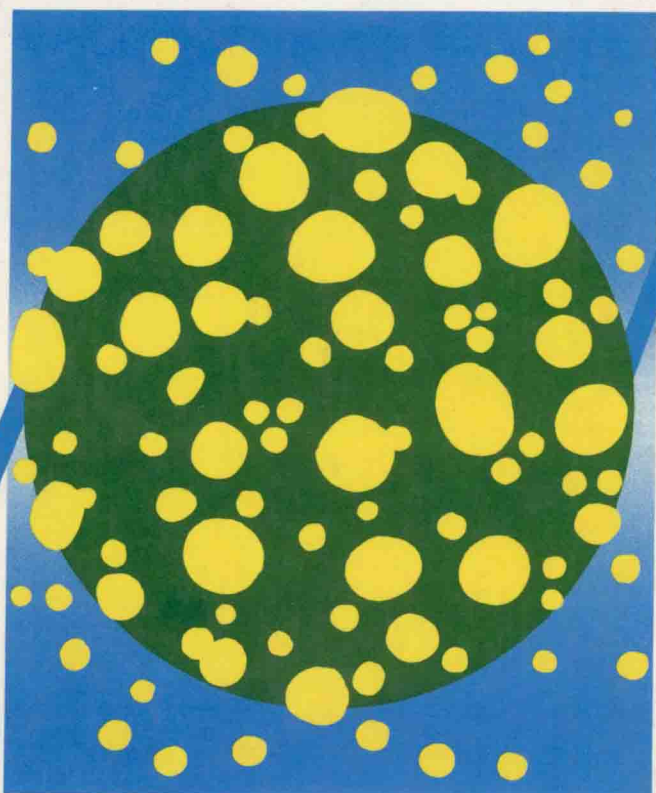


**ADVANCES IN  
MEASUREMENT  
AND CONTROL  
OF COLLOIDAL  
PROCESSES**



**R A WILLIAMS &**

**N C de JAEGER**

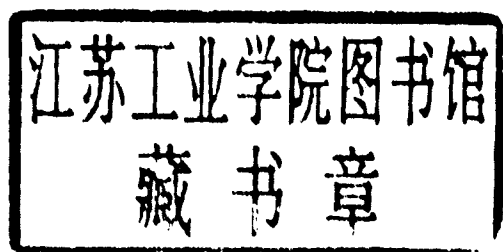
# Advances in Measurement and Control of Colloidal Processes

Edited by

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## PREFACE

### **Advances in Measurement and Control of Colloidal Processes**

**Edited by**

**R.A. Williams and N.C. de Jaeger**

This volume presents a selection of refereed and edited papers that were presented at the *International Symposium on Colloid and Surface Engineering* held in San Diego, under the co-sponsorship of the Fine Particle Society and the American Institution of Chemical Engineers, in August 1990. The emphasis of the conference, and of this book, was the practical measurement and exploitation of the principles of surface and interface science embracing a wide range of industrial sectors. Consequently, some of the latest thinking and practical techniques are reported here by industrial practitioners and university research groups.

The growing interest in the *engineering* of dispersed systems and interfaces reflects the importance of this subject area, being at the cutting edge of many technological developments in coatings, photographic imaging, microelectronics, pharmaceuticals, environmental control, biotechnology, food and chemical processing. These disciplines share a common foundation in the control and utilization of powder technology, surface chemistry, surface forces and interfacial phenomena. The contents of the book have been arranged under topics according to specific measurement techniques or phenomena, under the headings of *Processing and Characterization of Aggregated Materials*, *Developments in Instrumentation for Monitoring and Characterization of Dispersions*, *Controlled Particle Formation Technologies*, *Mineral and Inorganic Colloids – Micro and Macroscopic Characterization Methods*, *Measurement and Simulation of Complex Colloidal Processes*, and *Advances and Problems in Micron and Sub-micron Sizing Techniques*.

Our thanks are due to the members of the organizing committee, whose names are given elsewhere, and many others who participated in the Symposium and gave views on the work published herein.

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**PART I**

**PROCESSING AND  
CHARACTERIZATION OF  
AGGREGATED MATERIALS**



# EFFECT OF DOSING AND MIXING CONDITIONS ON FLOCCULATION BY POLYMERS

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Flocculation of suspensions by polymers can be greatly influenced by the dosing and mixing procedures used, especially for high solids concentrations. These effects can be explained in terms of several rate processes associated with polymer adsorption and particle collision. Break-up of initially-formed flocs can occur during rapid mixing and, by limiting this stage to only a few seconds, much larger flocs can be obtained. Slow addition of polymer, or the addition of a more dilute polymer solution can give great improvements in flocculation.

