TO MY WIFE

INVESTIGATIONS OF SOME ELECTROCHEMICAL AND COLLOIDAL PROPERTIES OF POLYMERIC FLOCCULANTS

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by

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ABSTRACT

The application of research to an industrial problem in the field of colloid science is described and the dual nature of the investigation is explained.

The first part deals with the theory of flocculation of colloidal suspensions by water-soluble polymers. Preliminary investigations into methods of assessing the interaction of Thames River mud with a proprietary 'mud remover' are discussed. An examination has been made of the effect of 45 polymeric flocculants and coagulants on mud suspensions. The optimum polymer-to-solids ratio has been determined for each polymer and estimates have been made of floc size and the degree of cohesion. A novel flow-cell has been devised to study the interaction of mud with polymeric flocculants during the process of mud removal under defined hydrodynamic conditions. Calculations have been made to determine the approximate shearing stress required at a horizontal surface to prevent sedimentation of mud particles within the cell. A comparison has been made of different types of polymeric flocculant as mud removers. The effects of combinations of flocculants and inorganic coagulants, and of mixed flocculants, have been studied.

The results provide substantial evidence for the theory that 'mud removal' is a special case of flocculation in general; both depend on adsorption of long polymers, leading to adhesion of adjoining particles by molecular 'bridging'.

The second part of the thesis is devoted to a study of the principal cause of corrosion at West Thurrock Generating Station and the unforeseen property of corrosion inhibition exhibited by proprietary flocculants.

An examination has been made of evidence of inhibition during experiments not designed to investigate corrosion aspects, but to observe mud polymer interactions. Simple qualitative confirmatory tests of the corrosion mechanism and its inhibition by flocculants

are discussed.

Potentiometric studies, capacitance and resistance measurements on cupro-nickel in aqueous 0.2 M NaCl solutions and the inhibiting effects of polymeric flocculants are described. The effect of polymer on the structure of the oxide films has been studied by electron microscopy. A mechanism for inhibition has been proposed; it is postulated that the adsorbed impurities (polymeric flocculant) influence the crystal morphology, leading to non-porous oxide films.

Appendices specify the polymeric flocculants investigated and give calculations of the statistical length of a polyacrylamide molecule in aqueous solution.

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FOREWORD

In Britain, the Central Electricity Generating Board (C.E.G.B.) is continuously faced with the problems of corrosion in its generating stations. In particular, corrosion of condenser tubes arising from the use of polluted estuarine river water for cooling is very evident and cases have occurred where the effective life of tubes has been greatly reduced by corrosion when compared to the expected life in service. Expensive cupro-nickel tubes have been developed to combat the corrosive effects of salinity in some waters. Tube failure in the condenser system of a generating station involves the 'shut-down' of plant and the consequent loss of power supply, and high maintenance costs.

Polluted river waters contain suspended mud which settles in the culverts, water boxes, strainers and condenser tubes, and by intimate contact with the tubes causes incipient corrosion, reduction in heat transfer efficiency and hence loss of vacuum and low overall efficiency of power generation. Typical methods of treatment and prevention of mud fouling of condenser systems are:

(i) manual cleaning of tubes and water boxes during maintenance shut-down - a most unpleasant task for operatives.

(ii) chlorination of the cooling water at the intake to prevent the formation of organic slime and reduce corrosion.

(iii) the Taprogge system of continuous cleaning of condenser tubes, which consists of introducing into the cooling water a quantity of sponge rubber balls having a density close to that of water and being of slightly larger diameter than the bore of the tube. Flow of water forces the balls through the tubes, automatically cleaning the surfaces. The balls are trapped at the out-let side and recirculated. Both chlorination and the Tapproge system require heavy capital outlay for the plant involved.

(iv) flushing with town-main water during overnight shut-down. This usually proves to be impracticable, particularly in densely populated regions consuming large quantities of water for domestic use.

Investigations by the C.E.G.B. have shown that the problem can be overcome by the treatment of river cooling water with a commercially available chemical referred to as a 'colloidal polyelectrolyte'*. This material is claimed to remove existing mud and silt while regular treatment prevents build-up of further deposits. Actual plant trials have shown the material to be effective in maintaining systems free from mud, halting corrosion and maintaining the thermal efficiencies of the tubes in pristine condition.

However, the 'polyelectrolyte' is expensive and even though use is confined to short periods at very low concentrations, when used in such large volumes of water (up to thirty six million gallons per hour for a large generating station) the costs are high.

It is significant that the 'polyelectrolyte' is claimed to flocculate mud; tests have confirmed this. Because of the similarity in the properties of the 'polyelectrolyte' and materials used in mineral processing for flocculation of suspensions for clarification and thickening and generally for solid-liquid separation, the C.E.G.B. initiated a research programme under the supervision of Dr. J.A. Kitchener (Reader in the Science of Mineral Processing , Imperial College) to study the colloidal properties of Thames River mud and to investigate the mode of action of 'polyelectrolytes' on mud, and consider alternative materials. This work has been carried out in the Surface Chemistry Laboratory in the Department of Mining and Mineral Technology.

* Although most technologists loosely refer to these materials as 'polyelectrolytes' they are more precisely 'polymeric flocculants', some being virtually non-ionic, some anionic, some cationic and some amphoteric.

During the course of the investigation it became apparent that it was essential to study two different aspects of the problem - namely, colloidal effects and corrosion protection. Although the two aspects may arise from similar fundamental surface phenomena, it was necessary to investigate the colloidal interactions of mud and 'polyelectrolyte' separately from the ability of 'polyelectrolytes' to inhibit corrosion of cupro-nickel in neutral aqueous environments. Accordingly, the work recorded in this thesis is presented in two parts.

PART I

COLLOIDAL PROPERTIES OF POLYMERIC FLOCCULANTS

1. INTRODUCTION

1.1 Stability of colloidal suspensions (sols)

Sols are stable dispersions of very small particles of a solid ('dispersed phase') in a liquid ('dispersion medium'). They are conventionally divided into two broad classes, lyophilic or lyophobic. Lyophilic colloids have a great affinity for the dispersion medium, and solvation plays an important part in their stability (1). Such colloids are now recognised to be true solutions of very large molecules such as natural macromolecular substances or synthetic polymers. Examples of lyophilic colloids are starches, proteins, high molecular weight water-soluble polymers - all exhibiting reversible solvation characteristics, resulting in true thermodynamic stability when dispersed.

In contrast, lyophobic colloids are suspensions of very small, insoluble, particles having little affinity for the dispersion medium. The surface properties of the particles play an essential role in the stability and behaviour of these systems. Lyophobic sols are metastable; work is required to prepare such dispersions and coagulation is spontaneous although perhaps extremely slow.

Between the two extreme classes, many systems exist which have intermediate properties. Clays are a good example of this type (2); in its sodium form montmorillonite is virtually a hydrophilic colloid, the individual lamellae spontaneously dispersing in water, but clays behave like a hydrophobic system in many respects, e.g. they are susceptible to flocculation by electrolytes of appropriate type. Clays also provide an example of the wide range of particle size which must be included in the definition of a suspension (3). The smallest particles in the range 0.1 - 1.0 μ behave almost as true colloids showing vigorous Brownian motion, appreciable diffusion and very slow settling;

but coarser particles are large enough to settle, under the influence of gravity, at an appreciable rate. The larger the particles, the less significant is the effect of surface properties. There is a continuous gradation from dispersions to coarse suspensions.

It is nowadays accepted that the stability of hydrophobic dispersions is dependent on long-range molecular forces that exist between the particles(4). Destabilization (coagulation) is considered as the aggregation of particles through the agency of the long-range forces of attraction overcoming the 'energy barrier' which otherwise prevents particles in a stable system from coming into contact. Generally the electrolytic nature of the surface of a particle creates the electrical double layer which provides the energy barrier necessary for stability; but other causes of stabilization such as steric interference(5) and hydration stabilization are recognised(6). In protected colloids, an adsorbed lyophilic compound converts an intrinsically lyophobic material into a lyophilic colloid.

The present discussion will be largely restricted to electrical interactions of particles as this is by far the most important factor in aqueous dispersions of coarse particles.

In contact with aqueous media suspended particles almost invariably aquire an electrical double layer(7) which arises from one or more of the following processes:

(1) ionization of ionogenic groups on the surface of the particles;

(2) unequal dissolution of ions from a crystal lattice;

(3) adsorption of foreign ions (e.g. surfactants) from the aqueous medium.

The charge on the surface of the particles is counter-balanced by counter-ions in the diffuse layer around them. Colloidal stability arises from the mutual repulsion of electrical double layers on adjacent particles. The repulsion of like charges of neighbouring double layers, if of sufficient magnitude, exceeds the London dispersion forces of attraction between the particles(4) and creates a net 'disjoining pressure'(8).

If, on the other hand, the London forces predominate, the system is unstable and particles aggregate. True colloidal systems are constantly subject to Brownian motion which causes frequent particle-particle collisions(9). The diffuse electrical double layer around the particles must have sufficient strength to preserve stability, the controlling parameters being the surface potential ψ_0 and the 'thickness' which is related by the Gouy theory to the Debye parameter of the solution. The quantitative theory of stability was independently developed by Derjaguin and Landau(50) and by Verwey and Overbeek(10) and is nowadays accepted as the basic theory of hydrophobic colloids.

The energy of attraction, V_A, between two spherical particles can be approximately expressed

$$V_A = -\frac{Aa}{12}\frac{1}{H}$$

in which A is the van der Waals attraction constant (Hamaker constant), a is particle radius and H the distance between two spheres(10).

The repulsive term, V_R, between two spherical particles is expressed approximately

$$V_R = \frac{\varepsilon a \psi_0^2}{2} \ln\left[1 + \exp(-\kappa H_0)\right]$$

in which ε is the electronic charge, a the radius of the particle, ψ_0 the surface potential, κ the Debye-Hückel function and H_0 the minimum distance of separation between two particles. The above equation is satisfactory for small values of surface potential but becomes less accurate for larger values.

It is common practice to employ in place of ψ_0 the experimentally determinable zeta potential, ζ, assumed to be the potential difference across the diffuse part of the double layer. Doubts are recognised in the significance of ζ. Its relationship to ψ_0 is controversial(11)(12); but in many colloidal systems there is no means of arriving at ψ_0. Furthermore, a rough correlation between ζ values and stability has long been known.

Electrical double layer repulsions cannot account for stability in all hydrophobic systems. For example, adsorption of highly solvated non-ionic detergents (e.g. polyethylene oxide derivatives) has been shown to produce stability of carbon dispersions in aqueous systems(6). Another factor particularly significant in relation to the theory of flocculation with polyelectrolytes, is adsorption of bulky macromolecules which prevent close approach of particles by steric hindrance(5). Neither solvated layers nor steric hindrance would account for stability without the additional factor that the London - van der Waals cohesive energy of adsorbed layers may not be very different from that of water: obviously if it were comparable to that of the particles themselves, the addition of an adsorption layer, however impenetrable, would merely cause an effective increase in the size of the particles. The important factor is that repulsion sets in at a distance between centres at which the net London - van der Waals attraction of the coated particles is still small. Calculations have been carried out to deal with this model.(13)

At the present time the problem is to calculate the law of force between interacting adsorption layers. Existing theory has been used by some workers to calculate the repulsion forces between back to back monolayers in lipid films(14); in addition a theory has also been developed based on the osmotic forces arising from interpenetration of solvated layers (which are regarded as thin layers of solution attracted to the surface of the colloidal particles)(15). At present such theories cannot be expected to yield more than order-of-magnitude estimates of the stabilization forces, but future refinement of the models seems feasible. Extending these principles from protected hydrophobic to intrinsically hydrophilic colloids, it follows that the characteristic features of the latter are:

(a) relatively small mass resulting in a sedimentation force that is small compared with diffusional forces; and

(b) low values of the London - van der Waals constant of the particles - generally because they are solvated, swollen, and even (e.g. with linear polymers in a 'good' solvent) highly extended.

Under these circumstances the thermal kinetic energy of the particles is sufficient to separate the particles and dispersion is a spontaneous process. It is understandable that in borderline cases a small change in the solvent can cause a transition from stability to instability (e.g. the precipitation of isoelectric protein by salt but the non-precipitation of either negatively or positively charged protein). Similarly the fractionation of polymers on a molecular weight basis can be interpreted on the basis of inter-particle potential energy in relation to the thermal energy, kT.

In contrast it is necessary to point out some of the factors governing the stability of hydrophilic systems. These systems are characterised by the formation of true solutions of molecules having colloidal dimensions in the range 1 mμ to 1μ. Although no satisfactory quantitative theory of solvation exists at present, it is apparent from their physical properties that hydrophilic colloids have a great 'affinity' for the solvent; the interaction can be ascribed to particular molecular groups which are ionic (e.g. $-COO^{-}Na^{+}$), or hydrogen-bonding (e.g. -OH) or merely dipolar (e.g. R-O-R'). Even when present in small quantities, hydrophilic colloids exert an appreciable effect on the viscosity of their solutions because of their extended molecular dimensions. Stability is partially attributed to the formation of hydrogen-bonds between the hydrophilic groups on the macro-molecule and water. The configuration in solution, solubility, physical and chemical properties, of macromolecules having ionogenic groups incorporated in their structure is a direct result of double layer repulsions between adjacent segments(16), ionization causes expansion of the random coil, whereas a high ionic strength of the solution reduces the effect by reducing the electric fields.

Coarse suspensions, such as those found in river water are subject to differential sedimentation, in accordance with Stokes's Law, since the limiting velocity of sedimentation is proportional to the square of the particle radius. In a polydisperse system such as a dilute clay suspension, it is necessary to consider the effects of particle size from two aspects - firstly, sedimentation and secondly, the influence of surface forces as compared with bulk properties. For very small particles the ratio of surface area to mass is high and surface properties such as double layer interactions and colloidal effects such as Brownian motion become significant, whereas sedimentation and inertia are the dominant factors for large particles.

Colloidal dispersions present special problems in the important industrial processes of filtration, thickening, de-watering and clarification(17);generally such separations are facilitated by a chemical treatment that causes the dispersed phase to aggregate. Destabilization of suspensions is brought about by the addition of controlled amounts of either electrolytes or polymeric flocculants (or both). Simple inorganic salts may act by reducing the potential of the electrical double layers, by increasing the ionic strength, or undergoing hydrolysis to form incipient 'flocs' (e.g. $Al(OH)_3$). In contrast, polymeric flocculants are water-soluble compounds of high molecular weight which adsorb on the dispersed particles and bring about aggregation by 'polymer bridging'.

Because of the fundamental differences in mechanism the suggestions of La Mer(18) will be adopted - aggregation of colloids by simple electrolytes will be called 'coagulation' and aggregation by high polymers 'flocculation'. The distinction is clear enough in extreme cases but it would be difficult to classify on this basis the action of polyethylenimine of low molecular weight. Both mechanisms are employed industrially and because of their bearing on the aim of this investigation they will be discussed in greater detail below.

1.2 Flocculation of suspensions by polymeric flocculants

Flocculation of hydrophobic suspensions has been the subject of much research in recent years and several excellent reviews and literature surveys exist(3, 17, 19). It is generally accepted that destabilization of suspensions by the addition of small quantities of organic polymers is caused by aggregation of particles through 'polymer bridging'. The mechanism of bridging is a two-stage process involving adsorption of a polymer molecule onto the surface of one particle and then adsorption of other segments of the same polymer molecule onto another particle. Adsorption of polymers onto solids can take place through the following types of bond:

1. Non-specific electrostatic attraction between the solid particles carrying an electrical double layer and polymer ions of opposite sign. Thus, a negative dispersion (e.g. a silica sol) is destabilized by adsorption of a cationic (i.e. positively charged) polyelectrolyte. Quantities of polymer in excess of that required for charge neutralization can cause reversal of charge and restabilization.

2. Electrostatic interaction between localized areas of charge on a heterogeneous surface and polyelectrolyte ions. Adsorption produces a reduction of the zeta potential - in this case the overall value for the surface. This is similar to type (1), e.g. flocculation of any mineral with a heterogeneous surface with a polyelectrolyte of opposite sign to the overall charge.

3. Electrostatic site bonding through the formation of chemical bonds between specific ions on the particle surface and functional groups on the polymer. The adsorption of polyacrylic acid onto a calcium-containing mineral leads to the formation of 'calcium acrylate'. Such adsorption takes place only when there is the possibility of chemical bond formation. Carboxylates, phosphates and sulphonates are functional groups on polymers which lend themselves to this type of bond. It is well known in the technology of flotation of minerals that anionic surfactants can often be attached to previously anionic

surfaces by the intervention of a di- or tri-valent cation - though the mechanism is somewhat controversial(20, 21).

4. Hydrogen-bonding between polymer and substrate. This type of bond is exhibited by molecules which have a hydrogen atom directly bonded to a strongly electronegative atom such as oxygen, nitrogen or sulphur. The bond arises from the sharing of the hydrogen between two electronegative atoms, the other being on a group on the surface of the particle. Single hydrogen-bond energies are not large - of the order of 8 - 10 kcal/mole - but polymers carrying many functional groups can lead to very large molar adsorption energies (high affinity) despite the fact that hydrogen-bonding on to a surface group means breaking two hydrogen-bonds with water. Evidence for hydrogen-bonding with relevant compounds has been provided by (22)(23)(24).

5. Dipole-dipole interactions have been suggested where none of the above seem applicable. A number of systems are known where adsorption of polymers on a surface possibly takes place through the interaction of non-ionic groups in the polymer molecules and the electrostatic field of the crystal lattice(25) - for example adsorption of non-ionic polyacrylamide onto positively charged fluorite (CaF_2). In the absence of hydrogen-bonding interaction between the dipoles of the polymer molecule and the electrostatic field of the crystal lattice is suggested. Combinations of the different attachment mechanisms may also operate in a particular system.

The second step in the aggregation process is the bridging of two or more particles by the same polymer molecule. Electrostatic interactions between polymer and substrate influence the efficiency of the process and charge neutralization between oppositely charged polymer and substrate facilitates bridging; but, in some systems, negatively charged particles (e.g.clay minerals) can be flocculated by a negatively charged polyelectrolyte and positively charged suspensions (e.g. fluorite) can be flocculated with cationic polymers. If polymer bridging is to cause successful flocculation, it is necessary to apply a concentration of flocculant which falls between fairly narrow limits. Too little will cause only a slight degree of flocculation, as only a fraction of the particles can adsorb polymer and be satisfactorily bridged; and flocs which do form have poor resistance to mechanical shear. Excess is adsorbed by all particles and saturates all available adsorption sites, which prevents polymer bridging and stabilizes the suspension(5).

There is much evidence in support of the bridging theory. For example, information gained by the mechanical destruction of flocs has proved useful(26). A flocculated suspension can be redispersed when subjected to mechanical shear forces; the resistance of flocs to agitation increases with increasing solids content of the suspension. As the recombination of broken flocs is determined by the time of freedom of the lose ends, they can be readsorbed on vacant sites on the same or other particles. At low solids content where inter-particle distances are greater and the number of particle - particle collisions smaller, there is a greater chance of readsorbing on the same particle to produce steric stabilization. Furthermore, it has been shown that flocs formed in the presence of excess polymer undergo more pronounced destruction during agitation as vacant sites adsorb fresh polymer as soon as they become available(27).

If dispersion of electrolytically coagulated suspensions is attempted by agitation no redispersion is observed and this itself is indicative of the fundamental differences between coagulation and flocculation mechanisms. Further evidence for the bridging theory is found in the correlation between polymer configuration and flocculation efficiency(98). Viscosity can be taken as an index of molecular extension in a polymer (a high viscosity indicates an extended molecule). It is reasonable to assume that if the molecule is caused to collapse through variation of pH, polymer bridging will not be so effective. This is found to be so in flocculating a fluorite suspension with anionic polyacrylamide; at low pH the viscosity is low (because of supression of ionization of carboxyl groups) and flocculation is poor, but when the molecule becomes extended at higher pH values flocculation improves markedly. Similarly, data obtained from infra-red spectroscopy and adsorption isotherms (28, 29) indicating adsorption of only a fraction of the functional groups of a polymer on a surface are also considered evidence for the bridging theory.Steric stabilization and the absence of further destabilization discussed in detail above, by further polymer addition is considered to be very important evidence for polymer bridging.

The bridging mechanism is affected both favourably and unfavourably by electrostatic interactions between polymer and substrate. Non-ionic polymers will not be affected by electrostatic effects and provided sites are available for bonding (e.g. for hydrogen bonding) flocculation can take place irrespective of the sign of the charge on the substrate surface. If the substrate and polymer are oppositely charged, bridging is facilitated because the polymer removes the electrostatic energy barrier between particles.

When polyelectrolytes are adsorbed, the zeta potential of the suspension changes and in addition to polymer bridging coagulation may be promoted. Similarly, the bridging mechanism may be activated by using simple electrolytes to overcome electrical repulsions between particles - a common industrial practice to economise on flocculants. The influence of electrolytes on stability will be considered further in section 1.4

1.3 Factors affecting flocculation

A number of other factors must be taken into account for a full explanation of flocculation and the efficiency of flocculants.

The efficiency of polymeric flocculants is primarily dependent on adsorption, whether it is electrostatic or chemical. The proportion of groups employed in adsorption is small; infra-red spectrophotometric evidence of polymethylmethacrylates adsorbed on silica(28) has revealed the proportion of attached segments to be about 0.4. This was attributed to lack of suitably spaced adsorption sites but the configuration of the adsorbed molecules may also be an important factor. It was also shown that the fraction of adsorbed segments was independent of the surface coverage and the proportion of attached groups independent of molecular weight, within a considerable range. The data show adsorption of amounts much greater than would be required for a flat monolayer but not as multilayers, which may be evidence for the bridging theory. The amount of polymer adsorbed from solutions of a given mass concentration increases with increasing molecular weight and, if a range of polymer sizes is present, fractionation takes place, a greater proportion of the higher molecular weight material being adsorbed(29).

