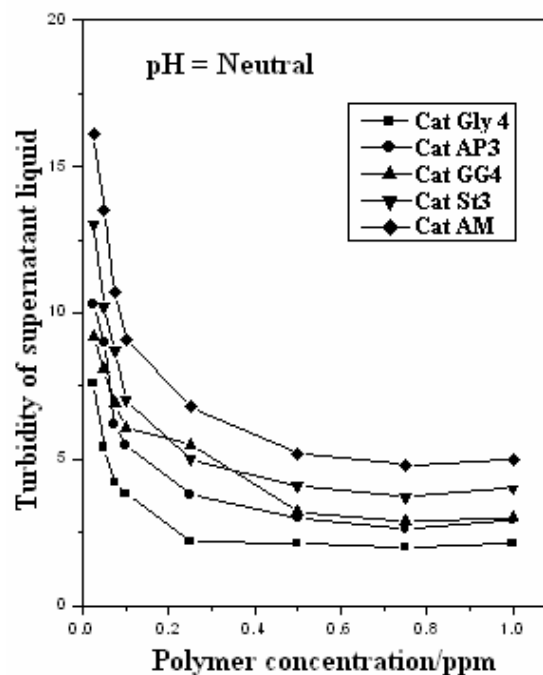


Figure 3. Jar test results in 0.25 wt. % silica suspension using several flocculants.

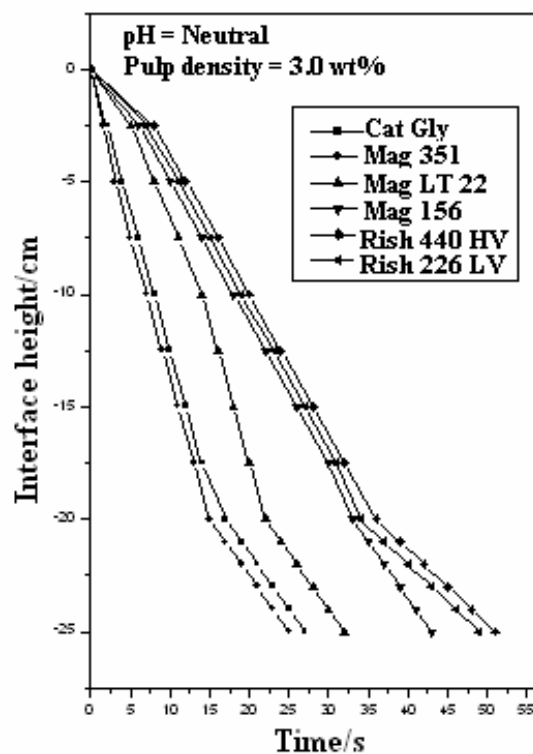


Figure 4. Settling characteristics of a silica suspension with addition of cationic glycogen (Cat Gly) and several commercial flocculants.

is inverted a number of times for thorough mixing. After that the cylinder is set upright and the height of interface between water and settling solid bed is measured over time. An example of such results is shown in Figure 4.

As can be seen in Figure 4, curves of the interface height as a function of time are linear, except for fairly short final parts which are concave. The linear parts of such diagrams thus provide us with the *settling velocities* y which are used as a measure of the flocculant efficacy of an additive in a given suspension medium.

6. PREDICTION OF FLOCCULATION EFFICACY

As already discussed in Section 4, the idea is to combine advantageous features of natural and synthetic flocculants. Thus for instance copolymers have been synthesized by grafting flexible polyacrylamide onto a rigid polysaccharide backbone. Grafted glycogen has shown very good performance in flocculation^{27,28} because glycogen has a highly branched structure and a high molecular weight. One of us has developed an Easy Approachability Model (EAM)². According to EAM, an increase in branching, in molecular weight and in subsequent grafting/ionic loading, the approachability of the contaminants towards the flocculant chains is enhanced – and so is the flocculation efficiency.

EAM helps in the choice of a flocculant, including a possible chemical modification of a given flocculant by grafting. A quantitative criterion would be still better. Discussing flocculation mechanisms above, we have pointed out how interaction of solid particles with polymeric chains affects the flocculation efficacy. This fits with the discussion by Kopczynska and Ehrenstein³⁵ how important are properties of interfaces in multiphase systems. However, one begins with a candidate polymer and the question is: will it serve well as a flocculant ?