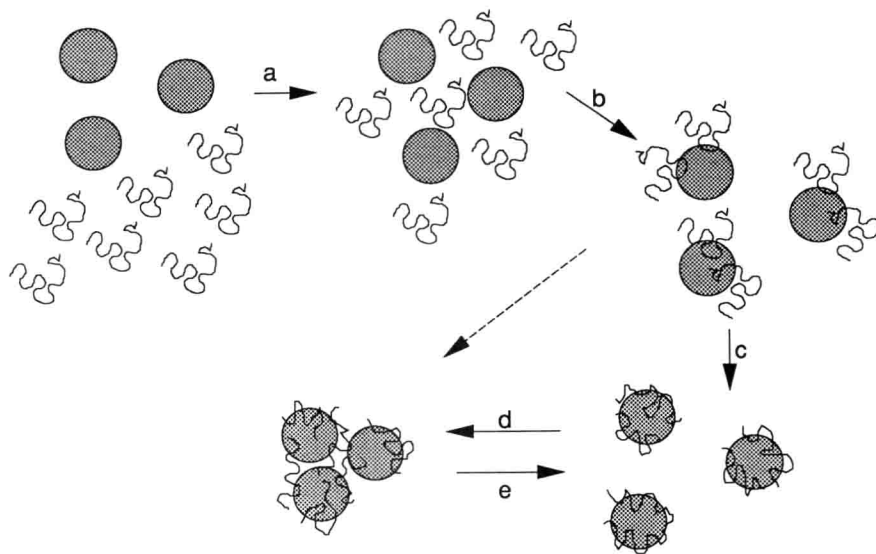
## 1 INTRODUCTION

Polymeric flocculants are widely used in solid-liquid separation processes, such as mineral processing, water treatment and many others. Their mode of action is broadly understood [1], although several uncertainties remain. In particular, it is known that precise details of dosing and mixing during polymer addition can have a great influence on the behaviour, but there is little systematic information on this point.

At the moment of addition of a polymer solution to a suspension of particles, usually under conditions of agitation, several processes are initiated, which are illustrated schematically in Fig 1.

- a) mixing of polymer solution throughout the suspension
- b) adsorption of polymer molecules on the particles, to give some degree of destabilization (either by charge neutralization or by giving opportunity for "bridging" between particles).
- c) rearrangement of adsorbed polymer molecules from an initially extended state to a flatter, equilibrium conformation.
- d) collisions between destabilized particles to give aggregates (flocs).
- e) break-up of flocs under the influence of applied shear.

These processes occur at different rates, which depend on a number of factors. Furthermore, they do not occur sequentially, but, to a large extent, concurrently, which makes the whole system difficult to analyse, but can help to explain the importance of mixing and dosing effects.



*Fig 1 Schematic diagram showing a) mixing of polymer chains among particles; b) adsorption; c) reconfiguration of adsorbed chains; d) flocculation and e) floc break-up. The broken arrow indicates the collision of particles before reconfiguration of adsorbed chains.*

## 2 RATE PROCESSES

### 2.1 Mixing

In many cases, effective polymeric flocculants are of quite high molecular weight and are added as rather viscous solutions. For this reason the thorough distribution of polymer throughout the suspension may take some time and small droplets of polymer solution may persist for an appreciable fraction of the mixing time. These could possibly act as "nuclei" for floc formation, although there is little evidence for such an effect [2]. If the time needed for a thorough distribution of added polymer among the particles is long relative to the adsorption and flocculation rates, there may be significant practical consequences. For instance, excess polymer may adsorb on a fraction of the particles, which could then become restabilized. This effect is thought to be responsible for the residual haze and poor filterability found for some flocculated suspensions [3].

There is a good deal of evidence, largely empirical, that a high degree of turbulence at the point of addition of polymer solution can have a beneficial effect on the flocculation process. This is especially the case for fairly concentrated suspensions, where adsorption and particle collision rates are rapid. For instance, Warden [4] found that the polymer-assisted thickening and dewatering of waterworks sludge could be greatly improved by careful attention to the polymer dosing point. It was shown that poor thickening was obtained at low and high values of applied shear, with intermediate values giving optimum results. There are many other applications, such as papermaking, where mixing conditions are known to be important.

Many laboratory flocculation trials are conducted in stirred vessels and the stirring rate can have a marked effect on the results. Such systems are complicated by the fact that there is a wide variation of effective shear rates (or energy dissipation) in a stirred vessel [5], so that floc formation and break-up may occur in different regions. It is typically found that flocs pass through a maximum size at some time after polymer dosing, and can show a marked reduction in size with continued stirring. These changes are reflected in dewatering rate [6] and settling rate [7], which also reach maximum values after a certain stirring time.