Temperature, in most cases, has little effect on flocculation although some systems have been reported in which a rise in temperature has improved floc formation(30) and others in which a rise in temperature has caused deterioration(31).

It is generally accepted that unattached 'loops' are free to form bonds when a polymer is adsorbed on to a solid surface; a hypothesis supported by adsorption isotherms showing adsorption and amounts greater than monolayer coverage but excluding multilayer coverage by the shape of the isotherm. The theory which postulates that loops extend only over a few segments unless the interaction energies are small, i.e. less than those due to hydrogen bonding, is substantiated by experiment (32). The size of the extended loops increases with increase in the molecular weight of the polymer(29) and for polyelectrolytes long loops exist under equilibrium conditions. This agrees with flocculation characteristics, as the process of flocculation is known to be very rapid where inter-particle distances are small but in some systems particles not immediately flocculated are stabilized(5,33). Examination of the 'haze' of stabilized particles left in the supernate after flocculation with a polymer dose in excess of the optimum value has shown that the particles carry a disproportionately higher dose of flocculant(26). The haze persists even after prolonged agitation and bridging of the particles does not take place between particles which have already adsorbed polymer. Stabilization becomes very pronounced in dilute suspensions where distances between particles are greater and bridge formation less likely because of the reduced frequency of floc forming collisions.

Effectiveness of polymeric flocculants is dependent on their high molecular weights. Although the addition of flocculant to a suspension brings about rapid destabilization and sedimentation, it has been shown that the kinetics of adsorption decrease with increasing molecular weight - possibly a result of slower diffusion, but the rate of settling increases(34). The higher the molecular weight and molar concentration the slower the time to reach adsorption equilibrium but the greater the number of molecules which are adsorbed in floc formation. Polymers with moderately short chains (e.g. mol. wt. 10^5) tend to produce unstable flocs: below a certain molecular weight (e.g. 10^4) polymers become ineffective as flocculants but retain some protective action(35).

Molecular weights are often characterised broadly by viscosity measurements and from the data the mean dimensions of the polymer molecules in solution can be calculated (36). The greater the end-to-end distance of the molecule, the greater the flocculating power, as there is a greater chance of bridging the inter-particle distances in a suspension. Similarly for a given chemical type of polymer, linear macromolecules are more effective flocculants than highly branched compounds of comparable molecular weight (37, 38). However, it has also been reported that branched chains improved the effectiveness of some starches(39); it was proposed that synthetic vinyl polymers, polyacrylamides and polyethylenes would also be improved as flocculants by chain branching(40).

The effects of substituting different functional groups in a polymer is demonstrated by the change in flocculation characteristics of partially hydrolysed polyacrylamide(41). Hydrolysis converts non-ionic $-CONH_2$ groups to $-COOH$ groups, a fraction of which are ionized at neutral pH values. It is found that there is an optimum degree of hydrolysis corresponding to maximum flocculation efficiency; it is generally accepted to be when about 30% of the amide groups are converted to carboxylic acid groups.

The addition of simple electrolytes has a dual effect on the flocculation mechanism; not only do they reduce the electrokinetic potential of the mineral particles but they promote adsorption of the polyelectrolytes onto the surface and subsequent flocculation (45, 46). At high negative values of zeta potential of mineral particles polyacrylamide is not adsorbed and the potential remains unchanged(43). Flocculation can only occur if the value of the zeta potential is reduced to about 30-40 mV - the addition of simple electrolytes or substitution of some of the amide groups with cationic groups in the polymer molecule will bring this about.

The viscosity of a solution of linear polymers is greatly influenced by the energy of solvation and therefore in aqueous solutions by the degree of ionization(42).

The polymer-solvent interaction parameters ψ_1 and K are expressed thus

$$J = (\psi_1 - K_1)\frac{\bar{V}^2}{V_1}$$

where ψ_1 is the parameter characterising the entropy of dilution of polymer with solvent, K_1 is the energy of interaction between polymer and solvent divided by kT, $\bar{V}$ is the specific volume of polymer, V_1 the molecular volume of the solvent and J is the parameter through which the free energy of the system changes during solvation(44).

Solvation of polymers depends on the following in increasing order of importance: dipole interaction, hydrogen-bonding and ionization; all three of which contribute to the polymer-solvent interaction. If the polymer is weakly hydrated and not ionized, the molecular chains exist as tight coils; but if the molecules are strongly hydrated and, especially if they are ionized, the molecules are, on the average, extended and therefore more suited to interparticle bridging. In accordance with the above it has been demonstrated experimentally that the variation in viscosity of hydrolysed polyacrylamide with pH is paralleled by a variation in the effectiveness of flocculation with pH (43)(98).

Excess polymer produces stabilization of suspensions, sometimes by increased electrical repulsion, but more frequently by steric stabilization; non-ionic polymers are excellent protective colloids. Although the optimum dosage (usually expressed industrially as a polymer-to-solids ratio) depends on conditions of addition and agitation of the suspension, it has been calculated to be at the point when about half the sites available for adsorption are covered(47).

Excessive mechanical agitation of flocs brings about irreversible destruction of flocs particularly for suspensions of low solids content flocculated with polymers of low molecular weight. Therefore in practice it is advantageous to ensure maximum floc growth by employing gentle agitation as soon as flocculant has been thoroughly mixed with the suspension.

In certain systems combinations of anionic and cationic polyelectrolytes added consecutively have been shown to be more effective than when they were used separately. Improved flocculation may be attributed to the replacement of hydrogen bonding between the flocculant and particles with electrostatic bonding between the highly charged positive and negative species - one of which is already adsorbed. The ratio of cationic to anionic material varies considerably with the nature of the suspension(48).

1.4. Coagulation by inorganic electrolytes

In addition to the above discussion of flocculation by polymers, it is necessary to consider briefly the effects of electrolytes on the stability of suspensions as a method of solid-liquid separation. Four different electrolytic effects which produce coagulation are distinguishable:

(1) Reduction of surface potential by control of 'potential-determining ions'. The surface potential ψ_0 is related to the concentration of the potential-determining species in solution thus

$$\psi_o = \frac{+RT}{F} \; Ln \left(\frac{\gamma \, C1}{\gamma \, Co} \right)$$

where C_1 is the concentration of the potential-determining species, Co the concentration producing zero point of charge and γ_1 and γ_o the activity coefficients at the concentrations C_1 and Co respectively. In practice the critical value of zeta potential for stability is in excess of about 30 mV.

(2) Indifferent electrolytes reduce the zeta potential through the electrostatic affinity of the counterions for the surface charge. The sign of the zeta potential does not change although its magnitude is dependent on the concentration of added electrolyte(49). As there is no specific interaction through adsorption with the particle, the charge remains constant but the thickness of the double layer (defined as the distance between a surface and its diffuse atmosphere up to the point at which the potential drops to 1/e or 0.37 of the value and normally designated $1/K$) decreases and the zeta potential drops; the effect is to reduce the electrostatic repulsion between particles and bring them within the long range forces of attraction to produce coagulation. If the charge on the surface is governed by adsorption of potential-determining ions, indifferent electrolytes have only a secondary effect on the potential determining function by affecting the activity coefficients of the same species in solution.

The conditions for stability predict a critical potential above which, and a critical electrolyte concentration below which, coagulation does not occur and are expressed for (a) low values of ψ_0 (50) (i.e. between 15 and 50 mV for particles of radius $< 10^{-5}$cm)

$$n = \frac{\psi_0^2 \varepsilon}{2kT} a$$

where n is a stability factor;

(b) high values of ψ_0'

$$\frac{C}{1000} = \frac{107 \varepsilon^3 (kT)^5}{A^2 Z^6 e^6 N} \gamma^4$$

γ is a function of the potential and approaches unity for high values and C is the critical electrolyte concentration.

3. Polyvalent ions (non-hydrolysing).

Polyvalent ions have a special affinity for a surface depending upon the valency of the counterion (adsorption of electrolyte is more pronounced the higher the valency). The effect of polyvalent counterions on a lyophobic colloid is twofold. Firstly, surface charge is reduced by adsorption of counterions into the Stern layer and the sign of the zeta potential is sometimes changed, if excess electrolyte is added; and secondly, the electrical double layer is collapsed. Co-ions have relatively little effect because their presence has no effect in reducing the zeta potential by adsorption unless, of course, the sol has undergone reversal of charge by addition of excessive quantities of electrolyte. It is important to distinguish between the effect of valency of the counterions on the Gouy layer as an electrostatic effect and the adsorption effects of polyvalent counterions into the Stern layer as being specific adsorption affinity.

In practice it is found that the higher the concentration of added electrolyte and the higher the valency of the counterion, the greater the degree of destabilization of sols. This effect is called the Schulze-Hardy rule. Theoretical calculations on spatial distribution have also shown that the degree of compression of the double layer is governed by the valency and concentration of counterions; but that the effect of co-ions is small(10)(50).

4. Hydrolysable electrolytes.

The fourth effect is destabilization of lyophobic sols brought about by hydrolysing electrolytes, a mechanism intermediate between flocculation and coagulation. Examples are iron or aluminium salts used in the coagulation of suspended matter in surface waters to make them potable(51).

The mechanism is controversial - two schools of thought exist at present. One postulates the adsorption of hydrolysed ions or small condensed species(52); the other emphasises the growth of tri-valent hydroxide coatings and subsequent particle bridging. In addition, other workers have reported the formation of polynuclear species of colloidal dimensions in solutions of tri-valent iron and aluminium.(54) The polynuclear species may bridge particles through complex formation of functional groups on the surface of the particles; not all the tri-positive ions are hydrolysed and doubtless they facilitate coagulation by electrostatic charge reduction.(53)

The effectiveness of hydrolysing electrolytes is dependent on pH; partly because of the influence of pH on rate of hydrolysis and partly because of the different species that form at different pH values. The second effect is illustrated in Fig. 1.1 in the diagrams of pH variation with concentration change on the two systems $Fe(NO_3)_3$ and $Al(NO_3)_3$(52).

1.5. Types of flocculant and coagulant available

A considerable number of materials used for destabilization and aggregation of suspensions are now available; some are natural products, some modified naturally occurring materials, and others entirely synthetic. It is impossible to place all the substances into well defined categories of chemical type, structure, molecular weight, etc., mainly because of the limited amount of information available from those manufacturers who are reluctant to reveal details of their products. Many products, however, are reasonably well

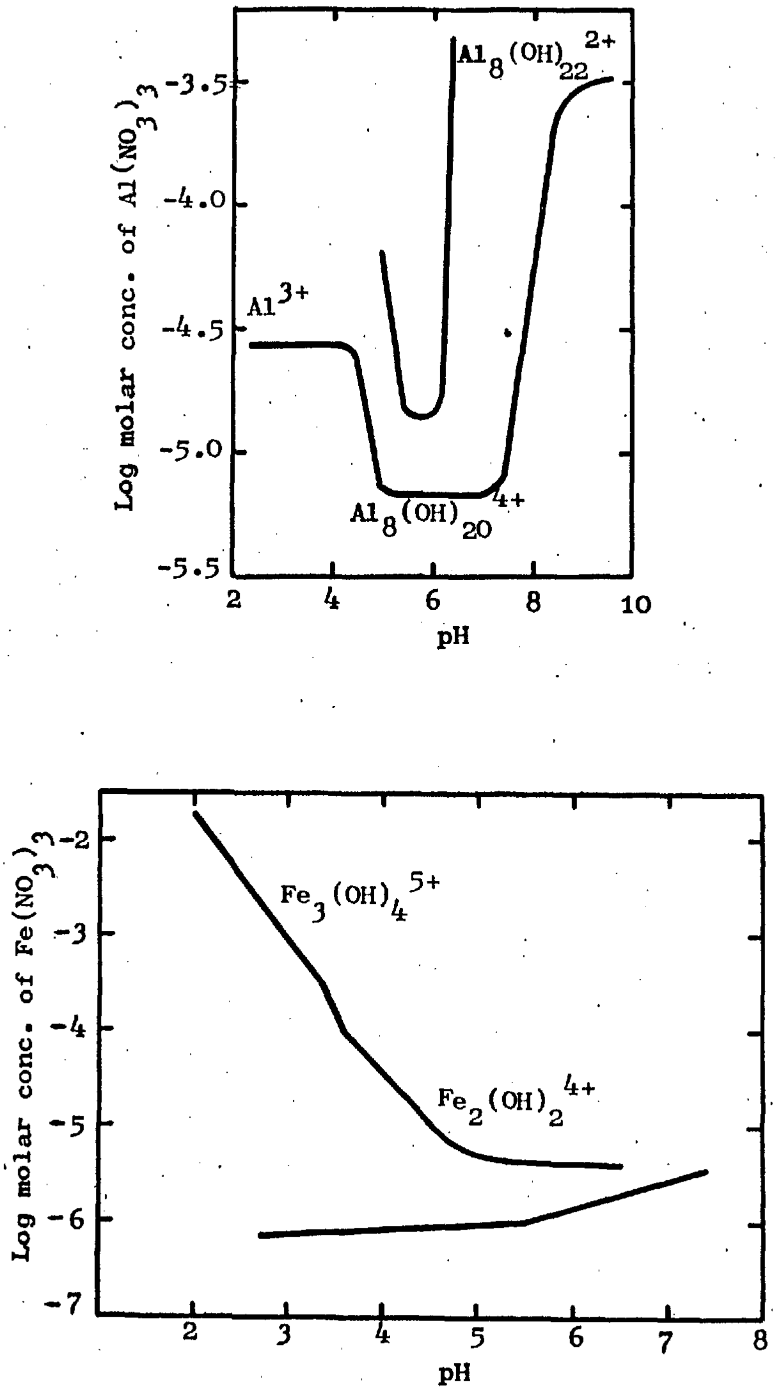


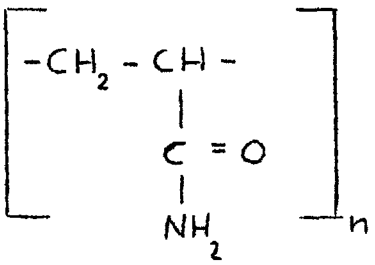
Fig. 1.1 Effect of variation of pH and concentration on the hydrolysis products for the systems $Al(NO_3)_3$ and $Fe(NO_3)_3$

characterised and it is convenient to employ the generally accepted classifications(19). Other substances not included in the following classifications are available and their omission does not preclude them from consideration as flocculants or coagulants. Indeed, some of the less well known materials are effective and cheap for specific systems.

The following classes are commonly recognised:

1. Synthetic flocculants based on polyacrylamide.
2. Other types of synthetic flocculant.
3. Naturally occurring organic materials of high molecular weight.
4. Hydrolysing metal salts.
5. Simple electrolytes.

1. Polyacrylamide flocculants are the most important type. Their efficiency surpasses that of any other flocculant at present available. The formula of non-ionic polyacrylamide is

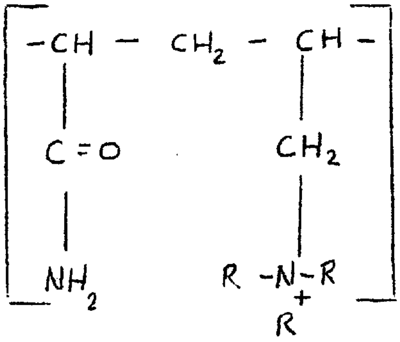


$$\left[\begin{array}{ll} -CH_2- & CH- \\ & | \\ & C=O \\ & | \\ & NH_2 \end{array}\right]_n$$

where n is commonly between 10^4 and 10^5. Preparation is usually from acrylonitrile itself prepared from sodium cyanide and ethylene oxide which is converted into the monomer acrylamide by saponification in the presence of sulphuric acid, and then polymerised to the required molecular weight.

Partial hydrolysis of the amide groups to carboxylate gives anionic polyacrylamide which has the advantages of improved solubility at higher molecular weights(56) and of negative charge which facilitates flocculation of positively charged particles. The maximum useful degree of hydrolysis, although dependent on the actual system, is when about 10 - 30% of the amide groups are replaced by carboxylate groups(41).

Cationic derivative is prepared by polymerization of substituted acrylamide (the substituent is a quaternary ammonium group) to produce a polymer structure in which some of the amide groups are replaced by quaternary ammonium ions of the form



Cationic polyacrylamides are particularly useful for negatively charged suspensions.

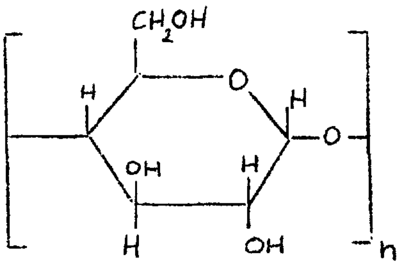
2. Other synthetic flocculants include polyvinyl alcohol, polyethylene oxide of high molecular weight and many others. They can be classified into four groups.

- (a) non-ionic polymers; for example, polyvinyl alcohol.
- (b) anionic polyelectrolytes; for example, sodium polyacrylate
- (c) cationic polymers; for example, poly-β dimethylaminoethylmethacrylate hydroacetate.
- (d) amphoteric compounds; for example,partially hydrolysed polyacrylonitrile.

3. Naturally occurring substances, although cheapest rather than most effective, are still widely used and can be grouped thus:

- (a) polysaccharides; for example, dextrin, starch and guar gum.
- (b) proteins; for example, casein glue, gelatin.
- (c) commercial mixtures or derivatives of the above substances.

The structural formula of starch is



The degree of polymerization, n = 60 - 1000, is low compared with that of synthetic flocculants. Starches are obtained from potatoes, wheat, maize, etc.; they are easily hydrolysed into polysaccharides of the same basic composition(55). They are practically non-ionic and presumably flocculate by hydrogen bonding and the bridging mechanism.

Proteins, such as glue, have been widely used for flocculating mineral slurries. The macromolecules consist of amino acid groups linked by polypeptide bonds $(-CH_2 - CO - NH - CHR)n$. Gelatin is versatile as a flocculant probably because of its amphoteric nature and is particularly effective (by comparison with other natural products), for clay suspensions, particularly in the presence of humic acids.

4. Hydrolysing electrolytes - for example, ferric chloride, aluminium sulphate, sodium aluminate - destablize suspension by a bridging mechanism brought about by the formation of polynuclear species(53) and eventually precipitation of the metal hydroxide. 'Activated silica' (57) can be included in this group; it is made by the treatment of dilute sodium silicate solution with acids or acidic salts. Colloidal silica is produced which undergoes condensation polymerization, eventually producing particles. Free OH groups on the surface enable the colloid to acquire a negative charge which causes it to mutually coagulate with positively charged particles. It is often used in conjunction with aluminium sulphate for water clarification.

5. Simple electrolytes - for example, sodium chloride, sulphuric acid, caustic soda and in fact, any strong electrolyte - can destabilise a suspension. Although increase of ionic strength leads to reduction of double layer repulsion the coagulation concentration varies from one colloid to another, depending on the magnitude of the van der Waals constant and the degree of hydration of the surface of the particles. There has been much speculation about hydration layers on surfaces, but little definite information exists. Older work ignored the influence of electrical double layers. When proper allowance is made, the thickness of the hydration shell on colloidal silica (a typical hydrophilic solid) appears to be only a monolayer in thickness(58). It has been reported recently that octadecanol remained stable under conditions where the zeta potential was reduced to zero. This is exceptional, as circa 30 mV is the accepted minimum for stability. Even allowing for the low value of the Hamaker constant for this system, it is not clear how stability can arise with a long-chain alcohol.

1.6. System under investigation

The system used for the greater part of the investigation of the colloidal aspects of Thames mud was a 'real' rather than a 'model' colloid, namely, a suspension of Thames River mud in Thames River water. Samples of mud were taken from the river bed at low tide near the cooling water inlets of the West Thurrock Generating Station. Although from the point of view of understanding colloidal behaviour and flocculation phenomena it is preferable to have a well defined system, this would have been incompatible with the technological problems involved.

No detailed characterisation of the suspension of mud in water was attempted, particularly as the dispersion was unstable because it contained coarse particles. It also contained about 4 wt% of organic matter and enquiries indicated that very little is known about the chemical constitution of organic residues, e.g. in sewage humus. However, certain information was obtained from X-ray analysis and considerations of the origin of the organic matter.

A sieve analysis on the wet mud is shown in Table 1.1

Table 1.1 Sieve analysis of Thames River mud
(particle size expressed as wt % of dry mud)

Particle size (μ)	% w/w
+250	1.0
-250 + 152	4.4
-152 + 76	18.3
- 76 + 53	10.7
+ 53 - 11	30
+11	34

The mud is essentially a mixture of clay minerals, silica silt and organic matter. A semi-quantitative analysis of mud oxidised with hydrogen peroxide to remove the organic matter is shown in Table 1.2(59). (The above analysis agreed in part with the findings of the Water Pollution Research Laboratory(60))

Table 1.2 Semi-quantitative X-ray diffraction identification of dried, oxidised Thames River mud.