The answer can be found in the mechanism of

flocculation described in the beginning of Section 3. We now consider experimental evidence in the light of the model. Several types of suspensions were investigated^{5,36}, containing in turn silica, iron ore, coal and manganese ore. For each system the flocculation efficacy was determined in terms of the settling velocity y and the radii of gyration; a variety of polymers with different chemical structures was so evaluated. The results are presented in Figure 5: settling velocities vs. the radius of gyration.

Figure 5 demonstrates the validity of the model⁵. Several flocculating agents were applied to each suspension system. In each such system application of a polymeric flocculant with a higher radius of gyration results in an increased settling velocity. This can be represented by a relationship valid for each system:

$$y = aR_G^b \quad (2)$$

where a and b are parameters characteristic for a given suspension medium, that is both the dispersed solid phase and the majority liquid phase. One can consider Eq. (2) as a quantitative formulation of the EAM discussed in the beginning of this Section.

Eq. (2) provides us with the desired capability to select efficient flocculating agents. Given a liquid system, we evaluate radii of gyration of candidate polymeric flocculants. The larger the radius of gyration, the higher will be the flocculation efficacy.

While our primary concern is water purification, Eq. (2) is general. The majority liquid phase does not have to be water.

Flocculation experiments are not 'colorful'. An instructional laboratory experiment is under development.

We began this article with stressing the need for water recycling. Water purified by flocculation cannot be used as potable – but it can be used as agricultural water. Whenever that is done, equivalent amounts of fresh water are saved. At the same time, rejection of un-purified water into the environment has been prevented.

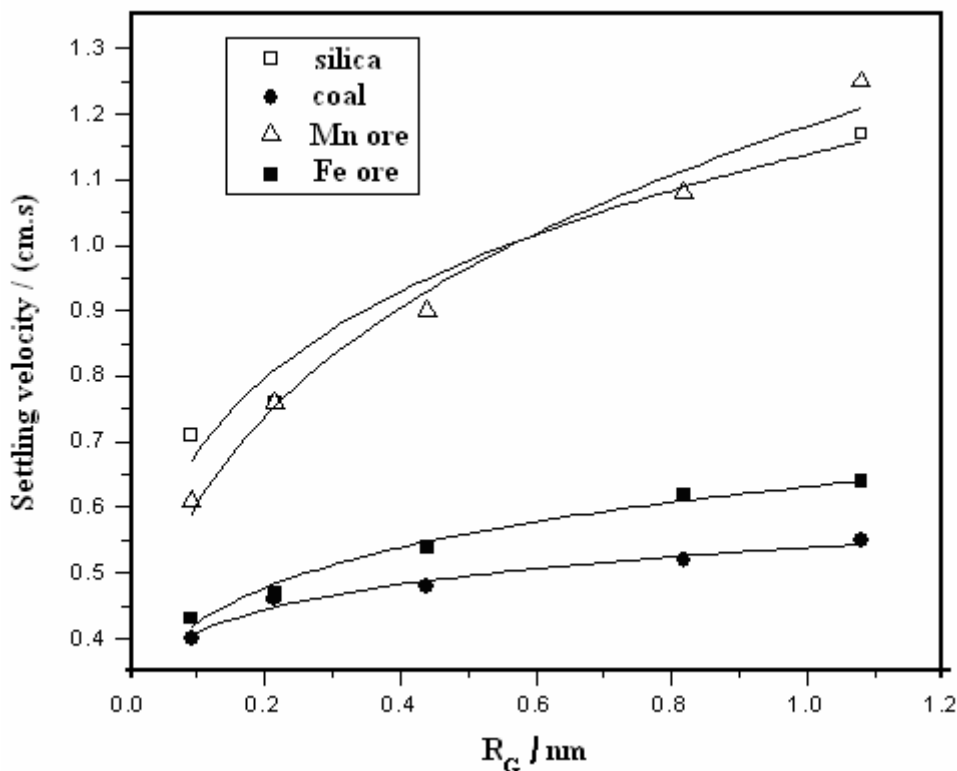


Figure 5. Flocculation settling velocity for several suspension media as a function of the radius of gyration of the flocculating agent. While for silica suspensions we have only two experimental points, the data have been sufficient to evaluate parameters in Eq. (2) and plot the curve.

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