By dosing polymer solution slowly or intermittently to a stirred suspension, considerable improvement in flocculation has been observed by Hogg [8]. In fact, Hogg showed that, in some cases, floc growth occurred only during polymer addition. It will be shown later that addition of polymer as a more dilute solution can also enhance the flocculation process. Clearly, these effects must be closely related with mixing, since the more slowly polymer is added, the less likely is local overdosing and flocs are not allowed to grow very rapidly during the very early stages of the process.

## 2.2 Adsorption

It seems reasonable to suppose that the adsorption of polymer molecules on particles is a process that occurs at a transport-limited rate, at least in the early stages, when the fractional coverage is still quite low. In that case, the rate of adsorption depends on the rate of arrival of polymer molecules at a particle surface, and the number of encounters in unit time and unit volume can be written:

$$J_{12} = k_{12}N_1N_2 \quad (1)$$

where  $N_1$  and  $N_2$  are the number concentrations of particles and polymer molecules respectively and  $k_{12}$  is the appropriate rate constant (see below).

In practice, a certain fraction of added polymer needs to be adsorbed on particles to give adequate destabilization and hence allow flocculation to occur under the given shear conditions. If this fraction is  $f$ , then the time required for adsorption can be derived simply, assuming that the particle concentration remains constant, giving:

$$t_A = -\ln(1 - f)k_{12}N_1 \quad (2)$$

A very important feature of this result is the inverse dependence on particle number concentration - the adsorption time will be lower at higher particle concentrations. The required time is also independent of the polymer concentration, provided that the same fraction of added polymer needs to be adsorbed. This last condition implies that the amount of adsorbed polymer needed to destabilize particles is proportional to particle concentration and that adsorption is essentially quantitative.

The adsorption rate constant can be estimated if it is assumed that both particles and polymer molecules can be treated as spheres. This assumption may seem unreasonable in the case of long-chain polymers, but such chains often adopt an approximately spherical, random coil, conformation in solution and can be treated, hydrodynamically, as equivalent spheres. The transport of polymer molecules to particles may be by diffusion (perikinetic) or under the influence of fluid motion (orthokinetic). In each case, the rate constant can be derived from the appropriate Smoluchowski expression (see Gregory [9]). For the perikinetic case:

$$k_{12} = (2k_B T/3\mu)(a_1 + a_2)^2/a_1a_2 \quad (3)$$

where  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\mu$  is the fluid viscosity and  $a_1$ ,  $a_2$  are the radii of the particles and polymer molecules respectively.

With suspensions subjected to agitation, as is always the case during polymer dosing, the orthokinetic result can be written:

$$k_{12} = (4/3)G(a_1 + a_2)^3 \quad (4)$$

where  $G$  is the velocity gradient or shear rate, which is assumed uniform.

A uniform shear rate is not a realistic assumption for the turbulent conditions encountered in polymer dosing and mixing applications, where turbulent eddies can play a role in polymer transport [10]. However, an appropriate mean value of the shear rate,  $G$ , (determined, for instance from the mean energy dissipation) can be inserted in eq (4) to give an approximate idea of the adsorption rate under non-uniform shear conditions.

The high shear forces present at a particle surface may reduce the adsorption rate and may even cause desorption of adsorbed polymer [11]. Although a quantitative analysis of this aspect is not yet possible, it may be one reason to expect an "optimum" mixing intensity for flocculation by polymers.

Rate constants calculated from eqs (3) and (4) show that orthokinetic transport will often be much more significant than diffusion in promoting particle-polymer contacts. This is the case for particles of about 1  $\mu\text{m}$  in size or greater and polymer molecules larger than about 0.1  $\mu\text{m}$ , with effective shear rates greater than about 50  $\text{s}^{-1}$ . Since typical polymer mixing conditions can correspond to shear rates of several hundred  $\text{s}^{-1}$  or greater, orthokinetic transport is likely to be important in most cases involving polymers of moderately high molecular weight. In such cases, the rate of polymer adsorption will depend strongly on the effective shear rate.

## 2.3 Reconfiguration

At equilibrium, an adsorbed polymer chain adopts a conformation consisting of *trains*, *loops* and *tails*, and a great deal of effort has been expended in both theoretical and experimental determinations of the segment density distribution as a function of distance from the adsorbing surface (see e.g. Cosgrove [12]). However, this equilibrium arrangement may be very different from the conformation of a polymer molecule in free solution and at the moment of initial contact with the particle.