Component	% by wt.
quartz	40 - 50
calcite	10
unidentified swelling clay mineral (probably montmorillonitic)	25
Mica	15
kaolinite	10

For comparison a typical analysis of fine suspended matter found in the river water at Barking and Gravesend is presented in Table 1.3

The carbon-to-nitrogen ratio of the organic component is about 10:1, the same as that for 'humus', the most oxidation-resistant product of the decay of organic matter found in soil(61). It is said to be 'a complex of lignin and protein'. In water humus behaves as an anionic hydrophilic colloid. Tests showed that the mud undergoes 'mutual coagulation' with a finely-divided strong-base anion-exchange resin, confirming its negative surface charge. The organic matter comes from sewage effluent(63). The discharge of organic matter into the river consumes most of the dissolved oxygen in the river below Tower Bridge. Table 1.4 shows the composition of a whole sewage before treatment(62). Although considerable effort is made to keep the biological oxygen demand of effluent discharged into the River Thames within certain limits, the river is overburdened and the effects are encountered at West Thurrock Generating Station where the oxygen level is low, (e.g. around 10% v/v the saturation level), compared to an unpolluted stretch where the oxygen reaches 100% of the saturation value of the river. The river near West Thurrock is subject to tides and contains appreciable quantities of salts. Salinity is in the range one third to two thirds that of sea water(60) Suspended matter varies greatly in quantity with depth, distance from bank, tide, season and weather, but an average figure is in the order of 300 p.p.m. (64).

The proprietary polymeric flocculant investigated initially in the present work was supposed to be of the polyacrylamide type; but the investigation was later extended to cover other types of flocculant, both natural and synthetic. It was convenient that the proprietary polymer showed identical properties to well-characterized flocculants of known composition. It was not, therefore, necessary to base the research on a particular, undisclosed, material.

Table 1.3 Analysis of suspended solids in Thames River water. Samples taken at Barking and Gravesend. (Data supplied by Gameson and Barret W.P.R.L.[(60)])

Component	Barking (wt. %)	Gravesend (wt. %)
carbon	9	9
nitrogen	0.9	1.0
sulphide	0.8	0.4
silica	36	36
sesquioxides	27	17
calcium	7	6
magnesium	0.6	0.5
loss on ignition	27	24
size (-200 mesh)	98	-

Table 1.4 Composition of whole sewage, expressed as concentrate of carbon in p.p.m. (Composition of Domestic Sewage[(62)])

Constituent	In Solution	In Suspension	Total
carbohydrates - (total)	21	12	33
amino acids - (free)	2	0	2
- (bound)	6	19.5	25.5
higher fatty acids	0	74	74
soluble acids	28.5	6.0	34.5
esters	0	37.2	37.2
anionic surface active agents	12	5	17
amino sugars	0	0.9	0.9
amide	0	1.2	1.2
creatinine	2.7	0	2.7
total - (by analysis)	82	218	300
- (by addition)	72.2	155.8	228
proportion accounted for, %	88.0	71.4	76.0

1.7 Aims of the investigation

Before the start of the investigation into the colloid chemistry of Thames River mud at Imperial College, it was known that a material marketed under the name "Zimmite" was claimed by the manufacturers to prevent accumulation of mud in industrial cooling systems and facilitate removal of previously deposited mud(65). This claim was borne out by experience at West Thurrock Generating Station where treatment of cooling waters had successfully prevented build up of mud in the condenser system and had eliminated the associated problem of corrosion(66).

Earlier work by the C.E.G.B. had shown that the product is an effective flocculant for mud, a property shared by a wide range of high molecular weight organic polymers. The investigation was aimed at establishing the following:

1. The mechanism of action of Zimmite .
2. Whether flocculation played a role in mud removal.
3. Whether the property of mud removal was peculiar to Zimmite or was shared by other polymeric flocculants.
4. The physical and chemical properties needed for an effective substitute.

Most of Part I of the thesis is devoted to the study of the mechanism of mud removal by Zimmite and the factors affecting it, but other systems are also considered. Evidence is presented for the validity of certain laboratory tests designed to estimate effectiveness of materials proposed as mud removers in industrial systems.

2. PRELIMINARY INVESTIGATIONS INTO MUD-POLYMER INTERACTIONS

2.1 Introduction

Thames mud dispersed in Thames River water is an unstable suspension: large particles settle within minutes from dilute suspensions and after several hours most of the smaller particles have also settled. On prolonged standing the supernatant liquid becomes practically clear - although removal of electrolytes (with mixed bed ion exchange resin) enhances the stability of the smallest particles indicating that the mud is slightly coagulated by the salinity of the water. The sedimentation of suspended matter in cooling water systems is a major cause of corrosion of condenser tubes and it has been known for some time that removing suspended matter from cooling waters, prior to passage through the condensers, will drastically reduce corrosion rates(67). Observations of the corrosion occurring in cooling water systems subject to polluted waters containing sedimenting suspended matter reveals that the corrosion appears beneath sedimented material (Section 8.1). If water without suspended matter (e.g. tap water) is used, no corrosion results.

It has also been established that when water containing suspended particles flows through condenser tubes, no sedimentation of suspended particles occurs if the average velocity is greater than about 1.5 ft/sec (68). At West Thurrock Generating Station the average velocity of water through the condenser tubes is 6 ft/sec and it is unlikely that matter will sediment from the cooling water under these conditions. However, in a large condenser cooling system there are many tubes and not all of them have water flowing through with the same velocity. Some tubes have a water velocity higher than the average, some lower, and some even have water flowing through in the opposite direction, because of poor hydraulic design of the end water-boxes(69). It is, therefore, probable that in some parts of the system the velocity of the water might be sufficiently low to permit sedimentation or deposition of mud.

Sedimentation takes place only in parts of the system where the Reynolds number is low, but sediment can sometimes be dispersed by increasing the shear stress at the sediment-water interface.(70)

If strict hydrodynamic principles were applied, no doubt condenser systems could be designed which would minimise gravitational sedimentation during flow of cooling water. Certain non-technical factors in the operation of generating stations influence fouling by mud. The demand for electricity for both domestic and industrial use varies greatly both during the day and the week. Consequently, during the periods of least demand, (overnight and at weekends), many generating stations (or sections of them) are shut down. The result is that large quantities of polluted cooling water remain stationary in condenser systems for many hours. Therefore, during shut-down, the mud sediments on to horizontal surfaces and in contact with the condenser tubes creates favourable conditions for corrosion. Although the majority of the sediment is swept away when circulation of water is resumed, mud is in contact with tube surfaces for sufficient time to start corrosion, and it is likely that the products of corrosion enhance the adhesion of the particles.

The reported explanation for the action of polymeric flocculants in reducing corrosion of the condenser tubes is that the material, a 'remover' of mud and silt, removes the cause of corrosion and thus halts the corrosion process(71). This interpretation appears obvious but it offers no explanation for the prolonged effectiveness of the treatment when it is confined in practice to a very small fraction of the total operating time, in a cooling system constantly subjected to polluted waters. Furthermore, the treatment with flocculant is carried out during normal passage of the cooling water - i.e. at a time when mud is not accumulating.

The preliminary investigations described in the following sections were designed to investigate the following:

1. The formation of mud sediment or mud deposits in a simple simulated condenser system.
2. The effects of addition of flocculant on deposits or sediments under simulated condenser conditions.
3. Direct interactions between mud and flocculants.

These experiments, although qualitative, influenced the planning of subsequent investigations.

2.2 Deposition and sedimentation of mud

2.2.1 Under conditions of turbulent flow

Suspended matter does not sediment from cooling water if the flow is sufficiently high; there exists a hydrodynamic 'lifting' phenomenon in a streaming liquid(72). However, this does not exclude the possibility of deposition of colloidal material from an unstable mud suspension(73). In order to study this aspect, an apparatus was constructed to simulate cooling water flow through a single condenser tube. The method used was that used by Sherry and Gill in a study of the effects of polyelectrolyte addition to circulating mud suspensions at West Thurrock. Their design was slightly modified and the apparatus used is shown in Plate 2.1 It consisted of two aspirator vessels connected through a horizontal length of cupro-nickel condenser tube (identical to the material used as West Thurrock) and a centrifugal pump circulated the suspension which was returned through a length of tubing. The system was flushed with oxygen-free nitrogen to minimise oxidation of the mud. The pump was fed by a variable transformer which had previously been calibrated for flow-rate of water against the voltage setting. The flow of suspension through the cupro-nickel condenser tube, 1" internal diameter, was turbulent at the velocities used, as indicated by the high Reynold's number. This is calculated to be 1.03×10^4 - far longer than the value of 2700 - 4000, taken as the onset of the transition from laminar to turbulent flow in circular pipes(74). But is in keeping with plant practice, where the flow of 6 ft/sec through the condenser tubes

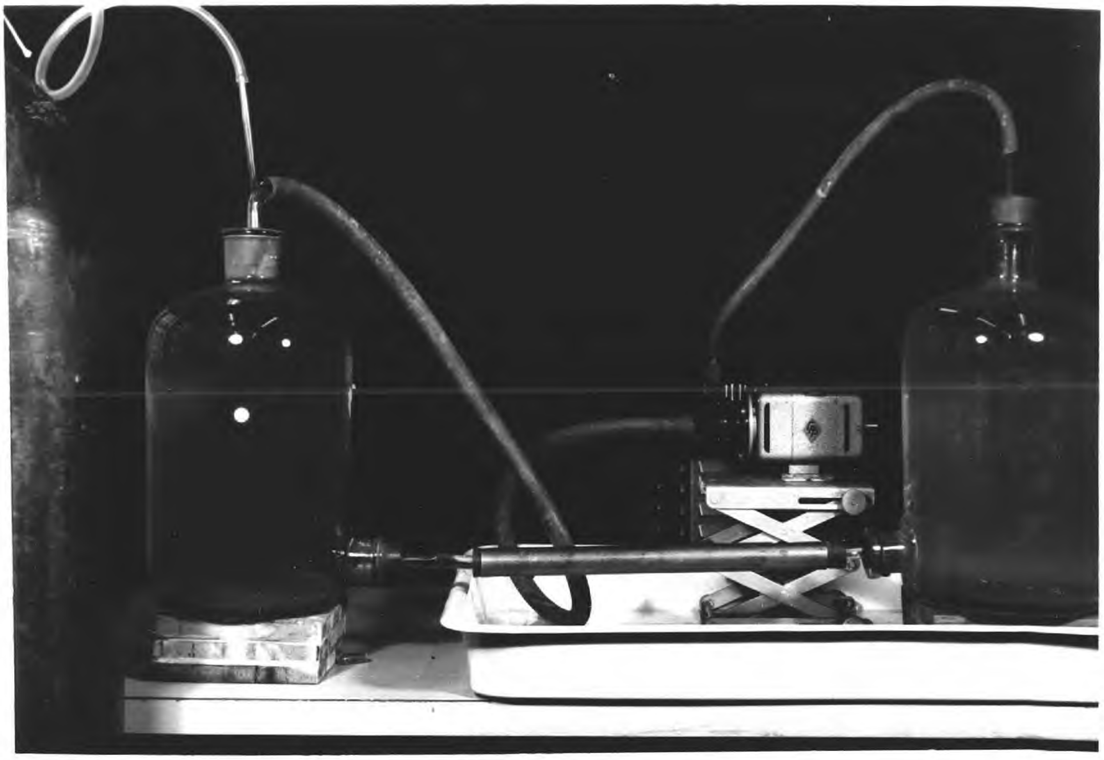


Plate 2.1 Apparatus used to simulate flow of water through condenser tubes (cupro-nickel) .

has a Reynolds number of 4.1×10^5 and is highly turbulent. The suspension used in the recirculating apparatus was made more concentrated than river water (1% w/v instead of about 0.05% w/v), in order to increase the rate of deposition or sedimentation. River water and samples ('bottom deposits') were obtained from near the cooling water intake at West Thurrock at low tide. Mud added to the system to give a 1% w/v suspension was thoroughly dispersed by the action of the pump. All experiments were carried out at room temperature (18°C); no temperature control was thought necessary in view of the fact that the yearly average cooling water temperature is 13°C. Experiments were carried out on the bases of continuous flow through condenser tubes and intermittent flow to simulate plant practice. The latter was achieved by incorporating a time-switch in the pump electrical circuit set for 12 hours on and 12 off.

Table 2.1 shows the qualitative results obtained with the apparatus for conditions of intermittent and continuous flow, and the effects of polymer addition. The results indicate that at no time was a significant macroscopic deposit or sediment formed in the horizontal condenser tubes at the flow rates selected to give turbulent flow. However, a very fine colloidal deposit of the finest mud particles (which resisted all attempts at removal except mechanical abrasion), became apparent when the surfaces of the tubes were examined (after drying) under a microscope. Large particles of mud and coarse sand sedimented in the aspirators in the regions of low flow rate and substantial deposits of mud were observed on the vertical walls where divergence of the flow produced eddying and stagnation. Sediment formed during 'off' periods in the tubes was quickly dispersed when flow was resumed. It was also observed that appreciable corrosion occurred only when sedimented mud remained in contact with condenser tubes during 'off' periods. Experiments in which a suspension was constantly circulated showed little sign of corrosion, apart from a thin, uniform, tarnish film on the previously bright cupro-nickel surface.

Table 2.1 Re-circulation of Thames River mud (1% w/v) in Thames water through cupro-nickel condenser tubes.

Re-circulation time and type	Deposition in condenser tube	Deposition in aspirators	Appearance of corrosion	Treatment	Observations
12 days continuous	none	deposition on walls	slight tarnish on tube surface	-	deposition on aspirator walls after 6 days
" "	none	" "	" "	'Zimmite' added (6th day)	suspension flocculated and wall deposits removed: mud resuspended and redeposited by 12th day
" "	none	" "	" "	'Zimmite' added (6th day)	polymer added (6th day) after removal of suspended matter: no removal of wall deposits
6 days intermittent	sedimentation in 'off' periods	" "	green corrosion products in lower half of tube	'Zimmite' added (6th day)	sediment formed in tubes during 'off' periods removed during flow: wall deposits removed
" "	" "	" "	" "	-	wall deposit removed on increasing flow-rate: deposit reformed at normal flow-rate
" "	" "	" "	" "	H_2O_2 added (after deposition)	organic component oxidised: deposit formed as usual
21 days intermittent	" "	" "	" "	-	removable cupro-nickel insert in circuit corroded
" " (aerobic)	" "	" "	slight tarnish (no corrosion)	-	aeration eliminates corrosion: deposit formed on wall

Mud which deposited on aspirator walls in regions of low flow rate was removed by addition of polymer, but no evidence for the actual mechanism of removal was forthcoming. The effects of polymer addition did not cause permanent removal of mud. During continued circulation the centrifugal pump subjected the flocs to a prolonged high shearing and re-dispersed the mud. Mud then re-deposited on the walls of the aspirator.

It was noticed that wall deposits formed from untreated suspensions were not removed during circulation of water treated with polymer, but containing no suspended matter. In other experiments lengths of glass tubing with the same internal diameter as a condenser tube were suspended in the aspirator in regions of low flow-rate. Mud deposited on them, but as the tubes were withdrawn for examination it was dislodged by the feeble shearing force of the draining river water.

In another series of experiments, samples of cupro-nickel were placed in the river at West Thurrock near the cooling water intake, with the intention of obtaining deposition of suspended particles on the horizontal and vertical surfaces of the specimens. However, no deposition or sedimentation was observed after prolonged immersion, the only observable effects being the appearance of a uniform green corrosion film over the whole surface of the specimens.

It became apparent that studying deposition and sedimentation of mud under turbulent conditions of flow was unsatisfactory as it gave no indication of the mud removal mechanism and did not provide a deposit or sediment suitable for more detailed observation. It also failed to provide a satisfactory basis for quantitative appraisal of mud removal efficiency by additives and comparison of different materials. As it was impracticable to obtain laminar flow or controlled hydrodynamic conditions in the recirculating apparatus, it was decided to investigate alternative procedures for obtaining deposits under controlled conditions.

2.2.2 Deposition under controlled hydrodynamic conditions

As observation of deposits had proved to be impracticable under turbulent conditions, an established method was tried, which gives, under prescribed conditions, laminar flow over a planar surface. This is obtained by rotating a disc in a horizontal plane in a motionless liquid of 'infinite' volume. The theory of the hydrodynamics has been fully set out by Levich(75). The diagrammatic arrangement is shown in Figure 2.1 Conditions for stream-lined or turbulent flow are dependent on such parameters as speed of rotation of the disc, smoothness of disc surface, disc radius, etc. The size of the disc and speed of rotation and other factors were all selected to give a Reynolds number for the system that would ensure stream-lined flow. Under conditions of stream-lined flow both the hydrodynamic boundary layer thickness and the diffusional boundary layer thickness remain constant over the whole surface of the disc. This method can be used to flow a suspension across the surface of a disc and if the suspension is undergoing slow aggregation particles will diffuse across the boundary layer and adhere through van der Waals forces to the disc surface(76). Unfortunately, although this method is satisfactory for monodisperse systems and systems with a limited size distribution, it is complicated for polydisperse systems with relatively large particles which move out of the stream-lines because of their inertia and deposit by 'impaction'. Nevertheless, the method was used in an attempt to deposit particles from a mud suspension and, if possible, observe their removal by polymeric flocculants.

Plate 2.2 shows the complete apparatus and the rotor and type of cupro-nickel disc used in the experiments. The constant speed, geared motor rotated the disc at 200 r.p.m. Discs were cleaned by refluxing in benzene, flaming for 5 seconds and immersing in 10% sulphuric acid(77). The discs were cemented with molten paraffin wax on to the face of the 'Perspex' rotor. The apparatus was virtually vibrationless. The vessel containing the suspension was raised to a predetermined position on a platform. (Ideally, the

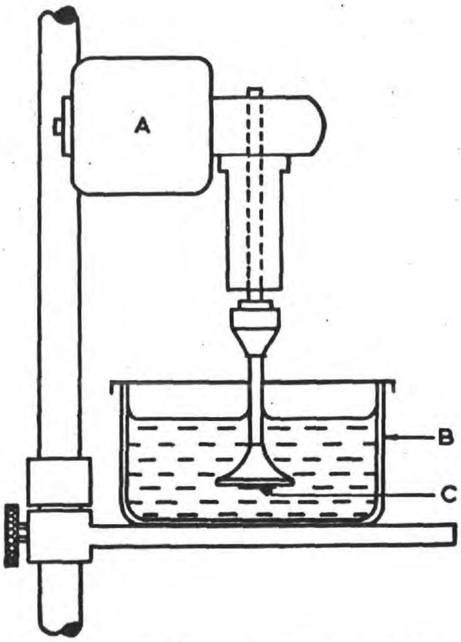


Fig. 2.1 Rotating disc apparatus for deposition under controlled conditions. (A) - constant speed motor; (B) - glass dish containing mud dispersion (C) - cupro-nickel deposition surface .

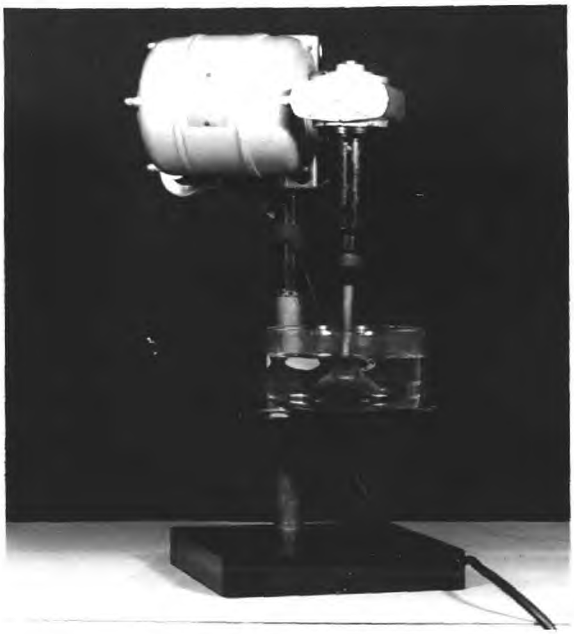


Plate 2.2 Rotating disc apparatus .

volume of the suspension should be infinite but in practice no edge effects are observed with a 12.5 cm diameter crystallizing dish, as long as the disc is more than 2 cm from the bottom surface of the dish). This arrangement suffered from the disadvantage that large particles were not kept in suspension because of constant sedimentation. The flow of suspension within the dish was not sufficient to keep all particles suspended and therefore these had no opportunity to deposit on the disc surface. This meant that only particles up to a limiting size could take part in the deposition process. The suspensions used in the experiments were carefully prepared in order to be as reproducible as possible. Preparation was carried out as follows:

1. Weighed samples of mud were centrifuged at 2000 r.p.m. for 10 minutes.
2. Sufficient centrifuged mud was weighed out to give a final concentration of solids of 1.0% (w/v).
3. The mud was thoroughly dispersed in water, first mechanically, then by ultra-sonics and then diluted to its correct volume in river water.
4. The suspension was allowed to stand for 5 minutes before being syphoned off at a depth of 15 cm. It was then ready for use.

This technique excluded very large particles and material not dispersed sufficiently during preparation. The optical densities of the final suspensions were consistent, indicating reproducibility. Suspensions used during deposition experiments were flushed with nitrogen to minimise absorption of oxygen and oxidation of the organic component of the mud. However, oxidation of the mud did not stop deposition but it was kept to a minimum to simulate practical conditions. Substantial deposition of mud could be obtained only on the discs by rotating them for periods of up to 16 hours; it was therefore convenient to prepare deposits overnight.

Although deposition of mud could be obtained and deposits could be removed by flocculants, which also prevented the formation of deposits, the technique proved altogether unsatisfactory for several reasons. Firstly, the deposition appeared to take place in two stages referred to as primary and secondary deposits. The primary deposition was originally thought to be a tenacious layer of very fine particles in immediate contact with the disc, but this was later shown to result from corrosion of the cupro-nickel surface. The secondary deposition, on top of the primary, took the form of a loosely adhering deposit (similar to that found on the aspirator walls in 2.2.1) and this was easily removed by gentle washing or even by careless removal of the disc from the aqueous suspension. Secondly, the addition of flocculant caused flocculation of the suspension and at the same time removed the secondary deposit from the surface of the disc, but it did not remove any primary deposit. Thirdly, prolonged rotation did not redisperse the mud once it was flocculated. Thus, no indication was obtained of the mechanism involved and it was not apparent whether flocculation of mud and sediment or a dispersion by a diffusion mechanism (peptization) was responsible (or perhaps both). Some of the more pertinent results obtained using the rotating disc are presented in Table 2.2

The experiments conducted with this technique gave little indication of the mechanism of mud removal although they again demonstrated the reality of the effects. However, the information gained from attempts at deposition under turbulent and stream-line flow not only helped in designing further experiments for studying mud deposition and removal, but indicated that 'Zimmite' might have some influence on the rate of corrosion of cupro-nickel in neutral saline waters. Observations on the corrosion of cupro-nickel and the influence of polyelectrolytes on corrosion is dealt with in Part II of the thesis.

2.3 Removal of mud sediment

In order to investigate reports that flocculants have an effect in facilitating removal of deposited mud a series of exploratory tests were tried.

Table 2.2: Effects of 'Zimmite' (20 p.p.m.) on primary and secondary deposits on cupro-nickel (16 hours rotation)

Suspension composition	Treatment of cupro-nickel disc	Observations
1% wt/v mud in river water: anaerobic		primary and secondary deposition
"	'Zimmite' added after 16 h.	secondary deposit primary intact
"	'Zimmite' added before rotation	slight discoloration of surface no deposition
"	mud floc. by 'Zimmite' redispersed before rotation	slight discoloration of surface: only secondary deposition
"	disc rotated in 'Zimmite' (2h) before rotating in 1% mud overnight	slight discoloration of surface: no primary dep. only secondary
Thames water: no suspended solids: anaerobic		primary deposit (soluble in HCl)
"	'Zimmite' added before rotation	slight tarnish film: no primary deposit

2.3.1 Erosion of mud

The technique tried for measuring erosion of sediment during flow was a modification of an engineering device, the 'Mercer gauge', which is used in the measurement of machined parts, e.g. cylinder bores. The principle is that fluid (air or liquid) at a constant pressure is forced into a cylinder through a nozzle of almost the same size as the internal diameter of the cylinder. The clearance between the measuring instrument and cylinder walls is registered as a pressure loss which can be directly and accurately interpreted as a diameter or volume.

The device used for measuring erosion of mud is illustrated in Figure 2.3. It consisted of two concentric tubes, the outer having a flange at its base, the other being fixed so that its end was in the same plane as the flange. The flange and inner-tube were placed almost in contact with the surface of a mud sample and water was passed through the inner tube under a constant head. At the onset of flow both concentric tubes were adjusted to give a reproducible water height (indicating the pressure drop between the inner and outer tubes). If the head of water remained constant then any change in volume, beneath the flange, indicative of erosion or removal of the mud, registered as a change in pressure (height) of the water.

The sediments used in these tests were prepared by centrifuging weighed quantities of mud under standard conditions. This produced a clear supernatant liquid and a consolidated bed of sediment. Because of the large quantities of water required, the river water was simulated by dissolving'sea water corrosion test tablets'(B.D.H.) to the appropriate degree of salinity.

Although changes in volume beneath the flange could be detected quantitative measurements proved impracticable because of the inherent lack of reproducibility of the surface of the mud. Tests did show, however, that water at a high flow rate, and consequently giving a high shearing stress, could erode away a mud surface, but the degree and rate of errosion could not be expressed numerically. No definite effects were observed when attempts were made to remove sediment by

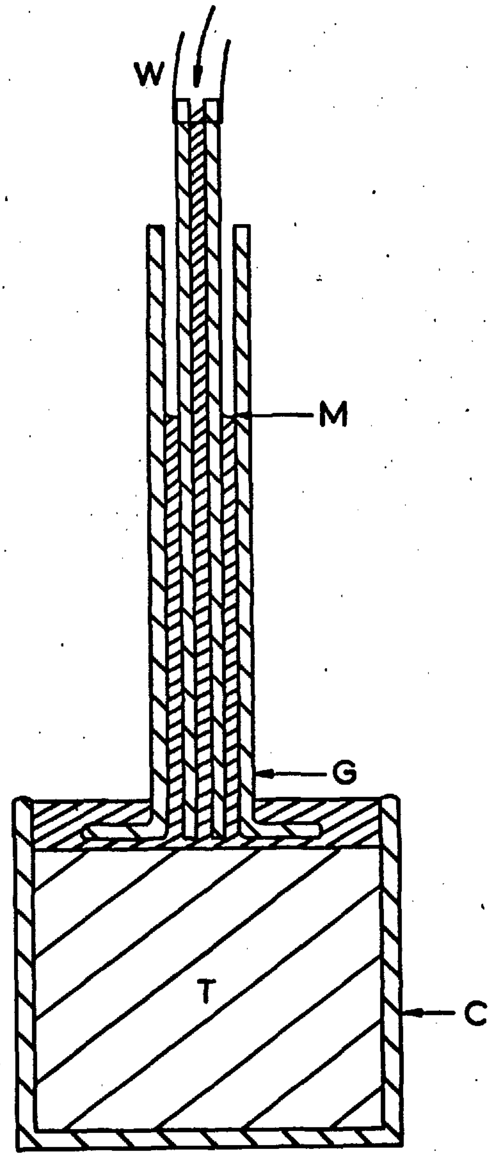


Fig. 2.2 Device for measuring erosion of mud ('Mercer gauge')

(G) - ground glass flange
(M) - meniscus
(W) - water from constant head supply
(T) - sample of Thames River mud
(C) - container

flowing water free from suspended matter, but containing flocculant over the surface. In other tests mud samples were allowed to sediment under gravity and were then subjected to similar errosion tests. These samples also proved unsuitable, probably because of the greater fluidity of the mud surface. Therefore this method of investigating mud-polymer interactions was abandoned.

The negative results in obtaining faster mud removal with flocculants than by untreated water indicated that sediment consolidated by centrifuging might be too far removed from the practical conditions of sedimentation under gravity. These considerations led eventually to investigation of thin layers of sediment (Section 4).

2.3.2 Resistance of mud to shear by cone penetrometer

Usually an effective flocculant produces large fluffy cohesive flocs. However, the patent(65) relating to the use of these materials claims: "even mud that has already settled in the cooling system is resuspended in the form of fluffy material that is easily removed by the flow of water. The function of the polymers here is contrary to what ordinarily would be expected." If this claim were justified the flocculant might be supposed to diffuse into a consolidated sediment and reduce the critical shearing stress necessary for flow(78): then without altering the flow-rate or the rate of shear at the mud-water interface dispersion of the sedimented mud might result.

Characterization of the rheological properties of mud sediments is difficult because of the dependence on their past history. However, a comparative technique for the rapid assay of 'consistency' is obtainable with a penetrometer(79). The device measures the depth of penetration of a needle or cone into a disc of the material under standard conditions of time, loading, shape of sample, temperature, etc. For the tests a 90° cone was made from polythene. The table on which the sample rested could be raised or lowered so that the surface of the mud was placed just in contact with the tip of the cone. The cone was released and after a period of 5 sec. was automatically arrested and the depth of penetration read off. Penetration depends on the yield value and apparent viscosity of the material.

A number of experiments were tried to establish the effects of diffusion of flocculants into the bulk of a mud sediment. Samples were prepared by centrifuging weighed amounts of mud under constant conditions and then transferring the sediment to 'Monax' dishes. Some of the samples were subjected to penetrometry tests before being placed in contact with flocculant solutions of varying concentrations. Some of the samples were left to stand under flocculant solutions; whereas with others the supernatant liquid was stirred. Samples obtained by sedimentation of concentrated suspensions, without consolidation by centrifuging, were also tested with the penetrometer. However, penetration values with these were not reproducible and tests on centrifuged material were more reliable.

Table 2.3 gives the results of these tests.

Table 2.3 Effects of 'Zimmite' on sediment viscosity.

Sample History	Treated with 'Zimmite' (20 p.p.m.)	Penetration depth (mm)	
		Before	after
Centrifuged 10 minutes	24 hrs static	9.7	9.7
"	24 hrs agitated	10.3	10.3
Sedimented	24 hrs static	17.5	17.5
"	24 hrs agitated	18.5	18.1

It is evident that a solution of flocculant in contact with a mud surface has no detectable effect on the apparent viscosity of the bulk of the mud. This indicated that attention should be directed to the influence of flocculent on thin, consolidated layers as penetration was evidently slight. That flocculants could, in fact, affect the consistency of the mud if conditions for interaction were favourable was proved by other penetrometer tests in which a dispersed mud was first flocculated by mixing with a non-ionic, anionic or cationic polymer and then consolidated by centrifuging. The results (Table 2.4) showed clearly that, notwithstanding the less dense packing obtained with flocculated sediments, the polymer strengthens the sediment (as indicated by reduced penetration). This is useful confirmation of the bridging theory and the concept of strong adhesion between particles flocculated by polymers.

Table 2.4 Penetration values of consolidated mud flocculated with organic flocculants

Material used for flocculation 10 ml (1 g/litre) / 100 g mud		Penetration depth (mm) after centrifuging		
No flocculant		Mean	value	9.7
non-ionic polyacrylamide		"	"	6.5
cationic	"	"	"	5.3
anionic	"	"	"	7.2

2.4 Flocculation of mud

A number of commercially available flocculants were tested as mud removers and found to be successful to a greater or lesser degree than Zimmite. Some correlation between flocculation and removal was suggested from comparison of the two phenomena. In practice it has been found that substances which bring about good flocculation of mud suspensions in general have good removal characteristics and conversely substances which produce poor flocculation tend to have poor removal properties. About fifty flocculants and coagulants were investigated experimentally as flocculants, and their direct interactions with mud suspensions observed. The materials were chosen to include all the major chemical types that are available commercially in bulk quantities. The experimental work described in this sub-section was carried out after the design and construction of the apparatus described in Section 3. However, the results of flocculation experiments were required so that semi-quantitative tests could be carried out in the apparatus and consequently they are included with the preliminary investigations. The technique used to obtain quantitative information about mud-polymer interactions was to determine the optimum solids-to-polymer ratio for each system under standard conditions. In addition, floc size was assessed and a visual appraisal made of 'floc cohesion' at the optimum dosage. The optimum polymer-to-solids ratio is generally accepted as the dosage of polymer for a given suspension which produces minimum turbidity when determined under standard conditions.(80) Curves of turbidity versus flocculant addition can be interpreted in terms of flocculation theory. Allowing for the imperfect mixing techniques employed, the values of optima obtained represent the optimum values for maximum floc size and minimum residual suspended solids under the conditions employed. Modification of the mixing technique so that polymer is adsorbed as nearly uniformly as possible reduces the optimum dosage for minimum turbidity but also reduces floc size.(81) It also reduces floc strength and cohesion. 'Overdosing' during normal mixing increases floc size but stabilizes particles overdosed during polymer addition. However, turbidity measurements were found to give reproducible results and tests were easily performed. The values of polymer-to-solids ratio at the optimum were used for subsequent mud removal experiments.

Details of the method used are as follows. A multiple stirrer was constructed (shown in Plate 2.3) which consists of a framework supporting a cross-member which carried the paddles and gears and drive shafts. A motor turned the drive shaft at 220 r.p.m. Although the motor speed could be varied it was considered justifiable to operate at a constant speed throughout rather than stirring at a high rate during polymer addition and then reducing the rate to help form larger flocs and promote clarification. The paddle speed of 220 r.p.m. could be considered a high rate of stirring, possibly leading to shearing of flocs; but this was offset by the design of the four bladed paddles. A feature of the stirrer was that each paddle blade could be raised to remove a sample under test without stopping the motor. The couplings, driving and paddle shafts, gears and shaft guides were made with 'Meccano' parts.

In the past square glass jars have often been used in flocculation tests, but these jars have been criticised on the grounds of inefficient mixing.(82) For the present experiments 600 ml standard 'tall-form' beakers were used and these proved to be satisfactory. The flocculation tests were performed as follows:

1. 24 g of wet mud (40% solids) were weighed out to give a 1% w/v suspension.
2. Mud was dispersed both mechanically and ultra-sonically in a Dawe 'soniclean' tank in a small volume of water.
3. The mud suspension was then dispersed in distilled water and diluted to a final volume of 2.4 litres, 400 ml being placed in each of six tall-form beakers.
4. Varying quantities of polymer solution were pipetted into each tap funnel, excluding the blank, in increasing doses. The volume was adjusted to 100 ml with distilled water and 100 ml of water placed in the 'blank' funnel.
5. The beakers were placed under the multiple stirrer and stirred for five minutes before running in the contents of the tap funnels.
6. After polymer addition the flocculating suspensions were stirred for a further three minutes.
7. The suspensions were removed from under the stirrers and allowed to stand for five minutes.
8. The supernatant liquids were drawn off at a fixed depth and the turbidity determined as % transmission in an E.E.L. photoelectric absorptiometer using a neutral density filter. A typical curve of transmission against dosage is shown in Figure 2.4 .

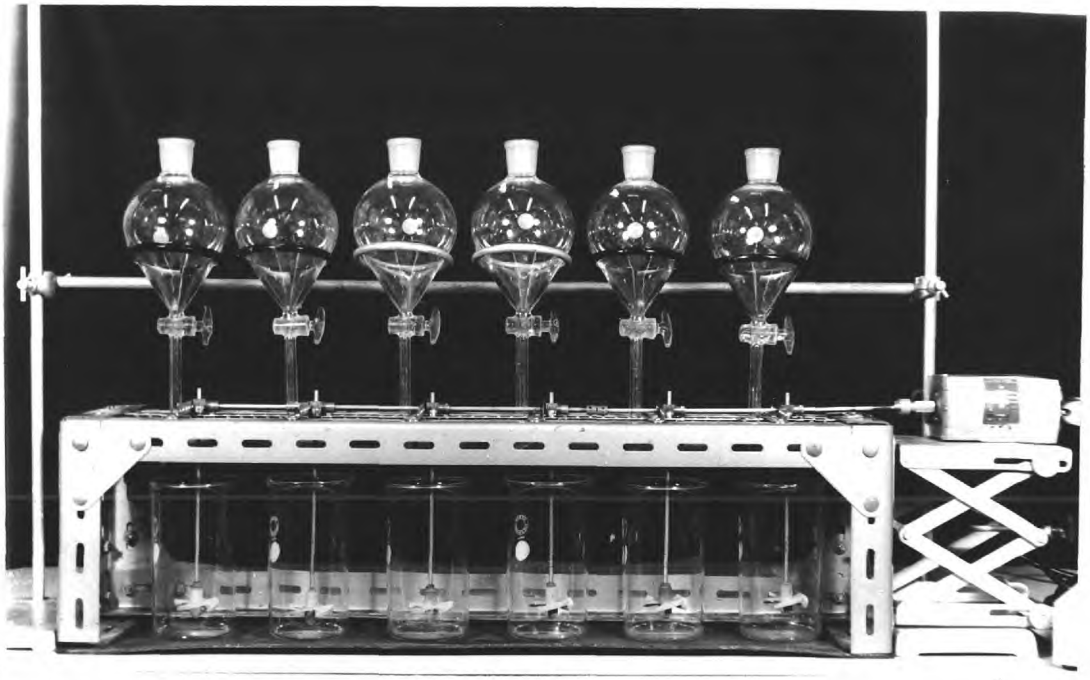


Plate 2.3 Stirring rig used to determine optimum polymer-to-solids ratio.

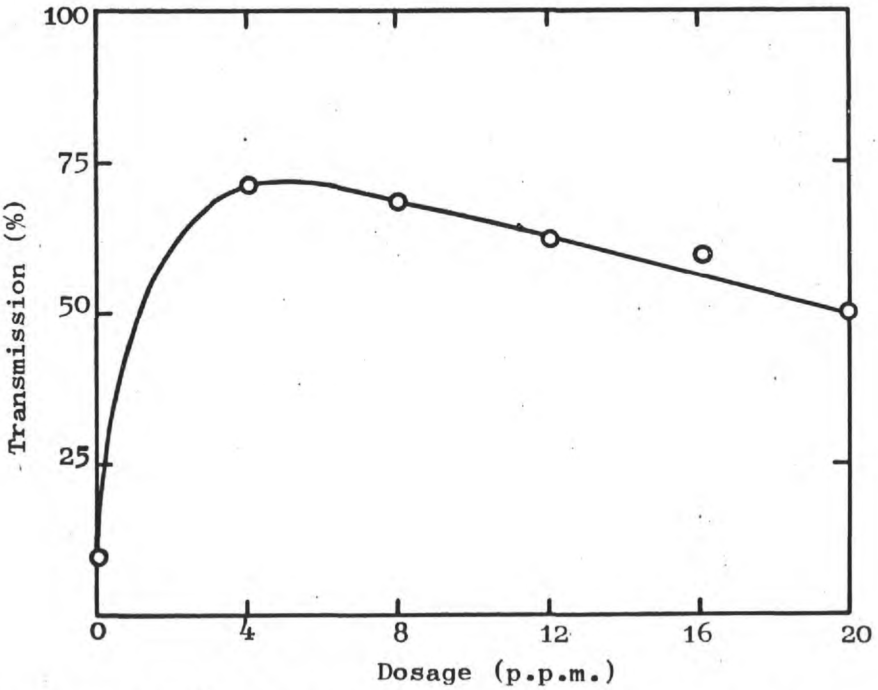


Fig. 2.3 Typical curve of transmission vs dosage for polymer flocculant and Thames River mud.

Once the optimum polymer to solids ratio had been determined, the average flocs size could be estimated for flocs formed under conditions of optimum dosage. The assessment was made by visual comparison of flocs with a 'floc comparator' (prepared by John Crosfield Ltd.). This was a chart illustrating a number of flocculated systems each having flocs between specific dimensions. The chart covered a range of floc sizes. The method provided only an approximate measure of particle size, but appeared to be adequate for the purpose of comparison of flocculants in this system. The degree of 'floc cohesion' was also visually assessed. It can be defined as the ability of flocs to aggregate or 'stick' together. It is a difficult parameter to measure and no method was devised for its assessment other than inspection of the flocs at the optimum polymer to solids ratio. For example, Plate 2.4 shows five flocculated systems exhibiting five degrees of floc cohesion. This method seemed unambiguous and served as a semi-quantitative index of cohesion. For convenience, a scale of from 1 to 5 was adopted to embrace the varying degrees of cohesion encountered in the flocculants tested. The degree of cohesion increased with number and the arbitary values are shown in Plate 2.4.

The three parameters, optimum ratio, floc size and cohesion are listed for each system investigated in Table 2.5. Details of the flocculants used, as far as is known, are listed together with manufacturers names in Appendix I.

The results obtained during the preliminary tests on flocculants were used in part for tests of mud removal efficiencies of selected flocculants. Results of these tests are reported in Section 4.

1

minimum
cohesion
encountered

2

3

4

5

maximum
cohesion
encountered

Plate 2.4 Chart illustrating estimated cohesion at optimum polymer-to-solids ratio.

1. Glue (hide)
2. Separan AP30
3. Separan C120
4. Zimmite
5. B.T.I. C110

Table 2.5 Values of optimum polymer-to-solids ratio, floc size and cohesion for flocculants tested (for type see Appendix I)

Flocculant	Optimum $\frac{P}{S}\frac{(mg)}{(g)}$	Floc size (mm)	Estimated cohesion
Aerofloc 550	2.0	0.3 -0.5	1
B.T.I. A100	1.5	0.75-1.0	2
B.T.I. C100	1.0	2.25-3.0	5
B.T.I. C110	1.25	3.0 -4.5	5
B.T.I. CL40	8.0	1.0 -1.5	3
B.T.I. CL80	8.0	1.0 -1.5	3
Flocbel FC10	0.75	1.5 -2.25	3
Flocbel FC11	1.75	2.25-3.0	3-4
Flocbel FC109	1.0	0.75-1.0	2
Floccotan	1.8	1.0 -1.5	3
Gelatin	1.6	0.5 -0.75	2
Glue (bone)	1.5	0.5 -0.75	1
Glue (hide)	1.0	0.5 -0.75	1
Magnafloc R139	1.0	1.5 -2.25	4
Magnafloc R140	1.75	2.25-3.0	4
Magnafloc R155	0.5	2.25-3.0	3-4
Nalco 670	0.5	0.5 -0.75	3
Nalco 632	0.6	1.0 -1.5	3
Nlaco 600	0.6	1.0 -1.5	3-4
Polyflok PX	6.5	0.3 -0.5	0-1
Polyflok 209P	1.6	0.5 -0.75	1
Polymer X-150	2.5	2.25-3.0	3-4
Polyox	0.5	1.0 -1.5	1
Powdaflok	-	no flocculation	0
Primafloc C3	2.0	1.0 -1.5	1-2
Primafloc C5	2.0	0.75-1.0	1-2
Primafloc C6	2.0	0.75-1.0	1-2
Primafloc C7	8.0	1.0 -1.5	2

Table 2.5 (cont.)