The time over which the equilibrium conformation is attained can have a great influence on flocculation, since it is very likely that bridging contacts will occur more readily when the adsorbed polymer is in an extended, non-equilibrium state. When there is strong interaction between adsorbing polymer segments and the particle surface, for instance between ionic groups of opposite sign, it is likely that a polymer chain will eventually lie flat on the surface, thus presenting no opportunity for bridging contacts. It could be argued that bridging contacts formed by polymer chains very soon after adsorption, or by simultaneous adsorption on two particles, would be weaker than those formed by adsorbed chains in a more "flat" configuration. In the latter case, more segments of the chain would be attached to the particles and this should result in stronger binding between particles. Also, the more extended chains would occupy a smaller fraction of the particle surface and so the collision efficiency might be lower (see below). These concepts are illustrated schematically in Fig 2 and may lead to a certain optimum reconfiguration time for bridging flocculation.

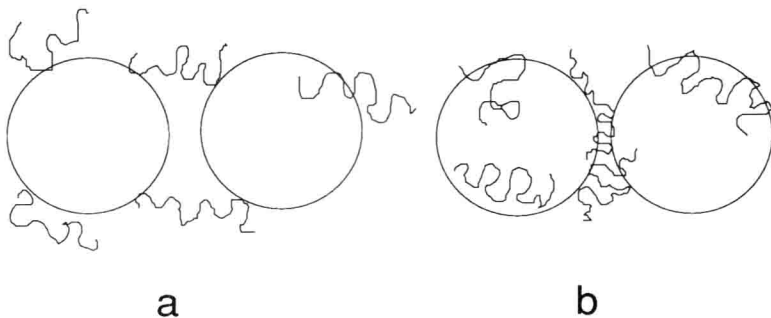


Fig 2 a) Bridging by adsorbed polymer chains before reconfiguration has occurred. b) Bridging by chains after some reconfiguration. In this case there are more polymer-particle contacts and possibly stronger binding.

Pelssers *et al* [13] assumed that adsorbed polymer chains would either be in an "active" or "inactive" state, the former corresponding to the extended, non-equilibrium condition in which bridging contacts are possible. After some time, relaxation to a flatter, inactive configuration occurs. The rate of this relaxation process depends on the nature of the polymer and the on the particle-polymer interaction, but characteristic times of a few seconds for polymers of several million molecular weight have been estimated [14]. These times fit quite well the flocculation data of Pelssers *et al* [13]. However, very much longer relaxation times (many minutes or even hours) are indicated from experiments of Pefferkorn and Elaissari [15], with quaternized polyvinyl pyridine of lower molecular weight ( $3.6 \times 10^5$ ).

At present, there is little other information which is of help in modelling the reconfiguration process under practical flocculation conditions. The effect of shear on the process seems to have been neglected.

## 2.4 Flocculation

The rate of flocculation depends on the collision rate of particles, given by eq (1), with  $N_1 = N_2$ , at least in the early stages of the process. Integration of the rate expression gives the characteristic flocculation time,  $t_F$ , in which the total number of particles is reduced to half the initial value:

$$t_F = 2/k_{11}N_0 \quad (5)$$

where  $N_0$  is the initial particle number concentration.

It has been shown previously [9] that this expression, applied to stirred suspensions and fairly high molecular weight polymers, predicts flocculation times considerably lower than adsorption times. Eq (5) is based on the assumption that every collision results in permanent attachment, but this will not usually be the case. If the fraction of particle surface with adsorbed polymer is  $\theta$ , and it is assumed that the only successful collisions are those between coated and uncoated surfaces, then it follows that the flocculation rate will depend on the product  $\theta(1 - \theta)$ . This leads to the well-known "half surface coverage" condition for optimum flocculation [16]. If the amount of polymer added to the suspension is not sufficient to give  $\theta > 0.5$ , then the collision efficiency should increase throughout the adsorption phase. It follows that there will be a certain time

after polymer dosing during which particles are not yet sufficiently destabilized for flocculation to occur. For dilute suspensions this "lag time" can be appreciable (several minutes). It can be reduced by increasing the shear rate, which increases both adsorption and flocculation rates. Such effects have been verified experimentally [17].

For more concentrated suspensions, polymer adsorption is sufficiently rapid for flocculation to begin almost immediately after dosing. In such cases, mixing and reformation rates need to be considered (see below).