Flocculant	Optimum $\frac{P}{S}\ \frac{(mg)}{(g)}$	Floc size (mm)	Estimated cohesion
Sedomax F	6.1	0.3 -0.5	1
Sedomax G	4.0	0.3 -0.5	1
Sedomax HP	1.0	0.5 -0.75	2
Separan AP30	1.0	0.5 -0.75	2
Separan C90	2.4	1.0 -1.5	3
Separan C120	2.5	1.0 -1.5	3
Separan NP10	1.4	1.5 -2.25	3-4
Separan NP20	1.9	2.25-3.0	4
Superfloc 16	1.5	0.75-1.0	3
Superfloc 20	1.5	2.25-3.0	4
Tragafloc	-	no flocculation	0
Tragora 40	1.5	$<$ 0.3	1
Tragora 55	2.0	1.5 -2.25	3-4
Tylose MH4000	-	no flocculation	0
Tylose CB4000	-	no flocculation	0
Tylose MH4000P	-	no flocculation	0
Wisprofloc P	2.0	1.0 -1.5	3
Wisprofloc 20	-	no flocculation	0
Zimmite	1.5	2.25-3.0	4-5
	Inorganic Coagulants		
Activated silica	-	no coagulation	0
Aluminium sulphate	25	0.75-1.0	1-2
Ferric chloride	13	0.75-1.0	1-2

3. DESIGN, CONSTRUCTION AND USE OF FLOW CELL

3.1 Introduction

Preliminary investigations into mud-polymer interactions showed that suspended mud can be both sedimented and deposited under certain conditions in an apparatus designed to simulate flow of cooling water through a condenser tube. The shape of the apparatus (Plate 2.1) permitted considerable convergence and divergence of flow, both of which gave rise to the hydrodynamic conditions of turbulent and laminar flow, eddying and stagnation(83). The velocities chosen to give turbulent flow in the condenser tube permitted sedimentation in each aspirator of coarse material only which, because of its inertia, remained undisturbed by the acceleration of deceleration of flow. The greater part of the mud was kept in suspension as the high Reynolds number at the horizontal surfaces or the aspirators did not permit much sediment to form. However, in other regions the flow became almost stagnant - the result of the combined effects of accelerating or decelerating flow passing through re-entrant orifices. This created regions where constantly replenished suspension was not subject to deterioration by sedimentation: the aspirator walls soon became covered with loose colloidally deposited mud. In addition, a very fine colloidal deposit formed on all surfaces throughout the apparatus, because the stationary boundary layer (existing at all liquid-solid interfaces, no matter what the hydrodynamic conditions are) permitted diffusion and deposition of the smallest particles.(73) The deposit was not easily visible except as a fine dust when the apparatus was examined dry. Observations on mud removal showed the effects of flocculants on sediment and deposit to be very similar, without revealing the mechanism involved. It is probable that mud fouling in condenser systems is a combination of sedimentation and deposition and that information gained from observations on the removal mechanism on either system would be applicable to both.

Following these earlier experiments, several 'flow-cells' were constructed, each producing divergence or convergence of flow over surfaces amenable to sedimentation. Sedimentation of a flowing suspension is dependent on such factors as the drag coefficient of the particles, terminal velocity, viscosity, shape of particles and the Reynolds number for the system(84). Therefore, in a system in which flow is accelerating or decelerating across a horizontal surface the change in Reynolds number, if sufficiently large, should create areas of sedimentation and areas of no sedimentation. In addition, a graded transition of sedimentation should exist between both areas. The Reynolds number for a system is proportional to the shearing stress - the internal surface force acting tangentially over the surface of elementary fluid masses, in addition to gravity. As the Reynolds number increases in a pipe, so does the shearing stress at the fluid-solid interface.

Initially, a uniform increase or decrease in shearing stress was achieved by flowing suspension through modified conical and spherical glass flasks. Both types used either vertically or horizontally produced areas of sediment formation in the regions of low shearing stress, and no sediment in the regions of high shearing stress. As in the preliminary experiments, mud was removed by the addition of small quantities of polyacrylamide. However, no other conclusions were gained from these experiments, as observation of the process of removal of sediment was obscured by the high solids content of the system and the shape of the cells. Further criticism of this type of cell was the difficulty in analysing the hydraulic flow of the suspension, particularly as the cells were not completely symmetrical, nor were the cross-sectional dimensions and construction of the cell adequate to ensure completely laminar or completely turbulent flow with the absence of stagnant zones. Therefore, experiments with these cells were discontinued.

The same ideas were incorporated in another design, but with greater attention paid to fundamental hydrodynamic factors required to set up controlled hydrodynamics and laminar flow.

3.2. Design of flow-cell

The following requirements had to be met in the design of the cell.

1. Laminar flow, combined with a graded shearing stress at a horizontal (or nearly horizontal) surface.
2. Easy observation of sediment formation and removal.
3. Structure to fulfil requirements of ease of fabrication, manipulation and cleaning.
4. Hydrodynamic requirements to be within limits imposed by pump performance and water supply available.

A tapering closed rectangular channel was considered suitable. It could be of 'Perspex' and glass, which facilitated observation in all parts of the system. Observation was also facilitated by its rectangular shape, as sediment would form on a nearly horizontal surface. Accelerated motion of a fluid as it occurs through a constriction is accompanied by a favourable pressure gradient which stabilizes the boundary layer and minimises energy dissipation. (Decelerated motion is accompanied by an adverse pressure gradient which promotes unstable eddy formation.(85)) The cell was designed to accelerate suspension from the thick to the thin end of the taper.

A maximum flow rate of 15 litres/min was the limit of the performance of the centrifugal pump and just below the maximum output of the laboratory water supply. As the flow was to be accelerated within the tapering region of the channel (for convenience called the 'wedge' it was necessary to establish laminar flow at the point of the highest shearing stress, this point being the thinnest part of the wedge. If the thickness of the wedge is 'w' at this point, then the width must be at least 10w in order to make edge effects on the velocity profile negligible.

This ratio was adopted and in addition a maximum value of 1500 was imposed on the Reynolds number to satisfy the conditions for laminar flow and provide a safety margin. For a liquid flowing through a circular pipe, the Reynolds number N_R is defined

$$N_R = \frac{Vd}{\nu} \tag{1}$$

in which V is the average velocity, d the diameter and ν the kinematic viscosity. In non-circular conduits it is necessary to adopt the 'hydraulic radius' concept.(86) The hydraulic radius R_h is the area, A, of flow cross section divided by the wetted perimeter. For a circular pipe diameter d, R_h is defined

$$R_h = \frac{\pi d^2}{4\pi d} = \frac{d}{4} \tag{2}$$

For a rectangular conduit of sides w and 10w R_h is defined

$$R_h = \frac{10w^2}{22w} = \frac{w}{2.2} \tag{3}$$

Combining equations (2) and (3)

$$d = \frac{w}{0.55} \tag{4}$$

To calculate w, the minimum thickness, at a flowrate Q litres/min.

$$V = \frac{Q\ 1000}{10w^2\ 60} = \frac{5Q}{3w^2} \tag{5}$$

Substituting equations (4) and (5) into (1)

$$N_R = \frac{5Qw}{3\ w^2\ 0.55\ \nu} \tag{6}$$

Re-arranging to obtain w,

$$w = \frac{Q}{0.33\ N_R\ \nu} \tag{7}$$

Substituting values of N_R and ν (at 20°C) in equation (7)

$$w = 0.202\ Q\ \text{cm}$$

The thickness w is the minimum value in cm in a rectangular conduit sides w and 10w at a flow rate Ql/min, at which laminar flow can be obtained. The imposition of a maximum value of 1500 on the Reynolds number means that w could be less than 0.202Q, but at the risk of entering the region of transition from laminar to turbulent flow.

In order to obtain truly laminar conditions in normal pipe flow, a minimum distance of 100 times the pipe diameter is required. In the case of the wedge 100w was taken as the minimum distance. An arbitrary value of 5w was adopted to give a wide range of shearing stress. As the flow rate of 15 l per minute would have resulted in a cell of about 300 cm it was decided to reduce the flow rate to 7.5 l/min. This reduced the overall length and permitted a wider variation in the choice of flow rates during experiments.

Fig. 3.1 shows a diagram of the cell together with final dimensions. However, the dimensions of the width and length of the cell do not correspond to 10w and 100w respectively. This is due to slight changes in the design during construction. The increased dimensions of the width and length of the cell help to stabilize laminar flow and in no way impair its performance. To minimise the turbulence within the channel the inlet box was designed to compress the flow through a 'short tube type' orifice. Flow of liquid to the exit box from the wedge was through a 'semi-rounded' orifice to eliminate turbulence within the wedge. During construction it became obvious that a symmetrical wedge would lack mechanical strength and possibly collapse as a result of the mass of water within the cell. The design was modified and a slightly unsymmetrical wedge was substituted. This offered the advantages of a horizontal surface, easier fabrication and added strength. This modification did not change the fundamental requirements of the cell, but did create an unsymmetrical velocity profile within the wedge, and consequently changed the gradation of shearing stress. The validity of the

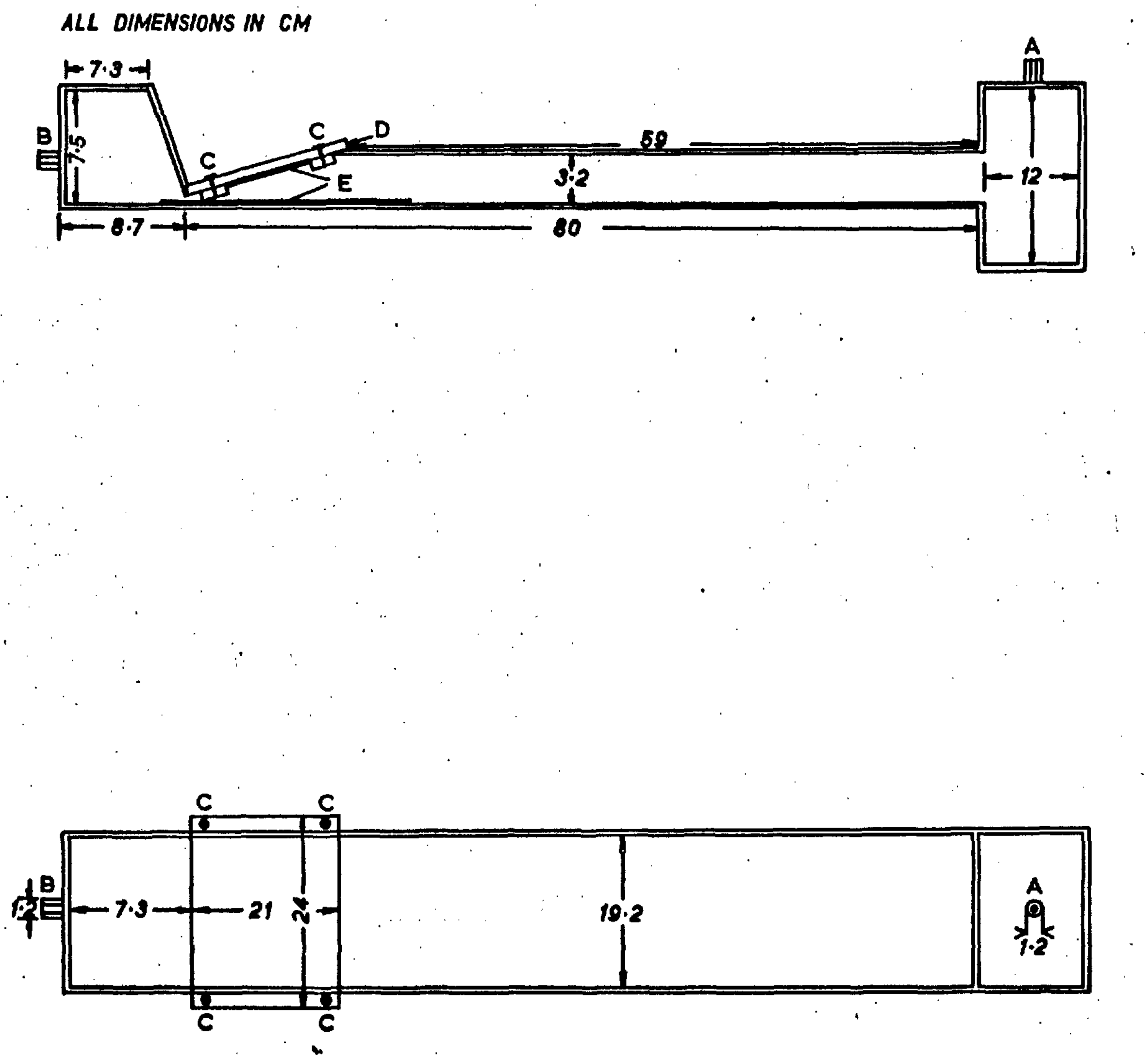


Fig. 3.1 Flow-cell used to observe the removal of sediment during flow.

(B) + (A) - exit and entry points
(D) - pressure plate
(C) - securing bolts
(E) - glass plates
(not to scale)

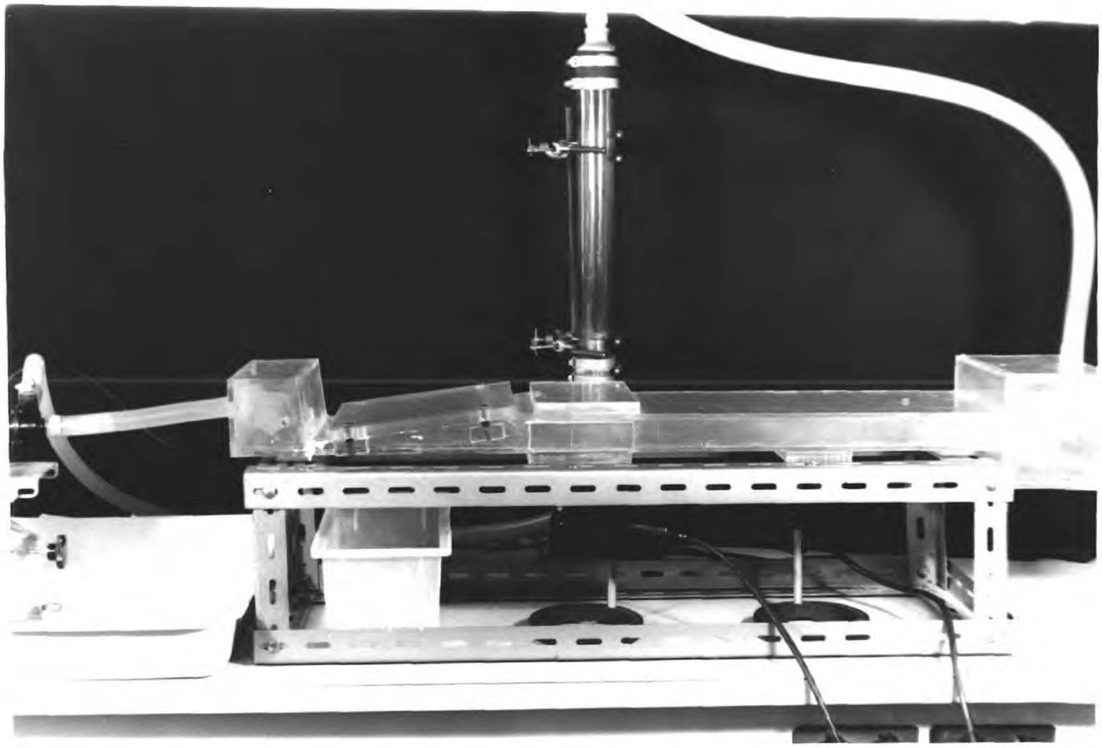


Plate 3.1 Flow-cell in circuit recirculating mud suspension under controlled hydrodynamic conditions .

modification was borne out by experiment as mud sedimented and/or did not sediment in particular areas according to the calculated shear stress.

3.3 Construction of the flow-cell

Plate 3.1 illustrates the complete flow cell on its stand, coupled to a centrifugal pump and 'Rotameter' flow-meter. Apart from the top surface of the wedge the whole cell was constructed from $\frac{1}{4}$" 'Perspex' sheet. It was made in two parts and cemented together, with additional support round the joint. For convenience, the wedge and exit box were made separately from the channel and inlet box. The top surface of the wedge was a glass cover plate which was sealed in position with silicone rubber moulding paste lightly applied to each side of the "Perspex" wedge and the edge opposite the exit. The moulding paste for the fourth edge at the point of exit was applied directly to the plate before it was placed firmly in position. A 'Perspex' pressure plate was then placed above the glass plate and held in position with four bolts, one at each corner and screwed into threaded 'Perspex' blocks cemented to each side of the wedge. The pressure plate ensured a water-tight seal and the silicone rubber moulding paste formed the gasket which established the seal. The seal could easily be removed or replaced. The pressure plate also prevented breakage of the glass plate in the event of sudden pressure build-up in the system. A thin glass plate was inserted in the cell before the top plate was placed in position. This provided replaceable top and bottom glass surfaces in the wedge portion of the cell. Although the joints of the cell were cemented together during construction with 'Perspex' cement, each joint was again liberally treated with 'Perspex' cement diluted with about 30% chloroform and then allowed to dry before use. This treatment prevented leakage and gave the apparatus additional strength to resist inadvertent pressure build-up of water inside the cell. Small holes were made near the inlet and exit in the top of the end boxes to release trapped air and facilitate filling and emptying the system. The holes were stopped with rubber bungs during experiments. The inlet and outlet orifices (shown in Fig. 3.1) consisted of short lengths of 'Perspex' tubing set flush with the interior walls and cemented into position. The flow cell was connected through a Charles Austen C16 centrifugal pump with 0.5" internal diameter clear p.v.c. tube. The tubing from the inlet and outlet was easily removed, and formed an effective water-tight seal without additional security. Elsewhere, expanding metal clips were used to prevent leakage.

The cell itself was mounted on a framework which permitted illumination from underneath and observation. Illumination was provided by two 60 watt lamps which also allowed the photographing of effects within the cell. The centrifugal pump was wired through a variable transformer. This enabled the flow rate in the cell to be varied. A tap funnel was mounted directly above the inlet box so that predetermined quantities of flocculant could be added to the system.

3.4 Use of the flow-cell

The following method was used for charging the cell with a mud suspension and making observations on mud-polymer interactions. The apparatus was set up as shown in Plate 3.1. The p.v.c. tubing was disconnected from the inlet box and the end placed in a sink. Both rubber bungs in the inlet and exit boxes were removed and the cell filled with tap-water. When this was done, the supply was removed, and the inlet tube and exit box bung replaced. The pump was then switched on and water circulated driving all the air trapped within the system into the inlet box. The water level in the inlet box dropped and allowed the addition of mud suspension and flocculant solution. The inlet tube was removed and held so that water did not drain back into the cell. At the same time, a quantity of dispersed mud was washed into the cell. The inlet tube was replaced and the water circulated at a selected flow-rate.

Mud dispersed throughout the cell during circulation and established a steady distribution between the suspended and sedimented phases. Sediment formed throughout the length of the parallel channel and partly within the wedge. As expected, there was a transition from a high to low sediment density per unit area within the wedge. After a fixed time, flocculant was added through the small hole in the inlet box and interactions between mud and flocculant could be followed and, if desired, photographed. Flocculant addition was made either directly by pipette or from a tap funnel.

Clearing of sediment and flocculated suspension was accomplished by removing the cell from the circuit and placing it, exit box downwards, in a sink. The bungs were removed and the whole cell was filled with clear water; failure to remove the bungs could result in pressure build-up in the system and cause damage. The water was then allowed to drain out rapidly and as it did so it carried out residual flocs and particulate matter. The cell was then replaced in the circuit and flushed with tap water for five minutes to wash out any unwanted material left in the Rotameter. From time to time it becomes necessary to clean the cell internally, as mud particles become lodged beneath the bottom glass plate and the excessive build-up of the fine colloidal deposit, mentioned previously, obscured observation of sediment, although it did not actually affect the working of the cell.

As mentioned in Section 2, slowly aggregating suspensions leave a deposit on surfaces, and the effect is greater if a suspension is allowed to remain stagnant in the cell. Particles deposited in this manner are very tenacious(87) and resist all forms of detergent except mechanical removal from the surface. For cleaning, the top glass plate and the silicone rubber gasket were removed and the cell scoured with a soft-bristled brush.

Experimental use of the cell confirmed that the design satisfied all requirements. In particular, graded sedimentation occurred where expected and at the flow-rates calculated to produce laminar flow. Establishment of laminar flow in the wedge was confirmed by injecting methylene blue solutions in water into the cell at the inlet and observing the flow patterns in the wedge.

Rapid sedimentation of mud from the suspension circulating through the cell occurred in both the channel and the wedge. Sedimentation in the wedge took the form of a decrease in the number of sediment particles per unit area from the thick to the thin end. The results of experiments carried out on the interactions between flocculants and mud are reported in the next Section.

In order to assess the hydrodynamic conditions in the cell which would permit or prevent sedimentation, it was necessary to determine the shearing stress at the wall and the change in velocity of water moving across the surface of the wedge(88). This was accomplished by measuring the 'head loss' in the system and determining the change in velocity of mud particles within the wedge. The head loss was measured by inserting two piezometer columns, not shown in Plate 3.1, into the channel portion of the cell and measuring the drop in energy line (head loss) between the two tubes. The change in height of the water meniscus in each tube was measured with a travelling microscope. Average velocities of particles in regions within the wedge were determined by timing the particles between fixed points. The average head loss $h_{L\ 1-2}$ for circular pipe flow between two points L_2 and L_1 is given by

$$h_{L,1-2} = T_o \frac{(L_2 - L_1)}{\gamma\ R_h} \qquad (8)$$

in which T_o is the shearing stress at the wall, γ the density of fluid, and R_h the hydraulic radius. Re-arranging equation (8), the wall shearing stress, T_o is

$$T_o = \gamma \frac{R_h\ h_{L\ 1-2}}{(L_2 - L_1)} \qquad (9)$$

Substituting into equation (9) values for γ, R_h, L_2, L_1 and $h_{L\ 1-2}$

$$T_o = 2.6 \times 10^{-3}\ \mathrm{g/cm^2}$$

This is the average wall shear in the channel at a flow-rate of 9.7 L/min. The velocity of particles moving across the bottom surface of the channel was assumed to be directly proportional to the shearing stress at this surface. Suspended particles do not move at exactly the same velocity as the fluid, but it was assumed that the drag coefficient remained constant within the region of laminar flow. The change in shearing stress decreases linearly from the wall, as expressed by

$$T = \mu \frac{dV}{dy} \qquad (10)$$

in which T is the shearing stress in the fluid at distance y from the wall, V is the velocity and μ the proportionality constant, which is assumed to remain constant as the velocity profile changes. This means that the shearing stress is directly proportional to the velocity of suspended particles at the sediment-suspension interface. During flow compression, the velocity profile became asymmetric because of the lack of symmetry of the wedge. The average velocity of particles in the channel was determined by finding the average time taken to move between two fixed points. Substituting in equation (10)

$$T_{o1} = \mu \frac{dV_1}{dy_1} \quad \text{and} \quad T_{o2} = \mu \frac{dV_2}{dy_2}$$

$$y_1 = y_2$$

$$\therefore \quad T_{o2} = \frac{dV_1 \, T_{o1}}{dV_2}$$

The shearing stresses at the bottom surface of the wedge at various distances from the point where the thickness equals w, at an average flow rate of 9.7 litres/minute are reported in Table 3.1

Table 3.1 Variation of shearing stress at lower surface of flow-cell (Flow-rate 9.7 litres/min)

Distance from wedge exit (cm)	Average shearing stress ($g/cm^2 \times 10^{-3}$)
0-5	76.1
5-10	20.0
10-15	8.7
15-17.5	4.4
50-55	2.6

4. RESULTS OF MUD REMOVAL EXPERIMENTS

Initial tests showed that when mud was circulated through the flow cell a demarcation between areas of sedimentation and no sedimentation was established in the region of graded shearing stress. At the highest shearing stress - at the thin end - very little mud sedimented; the amount of sediment at the thick end was similar to the amount sedimented per unit area in the channel, the difference in the shearing stress at the sediment surfaces being small. There was no sharp transition between the two regions of sedimentation and no sedimentation, partly because of the poly-dispersity of the clay minerals in the mud (Table 1. 1). But it was possible to set arbitrary limits on the transition zone between the two regions. The limits depended on subjective judgement by the experimenter, but changes in the boundaries during mud removal were unambiguous and there was no difficulty in observing other effects in the wedge. Although it was difficult to assess the extent of mud removal - particularly as most experiments were carried out in a recirculating system - it was possible to determine whether or not an additive did remove mud.

During re-circulation of mud in the flow-cell, the mud particles distributed themselves in the following way. Coarse silica and particles which were not throughly dispersed during the preparation of the mud suspensions settled in the inlet and exit boxes. Slightly less coarse material settled at the inlet end of the channel in the region of transition from turbulent to laminar flow. The finer material either remained suspended or sedimented in the channel or wedge, while the particles approaching colloidal dimensions remained suspended.

Mud particles rapidly established a balance between the suspended and sedimented phases, but it took much longer to establish an equilibrium between the two phases, i.e. the point at which no more particles sedimented during flow. However, there was no apparent difference between mud removal at the onset of demarcation - which occurred soon after the suspension was circulated - and removal after equilibrium sedimentation was established. The establishment of equilibrium did not affect the arbitrary demarcation zone and the only factor which did was a change in average velocity of water within the cell - a change in the flow rate changed the gradation of shearing stress in the wedge. In the flow-cell the transition zone for Thames mud occurred at approximately 8 cm from the wedge exit at a flow rate of 9.7 L/min and the shearing stress at this point was in the order of 20×10^{-3} g/cm^2. These values of shearing stress are approximate; errors are inevitable if a rectangular conduit is equated with a uniform pipe, particularly under conditions of laminar flow(86). In practice, sedimentation varies with the degree of coagulation and character of the mud, with the type, whether laminar or turbulent, and with conditions of flow in a condenser system(84,70).

4.1 Qualitative Investigations

The first tests in the flow-cell were designed to investigate qualitatively the action of flocculants on mud during removal. No information was obtainable on the exact dosages required, although from the experience gained at West Thurrock, an approximate value between limits was obtained. As in the flocculation of suspensions, the mud removal occurred within a wide range of dosages. In industrial solid-liquid separation the dosage of flocculants depends largely on the economics of use and the performance required. Often, in practice, the economic dose of flocculant is one tenth of the optimum value but the results obtained with the lower dosage are still satisfactory. Although experiments described in this section were all qualitative, there was no ambiguity in characterizing flocculants as mud removers or establishing the mechanism of removal.

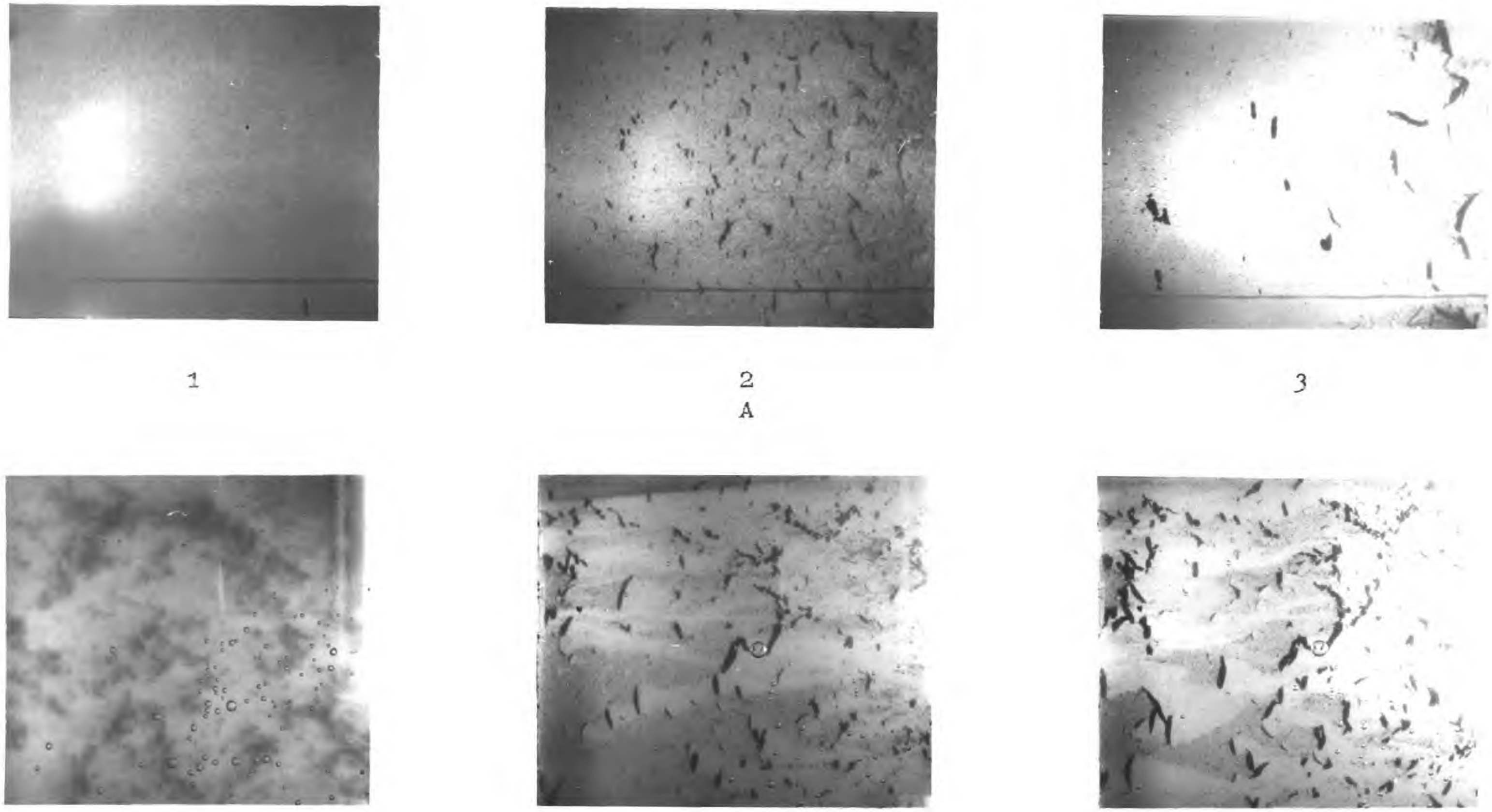
Preliminary tests were carried out in the cell with Zimmite (the proprietary material known to remove mud) to confirm that sedimented mud could be removed in this particular system. Tests were carried out with both tap water and simulated river water

(B.D.H. sea water test corrosion tablets dissolved to the approximate salinity of estuarine water). However, there was no apparent difference in mud — polymer interactions in the presence or absence of salts. Sodium sulphite was also added in some of the earlier tests to minimise oxidation of the organic component, but this was discontinued as the state of oxidation of the mud was found not to affect its response to flocculants. In all the tests with Zimmite, mud removal occurred after flocculation, but within minutes of its addition; the dosage was within the range known to flocculate mud suspensions of a similar composition and concentration.

The physical action of removal of mud is shown in the photographic sequences in Plate 4.1 (a) and (b). The sequence shown in (a) is the effect within the wedge - it shows the increase in floc size and partial removal of mud within the transition zone. The removal of sediment and transport of flocs in the channel is shown in (b). This test was extended to a number of other flocculants to establish if they removed mud in the same way. Although it was not possible to make a quantitative comparison between substances which removed sediment, it was possible to determine whether or not a substance would remove sediment. The qualitative results of the tests to establish which flocculants removed mud in the cell are shown in Table 4.1

In an attempt to make effects more marked, a 1.0% w/v suspension of mud in water was used at first; removal occurred readily at this concentration, but the high solids content obscured observation. The thickness of the sedimented layer prevented its complete removal as only the top layer could take part in the removal mechanism. At lower concentrations of mud, e.g. 0.15%, the layer of sediment on the bottom of the cell was thin enough to take part in removal. This effect was only observed in the channel; the clearance within the wedge was successful at both concentrations.

Recirculation of suspension was adopted because the large quantities of suspension required for a 'once through' system created handling difficulties, as found in an exploratory trial. This imposed restrictions on the experiments, but the effects observed were the



1 2 3

A

1 2 3

B

Plate 4.1 Removal of mud; (A) in wedge; (B) in channel; increasing with time 1 to 3; flow from right to left. (System Zimmite - Thames River mud)

Table 4.1 Qualitative results of the removal of sediment in the flow-cell containing Thames River mud suspension (0.15% w/v). Flocculant dose - optimum for clarification. Manufacturers specification of chemical types listed in Appendix I

Flocculant	Removal of sediment
Zimmite	++
B.T.I. C110	+++
Separan AP30	-
Primafloc C7	+
Floccotan	+
Tragora 55	+
Gelatin	+
Wisprofloc P	+
Powdaflok	-
Polyox	-
Separan C120	+
Polymer X-150	-
Cyanamer P250	++
Polyflok 209P	-
Primafloc C6	+

Degree of flocculation: (qualitative assessment)
+++ - very good
++ - good
+ - poor to good
- - slight or ineffective

Table 4.2 Qualitative results of sediment removal by inorganic coagulants on Thames River mud (0.15% w/v). Dosage - optimum for clarification

Coagulant	Removal of mud
Ferric chloride	none (coagulation)
Aluminium sulphate	" (")
Activated silica (arbitrary dose)	" (no coagulation)

Table 4.3 Qualitative results of Thames River mud removal 0.15% w/v) by flocculants in the presence of inorganic coagulants. Dosages - optimum for clarification.

Flocculant	Coagulant	Effect on mud removal properties
Zimmite	Ferric chloride	+ improved
"	Aluminium sulphate	+ "
"	Activated silica	+ no change
Separan AP30	Ferric chloride	- removal*
Separan AP30	Aluminium sulphate	- removal*
B.T.I. A100	Ferric chloride	- removal*
Floccotan	Ferric chloride	+ improved
Tragora 55	Ferric chloride	+ improved
Gelatin	Aluminium chloride	+ no change
B.T.I. C110	Ferric chloride	+ reduced
Polyox	Ferric chloride	- no change

* only slightly effective in the absence of trivalent iron or aluminium.

(+) - effective in absence of coagulant

(-) - ineffective in absence of coagulant

Table 4.4 Qualitative results of the interaction of flocculants and the sediment from various suspensions in flow-cell. Dosage - optimum for clarification.

Suspension	Flocculant	Result
London clay (0.2% w/v)	Zimmite	Removal of Sediment
Fluorite (1.0% w/v)	B.T.I. C110	"
"	Magnafloc R155	"
Kaolin (0.2% w/v)	B.T.I. C110	"
Bentonite (0.1% w/v)	" "	"

same for both systems. A constant head supply from a 60 litre aspirator was used for 'once through' tests, but the capacity of the container restricted tests to five minutes.

The removal tests indicated that good flocculants were good mud removers and poor flocculants poor removers. Other flocculants which had no effect on these mud suspensions failed completely to remove or displace mud sediment in the cell. Tests were also carried out on inorganic coagulants (Table 4.2) and combinations of inorganic and organic materials (Table 4.3). In addition, qualitative tests were carried out on other suspensions in place of rivermud to establish if their sediments could be similarly removed (Table 4.4).

It was next necessary to establish the mechanism of removal. All the tests, so far, had shown that polymer addition to the recirculating suspensions caused flocculation of the mud and then displacement or removal of the sediment through combination with freshly formed flocs. The critical step in the mechanism appeared to be the interaction between flocculated mud and sediment. The following three tests were decisive in determining the mechanism of removal and consequently are described individually.

Experiment 1

The flow-cell was charged with 15g of mud and circulation carried out for a time to allow sedimentation of mud. By carefully flowing in water at the same rate as the suspension was discharged, it was possible to replace the suspension with clean water containing no suspended matter. The correct dose of polyacrylamide (enough normally to effect removal) was added. Prolonged circulation of the clear supernatant liquid failed to dislodge the sediment. However, increasing the flow rate (which re-suspended some of the sediment and allowed it to flocculate and settle) resulted in partial removal of the mud by aggregation with settling flocs.

Experiment 2

Polymer solution was allowed to remain in contact (in the flow cell) with sediment prepared as in Experiment 1. Polymer solution was left in contact with sediment - in the absence of suspended matter - under both static and flowing conditions. Although several concentrations of polyelectrolyte were used, at no time was significant sediment removal observed.

In the flowing system slight removal was detected, but this was due to the dispersion of coarser material in the inlet and exit boxes and near the mouth of the channel under the action of prolonged circulation. Re-commencing circulation after static contact had no effect unless the flow rate was increased to the point of redispersion of sedimented material.

Experiment 3

The third test established the mechanism of removal. Sediment, again in the absence of suspended matter, was prepared as for Experiment 1. This sediment was then allowed to come into contact with a flocculating mud suspension passing 'once through' at the same rate as the supernatant liquid was recirculated. The flocculated mud was delivered from the 60 litre aspirator under a constant head. The result was gross removal of sediment in both the channel and the wedge, through the sticking together of sediment and flocculated material being swept through the cell.

This effect was confirmed by preparing sediment, flushing out suspended matter, and adding a small quantity of previously flocculated mud directly to the cell. Recirculation of the flocs at the same flow rate again produced removal of gross sediment. In both cases, flocs were transported by the water flow along the bottom of the cell, at the same time aggregating with the sediment and increasing in size.

The previous treatment of sediment in the cell with flocculant did not prevent the sedimentation of mud added during subsequent experiments. The presence of polymer had no effect on the fine colloidal deposit covering the interior walls.

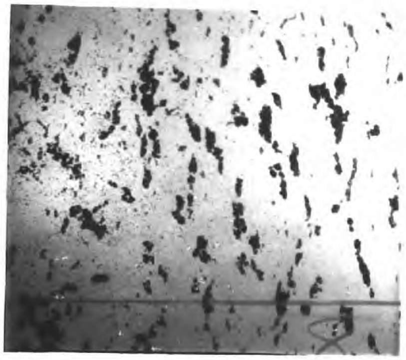
4.2 Quantitative tests

Once tests in the cell had been established as a reliable qualitative method of testing for sediment removal, the problem was considered of establishing quantitative tests for assessing optimum dosages and relative effectiveness of various flocculants. Several examples are shown in Plate 4.2 of the extent and efficiency of removal by various flocculants at dosages determined as the optimum for flocculation of suspensions. It can readily be seen that different flocculants interacted to varying degrees with the sediment, as manifested by the differences in floc size. Obviously a correlation existed between the ability of a material to flocculate a suspension and its ability to remove sediment from the same suspension in the flow cell.

In testing a flocculant to evaluate its efficiency as a clarifier in solid-liquid separation, it was convenient to determine the optimum polymer-to-solids ratio with respect to clarification, as described in Section 2.4. However acceptable this might be for clarification of suspensions, it is not justifiable to extend turbidity measurements to assess the optimum polymer-to-solids ratio for settling rate, filtration, etc. Although for some systems the characteristics of such curves might coincide, it is entirely by chance that they do.(89)

When testing polymeric flocculants for their effects on sedimentation rates, it is also convenient to follow the rate of settling of the solid-liquid interface. As the polymer-to-solids ratio increases and the optimum value of the ratio is approached, there is a corresponding increase in floc growth. As floc size increases, so does the settling rate, up to the optimum, beyond which floc size diminishes.

However, systems have been studied in which floc growth has not reached a maximum as judged by settling rate, but this continuous increase in floc size was not paralleled by a corresponding decrease in turbidity.(90) Turbidity curves follow the same pattern as above and increase beyond the optimum. In fact, turbidity reaches a



A

B

C

Plate 4.2 Removal of mud in wedge with

(A) Zimmite

(B) Floccotan

(C) B.T.I. C110

Flow from right to left

minimum at a comparatively low dosage. Theoretically, adsorption of polymer in excess of the optimum dosage for maximum polymer bridging produces stabilization of the suspension and limits the floc size. The absence of stabilization in some systems is almost certainly a result of inefficient mixing during addition of polymer, particularly at high solids content, when complete adsorption occurs on some particles before all the polymer has been added to the suspension. Added to the stabilization of some particles by disproportionate adsorption is the effect of small particles on floc forming kinetics - smaller particles have smaller inertia, which facilitates more rapid floc forming collisions and greater resistance to floc destruction under mechanical shear.

A similar technique was employed to determine the dosage of flocculant which brought about the most effective mud removal in the flow cell. The degree of removal was judged by the size of flocs formed during the removal process. The change in floc size was determined over a wide range of polymer concentrations, and each determination was carried out under identical conditions of mud-load, flow rate and time of floc formation. During the experiments, flocs were allowed to form under the same hydrodynamic conditions; it was assumed that the limiting floc size was a measure of its resistance to shear and a reliable index of the amount of sediment incorporated into the floc structure during removal.

In the system Zimmite — Thames River mud, floc growth reached a maximum at a dosage corresponding to the optimum polymer-to-solids ratio determined during the flocculation tests described in Section 2. Floc size also decreased when the optimum dose was exceeded. As with flocculation, floc size achieved during mud removal varied considerably with the nature of the organic polymer and the surface properties of the suspended particles. Average floc size was measured in the channel of the cell under constant shearing stress afterformation under standard conditions. Figure 4.1 shows the variation in floc size with dosage for Zimmite and 0.15% Thames River mud in water after ten minutes growth (following a ten minute equilibration period). Superimposed on the same graph is the turbidity curve of the earlier flocculation test. Curves of floc size against dosage were determined with flocculants representative of the major types available and are presented in Figures 4.2, 4.3 and 4.4.

Industrially, the effectiveness of flocculants can be improved and dosages reduced by pre-treating suspensions with inorganic electrolytes - in particular, trivalent iron and aluminium salts are used. The effectiveness of some polymeric flocculants for mud removal was also improved by the addition of trivalent iron or aluminium salts to the cell prior to the addition of flocculant. Figure 4.5 shows the effect of varying dosages of iron and aluminium salts on floc size at the optimum polymer-to-solids ratio for the system Separan AP30 + mud (previously found to be virtually ineffective in the absence of electrolytes). Figure 4.7 shows the effect of varying polymer dosage at the optimum iron concentration (taken from the graph of variation of floc size with concentration of ferric ion at the optimum polymer dose - Figure 4.6 - for Zimmite and mud suspension.

The effect of ferric ion addition (at the optimum concentrations determined from Figs. 4.1 - 4.4) on the optimum floc size of the flocculants representative of each class is shown in Table 4.5. The effectiveness of trivalent ions on coagulants is dependent on the pH of the suspension as the rate of formation and type of species instrumental in bringing about destabilization is dependent on pH(52). The effect of variation of pH on floc size at the optimum concentration of Separan AP30 (in the presence of trivalent iron and aluminium at their predetermined optimum concentrations) is shown in Fig. 4.8

Oppositely charged mixtures of cationic and anionic flocculants added consecutively have also been proposed to improve flocculant efficiency in industrial processes(48). Several tests were carried out on combinations of cationic and anionic flocculants. The results, reported in Table 4.6, showed examples of the formation of larger floc with combined flocculants than with either component separately.

Table 4.5 Effect of prior addition of Fe^{3+} ions (5 ml 50 g/1 $FeCl_3.6H_2O$) on floc size during mud removal. Flocculant dosage optimum for systems in absence of inorganic coagulants.