## 2.5 Floc Break-up

In a sheared suspension, flocculation proceeds at a rate which depends on the applied shear rate, but floc growth cannot continue indefinitely. A limiting floc size is usually observed, above which breakage to smaller units occurs. The limiting size depends on the shear rate and on the strength of the flocs, which is largely determined by the amount and type of polymer used. In typical stirred vessels there is highly non-uniform distribution of energy dissipation (and hence of shear rate). This means that flocs formed in low-shear regions may be disrupted in regions of more intense shear (for instance, near the tips of rotating blades).

It is generally found (see, e.g. Mühle and Domasch [18]) that the maximum stable floc size  $d_{\max}$  depends on the energy dissipation per unit mass,  $\epsilon$ , according to:

$$d_{\max} = C\epsilon^{-n} \quad (6)$$

where  $C$  is a coefficient which depends on the nature of the particles and the flocculant and the exponent  $n$  is often in the range 0.2 - 0.4.

Long-chain polymers giving bridging flocculation lead to much stronger flocs (higher  $C$  values) than simple salts. Polyelectrolytes acting by charge neutralization give flocs of intermediate strength. The nature of floc breakage under the influence of shear can be of essentially two types: large-scale splitting into fragments of comparable size or erosion of primary particles or microflocs from the outer floc surface. The latter is thought to occur mainly for quite small flocs (smaller than the turbulence microscale), whereas larger flocs are subject to splitting. Typically, flocs formed by polymer bridging can have diameters approaching 1 mm, which is larger than the microscale of turbulence (of the order of 100  $\mu\text{m}$  in most cases).

A very important point concerning floc breakage is that it is often irreversible in the case of polymer bridging. Although flocs formed by long-chain polymers are more resistant to breakage, they tend not to re-form if breakage does occur. When charge neutralization is the mode of action, flocs are generally weaker, but can re-grow after breakage if the shear rate is reduced [19]. Irreversible floc breakage has important implications in choosing the duration and intensity of mixing during polymer dosing.

## 2.6 Overall Process

After considering the various stages in Fig 1 separately, it is worthwhile to look again at the effect of mixing conditions, in the light of the other processes. The table below shows the effect of particle concentration and mixing rate on the rate of the various steps. A "-" indicates little or no effect expected. In other cases the number of "+" signs indicates the estimated importance of the effect. For instance, both adsorption and flocculation rates are expected to depend on the square of the particle concentration and so both are given a "++" rating in the appropriate column. Where there is some uncertainty, for instance over the effect of particle concentration on floc break-up (since the



effect of particle collisions on break-up is not well-established), then a "?" sign is included. The final column contains estimated times for the processes, assuming laboratory-scale stirred reactors and a realistic range of particle concentrations and stirring rates.

Step	Effect of:		Typical time scale
	Particle Concentration	Mixing Rate	
Mixing	-	+	Seconds
Adsorption	++	+	0.5 s to minutes
Reconformation	-	?	1 s to hours (?)
Flocculation	++	+	0.1 s to minutes
Floc break-up	+	+++	Seconds

If the polymer solution is dosed as a small volume of a fairly concentrated solution (typically of the order of 0.1%), then the time required to achieve complete distribution throughout the suspension in a stirred reactor might be of the order of several seconds. During this time polymer adsorption may occur to an appreciable extent, and in a non-uniform manner (i.e. some particles receive excess polymer). Furthermore, these particles may undergo many collisions during the mixing time, so that flocs may form. The extents of adsorption and flocculation depend on the stirring rate and the particle concentration, whereas the mixing time depends primarily on the stirring rate and not on the particle concentration. This means that, as the particle concentration is increased (with a proportionate increase in polymer concentration), there should be an increased chance of flocculation occurring before complete mixing has been achieved. In a stirred vessel these "premature" flocs may be disrupted in regions of high shear and the fragments may not re-flocculate. If complete mixing of polymer could be achieved *before* any adsorption and flocculation were allowed to proceed, then it is likely that a more uniform flocculation process would be observed.

The reconformation process does not depend primarily on either the stirring rate or the particle concentration. As these parameters are increased, so is the particle collision rate, thus increasing the chance of bridging contacts forming through adsorbed polymer chains in a non-equilibrium configuration. This should give improved flocculation, although there is little experimental evidence on this point. Since estimates of typical reconformation times range from seconds to hours, it is likely that this is an important effect in most practical applications of polymeric flocculants, with fairly concentrated suspensions. In such cases particles would collide many times before adsorbed polymer had adopted an equilibrium configuration.

### 3 EXPERIMENTAL

By way of illustration of some of the concepts outlined above, some examples of mixing effects in the flocculation of clay suspensions by a high molecular weight cationic polyelectrolyte will be given. These are taken from more detailed results to be published elsewhere [20].