Flocculant	Max. floc size (cm) (polymer only)	Floc size (cm) after addition of coagulant and polymer
Zimmite	1.60	3.09
B.T.I. C110	6.3	3.39
Separan AP30	0.31	1.51
Floccotan	0.62	0.41
Tragora 55	1.15	1.25
Polyox	ineffective	ineffective
Gelatin	0.23	0.74
Wisprofloc P	1.52	0.75
Polyflok C6	1.58	0.90

Table 4.6 Effect of combining anionic and cationic flocculants on floc size (numbers in brackets indicate order of addition)

Cationic flocculant and floc size (cm)		Anionic flocculant and floc size (cm)		Combination floc sixe (cm)	
Tragora 55	0.46	AP30	0.16	cat-(1) an-(2)	0.68
"	"	"	"	cat-(2) an-(1)	0.69
B.T.I. C110	1.95	"	"	cat-(1) an-(2)	1.77
" "	"	"	"	cat-(2) an-(1)	0.90
Primaflok C6	0.37	"	"	cat-(1) an-(2)	0.90
" "	"	"	"	cat-(2) an-(1)	0.88

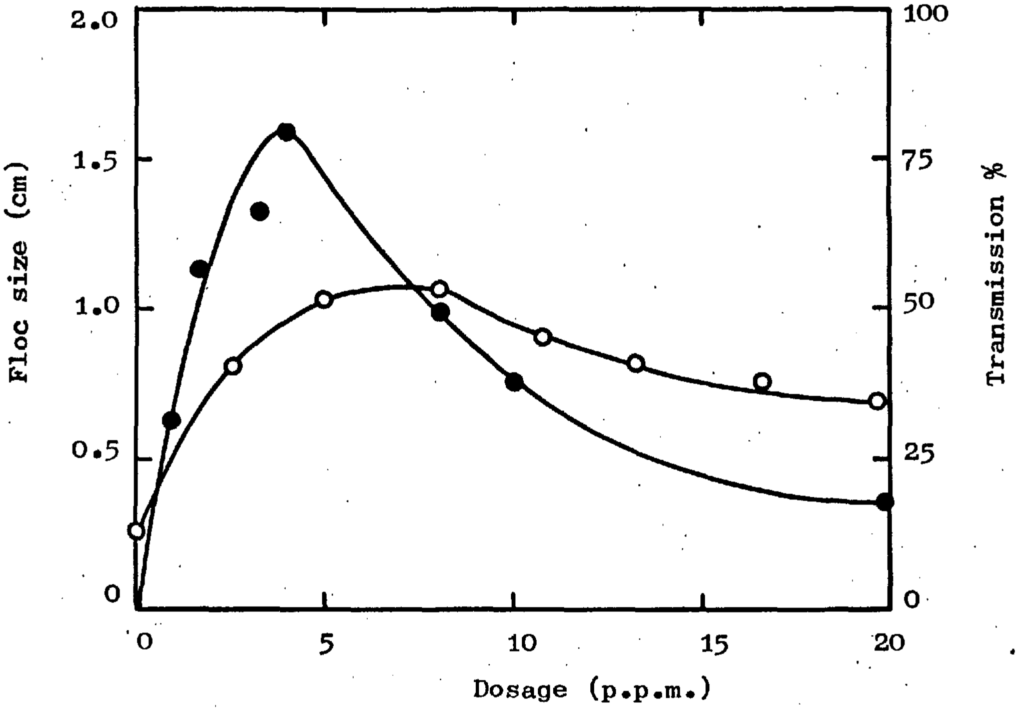


Fig. 4.1 Variation of floc size (●) in flow-cell channel with dosage for system Thames River mud (0.15% w/v) - Zimmite. (o) Transmission curve vs dosage curve for same system.

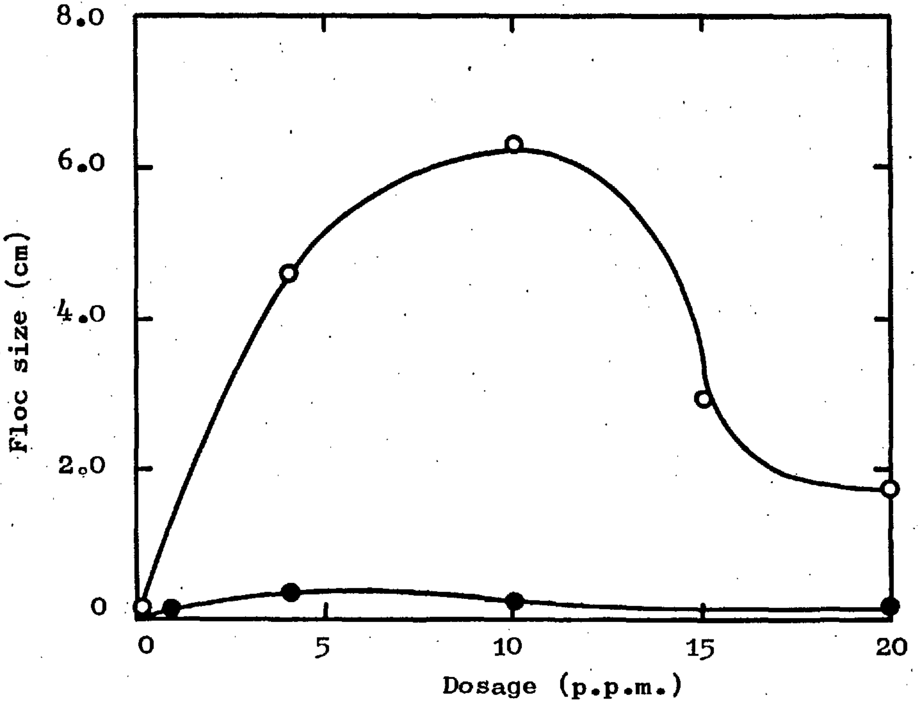


Fig. 4.2 Variation of floc size with dosage for system Thames River mud (0.15% w/v) - o; B.T.I. C110; ●, AP30.

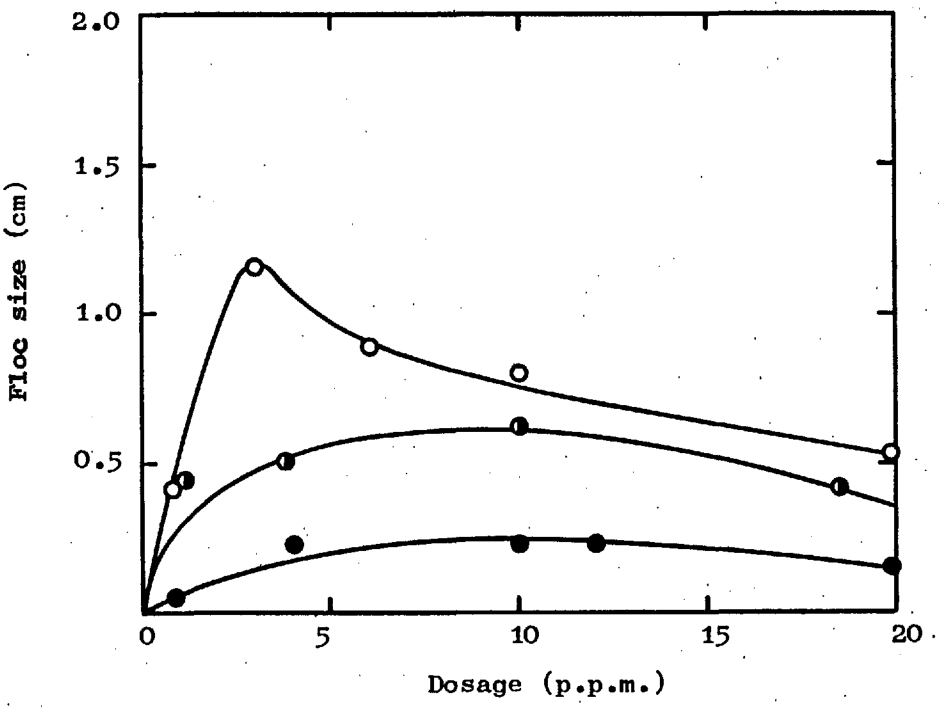


Fig. 4.3 Variation of floc size with dosage for system Thames River mud (0.15% w/v) - o, Tragora 55; ●, Gelatin; ◐, Floccotan (Floccotan dosage x 2)

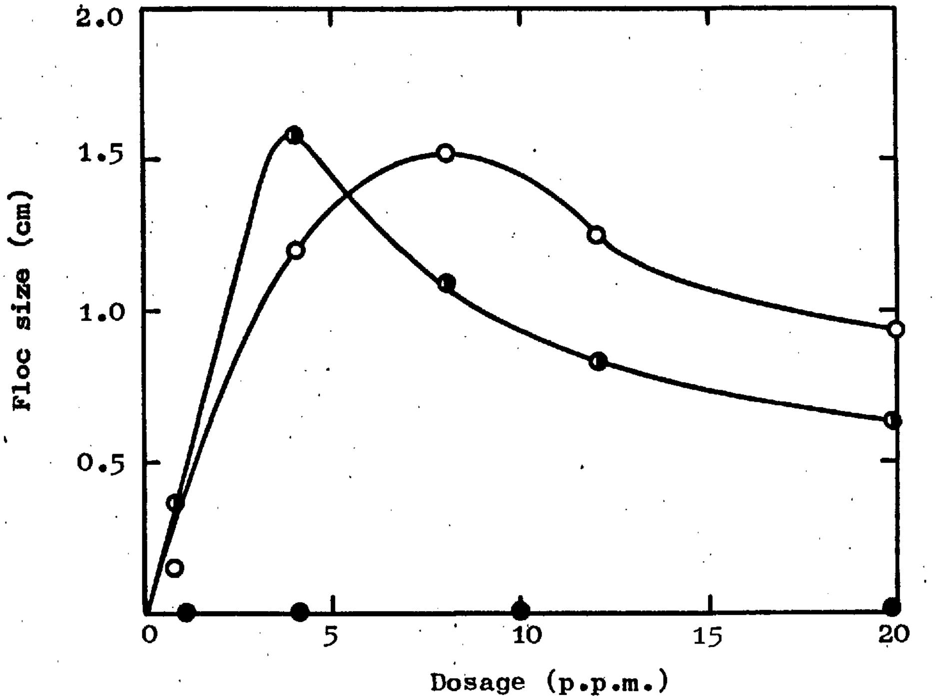


Fig. 4.4 Variation of floc size with dosage for system Thames River mud (0.15% w/v) - O, Wisprofloc P; ◐, Primafloc C6; ●, Polyox. (Primafloc dosage x 5)

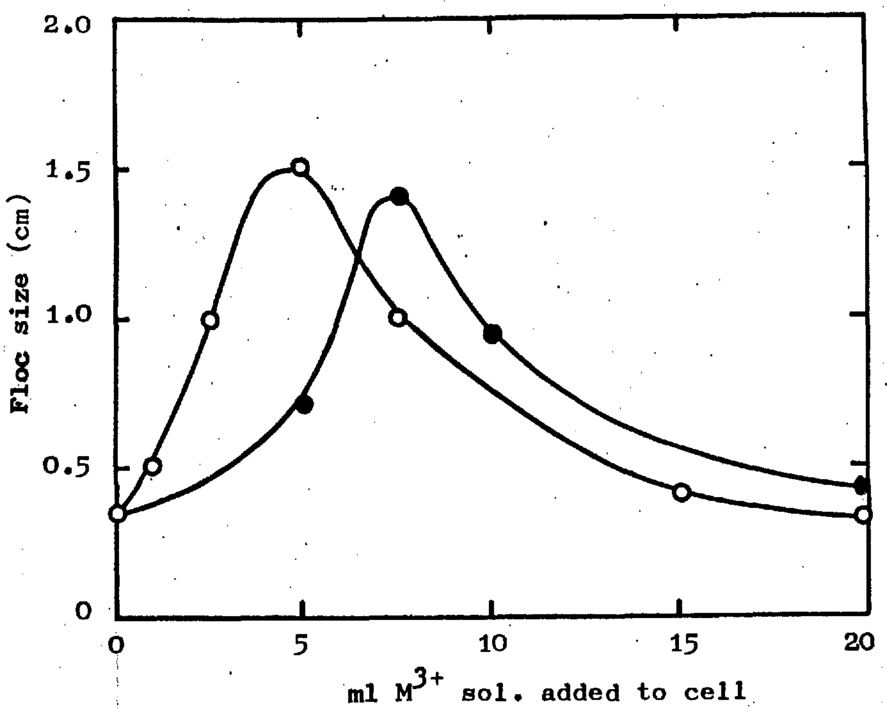


Fig. 4.5 Variation of floc size with concentration of M^{3+}: o, $FeCl_3$ 6 H_2O (50 g/l); ●, $Al_2(SO_4)_3$ (50 g/l) Flocculant AP30 at optimum dosage - 4 p.p.m.

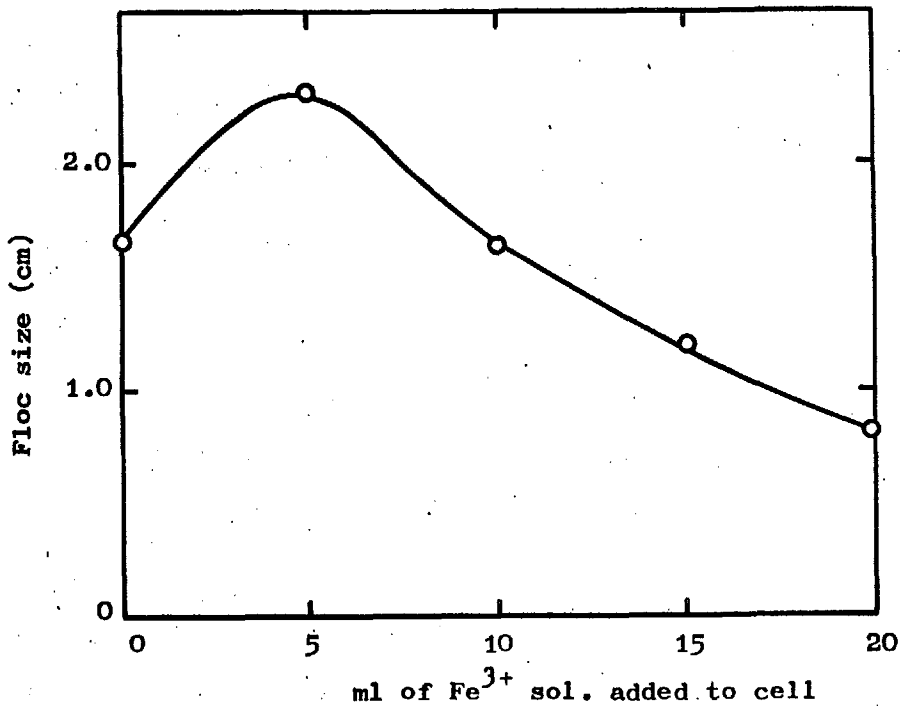


Fig. 4.6 Variation in floc size with concentration of Fe^{3+} (50 g/l $FeCl_3$ 6 H_2O) at optimum Zimmite dosage - 4 p.p.m.

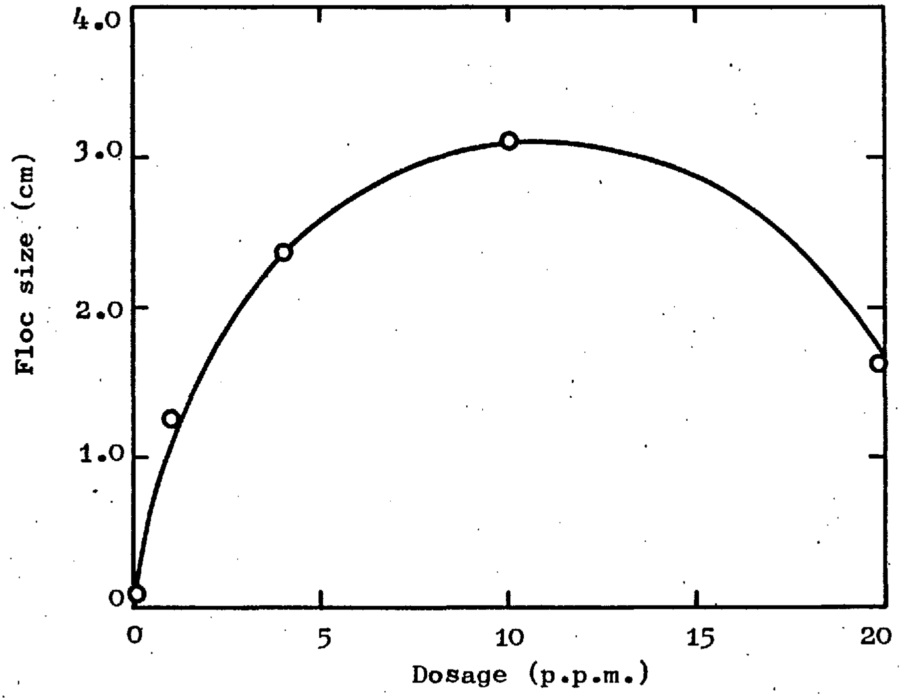


Fig. 4.7 Variation of floc size with dosage of Zimmite in presence of Fe^{3+} at optimum dosage (5 ml of 50 g/litre $FeCl_3$ 6 H_2O)

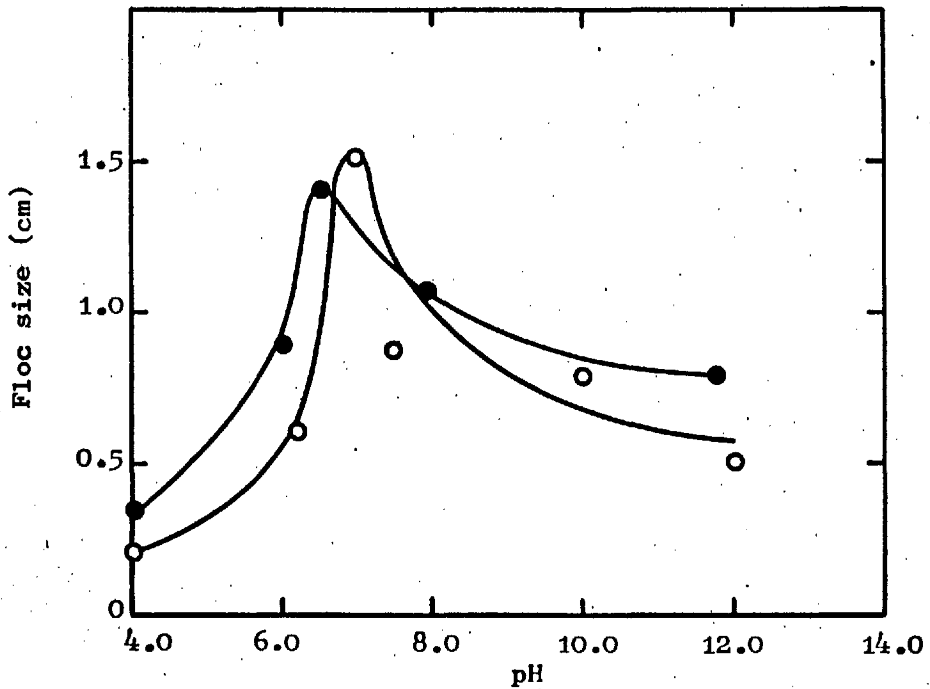


Fig. 4.8 Variation of floc size with pH. System Thames River mud (0.15 % w/v) - AP30 - M^{3+}. Flocculant and coagulant at optimum dosages: ●, Fe^{3+}; o, Al^{3+}

5. DISCUSSION

5.1 Mechanism of sediment removal

Although there are some reports in the literature on the action of organic polymers as removers of accumulations of mud and silt in industrial cooling systems,(71,91) no satisfactory explanation of the mechanism has been offered. Whilst there is a tenuous explanation of the effect of polymeric flocculants preventing suspended material from sedimenting in a cooling system, there is no explanation for the removal of existing sediment or deposits.(71) The explanation offered is that flocculation substantially reduces the adhesive forces between particles and substrate (tube walls), by reducing the points of contact, and prevents adhesion of material. This implies that polymer diffuses into a sediment or deposit and lowers its 'adhesion' to a surface - although in static systems some agitation is required for it to be effective.

In practice, under conditions of laminar flow for the system Thames River mud - tap water, material does not deposit in the region of the flow cell where the shearing stress is greater than 20×10^{-3} g/cm^2. However, once the particles are deposited, the shearing stress required to re-suspend the sediment in the absence of flocculants is greater than the critical rate above which sedimentation does not occur. In fact, a particle incorporated into a sediment requires more energy to free itself than is required to keep it suspended; the van der Waals attraction forces as well as frictional forces must be overcome before removal is possible.

Most of the polymeric flocculants investigated in the flow cell exhibited the property of sediment removal, both for Thames mud and other minerals (Tables 4.1 and 4.4). In every case involving removal the mechanism followed the same sequence, as follows:

1. Flocculant added to the cell is rapidly adsorbed by the mud particles (the kinetics of polymer adsorption are such that almost all the total amount adsorbed is adsorbed within seconds of addition(92)). Small aggregates of mud particles form and settle out of the hydro-

dynamic flow on the sediment. At the same time they are undergoing orthokinetic flocculation (floc growth) by collision with other freshly formed flocs and individual particles; the size of the flocs depends on the flocculant and the nature of the suspension. The 'sedimentation of flocs' conflicts with the view expressed in the patent that 'contrary to normal practice, the mud remains suspended as loose fluffy flocs' - a hypothesis incompatible with present-day theories of solid-liquid separation with organic polymers.

2. The next stage is the further growth of flocs by incorporation of sediment (which has already adsorbed polymer) and movement of flocs across the surface of the cell in the direction of flow. The macroscopic effect is similar to 'snow-balling'; but, rather than discrete spherical flocs, the flocs are extended along an axis normal to the flow and the effect is that of peeling or 'carpet-rolling' (Plate 4.1). If the sediment is present as a thin layer, most of it is incorporated into the floc structure; if it is a thick sediment, only the top layer is incorporated into the growing flocs.

When flocculated mud settles in a pipe, it does not remain stationary (even though the adhesion to the underlying sediment substrate may be increased by polymer bridging, as is found during floc growth) but rolls downstream. There are two contributing factors to this phenomenon:

1. A particle (in this case a floc) at the fluid-solid interface in a pipe through which fluid is flowing is subject to a velocity gradient which gives rise to a variation in pressure across the surface of the particle. The effect is equivalent to the variation in pressure resulting from the rotation of a particle in a fluid stream (the 'Magnus effect'). The imbalance of pressure forces gives rise to a net force on the particle directed towards the axis of the pipe, called the 'lift force'. Because of eddies, the lift force, T_L, on the particle is asymmetric and higher on the upstream side. The lift force is displaced in front of the centre of gravity

and together with the drag force tends to make the particle roll downstream ("carpet rolling" of flocs). The drag force is the force acting on the particle in the direction of flow and is greater nearer the wall of the tube because of the parabolic velocity profile(93). During movement downstream the rolling flow leads to contact with more sediment and collisions from other sedimenting flocs. Thus the growing flocs roll across the sediment and are eventually swept out of the cell.

2. The second factor is the change in rheological properties from sediment to flocculated material. Normally, sedimentation of non-spherical clay minerals or electrolytic coagulation produces sediments which are subject to a more efficient packing (indicated by their smaller floc volumes) than sedimented flocs. The closer packing of sediment results in a material which has a high degree of internal friction giving rise to dilatancy under applied stress (the shearing stress of water flow). Although the extent of dilatancy is not very pronounced, it is sufficient to prevent movement of sediment subject to a lift force. Flocculated material, however,has a larger floc volume because of the random arrangement of particles (van der Waals forces become insignificant) and consequently a reduced internal friction. This imparts a thixotropic character to the flocs, which tend to flow rather than roll as a rigid sphere under the influence of drag and lift forces. Recently it has been shown that low concentrations of long chain molecules can greatly reduce turbulent friction on bodies moving through the fluid or on surfaces past which if flows.(94)

In a recirculating system floc growth and movement do not proceed indefinitely; after a time the flocs reach a limiting size governed by the nature of the polymer, the surface properties of the suspension and the velocity of suspension in the cell. Floc movement is also affected by the spontaneous dewatering of flocs. Initially, floc density is low - freshly formed flocs have a very open structure - and the lift and drag forces are sufficient to move the rolling floc further downstream. However, the flocs undergo compression (density increases) and reach a point at which gravitational force overcomes the combined drag and lift forces (which diminish as the flocs dewater) and floc rolling ceases. In a closed system, all the suspended matter (excluding that which is produced by floc degradation or which does not take part in the flocculation mechanism) is incorporated into rolling flocs and floc growth is limited by the absence of freshly forming or recombining flocs. Flocs which reach the wedge before collapse of the open structure prevents further movement are accelerated through the wedge under the influence of the graded shearing stress and are swept out of the cell before they are destroyed by the action of the centrifugal pump. Dispersed flocs can reform in the inlet box and proceed down the wedge, but degraded flocs are not so effective in the removal mechanism, and quickly come to rest in the channel part of the cell. In a once-through system, flocs are swept out of the system and do not re-enter, whilst existing flocs grow continuously under the influence of fresh flocs constantly forming upstream.

Important evidence for the mechanism proposed above is the lack of removal of sediment in the absence of suspended matter. If no floc-sediment collisions are possible, then removal cannot take place, irrespective of the concentration of polymer or the hydrodynamic conditions. The addition of fresh flocs to a system creates the necessary conditions for mud removal (Section 4.1 Expts. 2 and 3) - floc sediment collisions are still effective and floc growth proceeds even though the sediment has not previously adsorbed polymer. The same mechanism applies to the removal of wall deposits, mentioned in Table 2,1 Floc — deposit collisions are responsible for any removal - removal again being prevented in the absence of suspended matter. The prolonged recirculation tests in the flow-cell also excludes the possibility of diffusion of polymer (and reduced adhesion) into the sediment.

To remove mud from filters and coolers, the technique is to fill up the equipment with 'Zimmite' solution and allow it to stand overnight (with agitation). Without doubt, the agitation resuspends sediment which flocculates and is responsible for floc-sediment collisions. In addition, turbulence created during filling and emptying facilitates floc formation. The thixotropic nature of the settled flocs permits easy removal during emptying of the equipment.

5.2 Comparison of removal efficiencies and determination of optimum polymer dosage

Figures 4.1 - 4.4 show the variation of floc size with dosage for a number of polymer-mud systems. The range of floc sizes at optimum dosage extends from 0.23 to 6.3 cm under the particular conditions employed. Earlier flocculation tests with the same materials showed a wide variation in their interaction with mud suspensions (Table 2.5).

Flocculants which produce large flocs with Thames River mud suspensions (e.g. B.T.I. C110) and are estimated to have a high degree of cohesion produce large flocs in the flow-cell; conversely; flocculants which produce small flocs (e.g. Separan AP30) and have little cohesion are almost ineffective in the cell and produce very small flocs. The same correlation applies to the other materials tested both as flocculants and mud removers. This evidence suggests that the factors which govern flocculation efficiencies (e.g. structure, molecular weight, chemical type, etc.) are also responsible for the effectiveness of flocculants as mud removers.

In accordance with the above, the optimum polymer dosage for removal is taken as that which produces the largest floc size. The conditions in the flow cell are defined hydrodynamically and floc growth takes place under favourable conditions of low shearing stress, laminar flow, and on a horizontal surface. In industrial systems, conditions in pipes under turbulent conditions are very different and so the optimum dosage may also be different.

It has been suggested earlier (Section 4.2) thatturbidity measurements are valid only in determining the degree of clarification by polymeric flocculants and do not necessarily correlate with the characteristics of settling rates and filterability of flocculated suspensions. In practice, certain polymer-solid systems show optima for turbidity, filtration rates and settling times which correspond well, and some systems do not. This evidence emphasises the importance of hydrodynamic conditions during the addition of flocculant to a suspension; conditions should be such as to eliminate non-uniform adsorption as far as possible.

A comparison of floc growth variation with dosage during removal and turbidity variation with dosage during flocculation (Fig. 4.1) for the system Thames River mud - Zimmite, shows that the optima for clarification and removal coincide. This applies roughly also to some of the other flocculants tested as mud removers (turbidity curves of which are not reproduced), although coincidence is not always exact. It is probable that flocculant added to the flow cell diffuses slowly (as demonstrated by the flow pattern of dyes) and is comparable to incremental addition of flocculant to a suspension. In flocculation tests this gives the maximum rate of settling of flocs, indicative of larger flocs and more effective bridging(95).

In the light of this evidence, it may be feasible to determine the optimum removal dosage for industrial purposes from turbidity measurements. But it would not always be reliable to extend this to comparative tests between flocculants, in view of the excellent clarification achieved with 'quasi-flocculants' such as polyethyleneimine.

5.3 Factors governing removal of sediment

In solid-liquid separation by flocculants, the intrinsic nature of the suspension and the flocculant governs the performance of the operation. Industrially, factors such as filtration rate and clarification, etc., influence the choice of flocculant. However, when a flocculant is to be used for mud removal, floc size is the parameter which reveals the effectiveness for mud removal, and when determined under standard conditions it provides a method of comparing flocculants and determining optimum dosages.

The factors which govern floc growth can be classified into hydrodynamic and chemical.

Hydrodynamically, floc growth is determined by the shearing forces imposed by flow. Certain flocs are more resistant to shearing forces than others, and consequently, during floc growth, by incorporation of sediment, a limiting size is reached beyond which the cohesive forces of the flocs are insufficient to hold them together. In addition, the spontaneous dewatering of flocs affects floc size (collapse of flocs is accompanied by a reduction in lift and drag forces). At higher flow rates, lift and drag forces are less easily offset by collapse of floc but the flocs are subject to greater shearing forces. Increase in the flow rate in the cell causes movement of flocs already at rest, but is often accompanied by rupture of flocs. It is possible, however, that once sediment is incorporated, partial destruction of flocs does not deteriorate sediment removal, particularly in a 'once through' system.

Irrespective of the limits imposed on floc growth by shearing forces and collapse of floc structure, the direct interaction between suspension and polymer is the major factor governing floc growth and, hence, removal. Table2.5lists all the materials investigated as flocculants for Thames River mud, and shows the floc size and estimates of cohesion of floc size formed under standard conditions. Materials representative of each class were investigated as mud removers and will be discussed individually with respect to their colloidal behaviour with mud. It is important to point out that the organic component in the mud had little effect on polymer-mud interactions. In fact, it is likely that the organic material - which is protein like in character - excludes some adsorption sites, but adsorbs some flocculants itself; it is known, for example, that an emulsion stabilized with casein can be flocculated with a cationic polyacrylamide(96).

As a class, the polyacrylamides, particularly the cationic polyacrylamides, are clearly the most effective removers of mud at present known. The materials used are linear polymers and have molecular weights around 6×10^6, and even in the absence of ionogenic groups (e.g. COO^-) have an end to end distance in excess of other flocculant molecules (Appendix II contains calculations of the average length of a non-ionic polyacrylamide molecule of molecular weight 6×10^6). The introduction of ionogenic groups such as a quaternary ammonium ion gives the molecule a cationic function and extends the molecule appreciably in solution. Both the opposite charge (intensifying adsorption) and increased length of the molecule make it even better for polymer bridging of mud (itself negative). However, anionic polyacrylamide has a reduced effectiveness, despite its extension in solution; the degree of flocculation of mud suspensions is small and mud removal almost zero. The negative character of the carboxyl group reduces the adsorption of the molecule onto negatively charged surfaces, though this is not completely prevented. Both the non-ionic and the cationic polyacrylamides form large cohesive flocs which resist destruction under the shearing forces in the cell. Presumably the length of the polymer molecules imparts a high degree of flexibility to the floc structure.

Cationic polyethyleneimines flocculate mud suspensions and leave very little residual turbidity. Their low molecular weight and positive charge makes them good coagulants rather than flocculants; floc size is small and the estimated degree of cohesion low. They bring about mud removal in the flow cell, but the floc size is smaller than that attained with non-ionic polyacrylamide.

Glues were found to be effective as flocculants, but clarification was poor, the size of the flocs small, and the estimated cohesion low. Gelatin produced very little mud removal in the flow cell - probably because it is a relatively low molecular weight polymer of low solution viscosity which is not adsorbed onto clay mineral surfaces as strongly as other flocculants.

Two modified natural products, Tragora 55 (a cationic starch) and Floccotan (modified tannin) were found to produce good clarification of mud suspensions. Both were tried in the flow cell. Tragora 55 gave a floc size almost equivalent to that produced with the polyethyleneimines, but Floccotan gave very small flocs and appeared to be more like a coagulant than a flocculant.

A number of other starch products were tested as flocculants, but were found to be ineffective, apart from Wisprofloc P (a modified starch; cationic in nature). This material removes mud and produces a floc size comparable to Tragora 55.

"Polyox" (presumably high molecular weight polyethyleneoxide) was ineffective as a flocculant and had no detectable effect on mud sediment in the flow cell. Although it is supposed to be linear and of high molecular weight (about 10^7), it showed no signs of flocculation of mud particles. It is not possible to determine if adsorption has taken place but it must be assumed that in this particular system, its ability to form hydrogen bonds is poor. Detergents of similar chemical structure, i.e. $ROCH_2(OCH_2)n^-$ are universally adsorbed presumably by physical adsorption of the non-polar part of the chain onto non-polar areas of the substrate.(97)

5.4 The effects of added electrolyte

Figure 4.5 shows that the addition of tri-valent iron or aluminium salts to the flow cell prior to the addition of Separan AP30 (anionic polyacrylamide) had a marked effect on the interaction between mud and polymer. This test was also carried out for the other materials and the influence on floc size is shown in Table 4.5. The optimum concentration of Fe^{3+} and Al^{3+} was well below the amount required for complete coagulation of mud suspensions. The mechanism of 'sensitization' is dependent on two factors: firstly, adsorption of a hydrolysis product, such as $Al_8(OH)_{20}{}^{4+}$ results in charge reduction on the surface of the suspended particles and provides positive adsorption sites which are available to anionic polyacrylamide. Secondly, it partly coagulates the mud itself, either through polynuclear complex formation, or bridging by colloidal metal hydroxide (the mechanism is controversial), in addition to electrolytic coagulation by unhydrolysed metal salt. Above the optimum concentrations of Fe^{3+} and Al^{3+}, the floc size decreased and the form of the floc changed from floc-rolls, normal to the axis of flow, to discrete amorphous flocs. It is likely that coagulation by trivalent salts produces weak particle-particle bonds which have little resistance to the shearing force of the flow or the pump; unlike unaided floc formation, floc destruction is not then reversible. Anionic and non-ionic flocculants at the optimum M^{3+} concentration produce larger flocs, because the discrete particles which adsorb the polymers are larger than those found in untreated suspensions. And increased affinity for anionic polymers occurs by virtue of more favourable electrostatic effects. A larger particle size may, however, result in easier floc destruction at high shear rates. There is a reduction in floc size when cationic polymers and ferric ions are used together - similar charges on both adsorbent and adsorbate reduce the adsorbability of the polymers.

In all the tests, the pH of the suspension was around 7.0. The coagulation of sols by polyvalent hydrolysing ions is dependent on pH(52). Not only is the rate of hydrolysis governed by pH, but also the species formed (Figure 1.1). In an attempt to establish the optimum pH for the sensitization of Thames River mud by trivalent metal ions, floc size was measured at different pH values (Figure 4.8). The curve shows a maximum floc size for Al^{3+} and Fe^{3+} at pH 7. Above pH 7, the floc structure changes to discrete spheres characteristic of coagulation by M^{3+}. Below pH 7 floc structure does not appear to change drastically, but the size is smaller, and at lower pH values, hydrolysis ceases altogether. However, the change in pH may alter the surface properties of the clay mineral adversely, making it less negative at low pH, and more negative at higher pH. In addition, the viscosity (related to the dimensions) of the anionic material changes appreciably over the pH range investigated and, in consequence, the degree of effectiveness of the flocculation process changes also. Figure 5.1 shows both the change in viscosity and the effectiveness of flocculation with pH for the system Separan AP30 and fluorite.(98) The maximum viscosity and effectiveness is reached at pH 9, but for a clay system the adsorbability of AP30 may well be reduced as a result of an increased ζ potential. Also, electrolytes influence the configuration of the AP30 molecule and reduce its solution viscosity and therefore its effectiveness - unhydrolysed Fe^{3+} may contribute to this.

5.5 Combinations of organic polymers

Oppositely charged polymeric flocculants have sometimes been used industrially in combination to enhance solid-liquid separation. Table 4.6 shows the floc size produced by two materials added consecutively, compared with the floc size when used alone. In each test the anionic material was Separan AP30 (a good flocculant for positively charged suspensions). Three different cationic polymers were used in combination with this anionic polyacrylamide: cationic polyacrylamide, cationic galactomannan, and a polyetheneimine.

Added first, the cationic polymers readily adsorb on the negatively charged mineral suspension and bring about flocculation. The addition of the anionic material through electrostatic attraction (and possibly hydrogen-bonding) increases the degree of flocculation - it has the advantages of high molecular weight and high molecular extension. If Tragora 55 and Primafloc (both of relatively low molecular weight) are used, the order of addition makes little difference to floc size, although the flocs are greater in size than when the two materials are used individually. It is probable that the advantage of the molecular extension of the AP30 manifests itself irrespective of the order of addition. However, in the case of

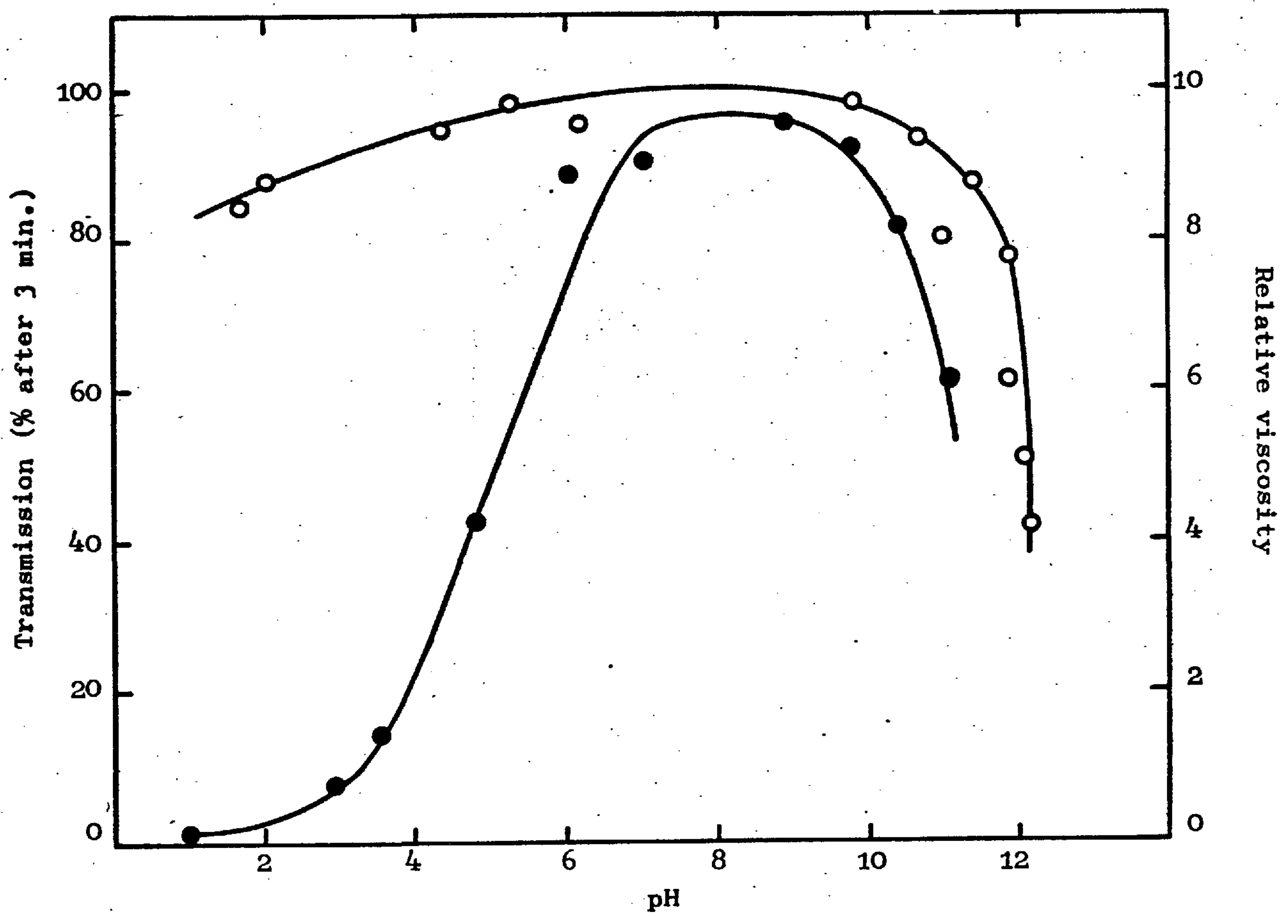


Fig. 5.1 The effect of pH on the (o) flocculation of fluorite; and (●) the relative viscosity of the flocculant (0.01% solution of AP30)

cationic polyacrylamide, the order of addition does affect floc size. If the cationic material is added first, it readily adsorbs on the particle surface, and presents sites available for adsorption of anionic polymer which may well reduce the molecular extension of the cationic material and hence its effectiveness. If the anionic material is added first, adsorption of anionic material is slight and much of the molecule remains unadsorbed. The remainder is free to react with cationic material and so the effectiveness of both the cationic and anionic material is further reduced; solutions of cationic and anionic polyacrylamide form a precipitate on mixing - no doubt due to mutual neutralization of ionic groups.

The method of addition of polymer, the time between consecutive doses, and the order of addition, are variables which might affect the performance of the system and justify further investigation, in an attempt to optimise the process.

5.6 Other systems

During the course of investigations into mud removal in the flow-cell, a number of other systems were tested qualitatively. Table 4.4 gives the result of the test in which sediments from suspensions of 'model' colloids were cleared in the channel of the flow-cell - the mechanism being the same. The materials used covered a wide range of particle size, although for each individual material particle size distribution was within fairly narrow limits. Observations showed that a reduced polydispersity reduced the degree of sediment incorporation into floc growth - even though the flocculation of the suspension by polymer was good. This evidence indicates that appreciable amounts of material must be present in the supernatant liquid for effective removal.

Apart from the materials tested as mud removers and recorded in Table 4.1, others were also examined to justify the selection of representative materials for the quantitative assessment of mud removal. No ambiguities arose among the materials of known chemical type which were tested.

Inorganic coagulants tested by themselves (Table 4.2) showed no macroscopic removal properties, although they did coagulate the suspension. Activated silica, recommended by some workers as a coagulant particularly useful for clays, had no influence on the stability of Thames River mud suspensions, nor did it 'activate' polymeric flocculants.

6. SUMMARY OF CONCLUSIONS

1. Observations on Thames Rives mud suspensions flowing under controlled hydrodynamic conditions in a specially designed flow-cell showed that particles sedimented on a horizontal surface subject to a shearing stress of less than 10-20 x 10^{-3} g/cm^2. It is probable that macroscopic colloidal deposits which form at other surfaces do so only below a critical shearing stress, although the magnitude has not been determined. The distribution between suspended and sedimented phases depends on the size distribution of the suspension, the degree of destabilization and the hydrodynamic conditions.

2. The mechanism of mud removal by organic polymers has been established and found to correlate with flocculation of mud suspensions in all respects; in particular the dependence of removal on the mutual adhesiveness of flocs and the flexibility imparted to floc structures by the high molecular weight organic polymers. Factors which determine the characteristics of floc formation (e.g. molecular weight, configuration, etc.) also govern mud removal. The only basic difference between flocculation (for which theory and practice are well established) and mud removal is in the initial rheological states of the two systems. In flocculation of suspensions, all the particles are suspended before flocculation, whereas in mud removal, particles are not only suspended but also sedimented - a state which does not exclude sediment from taking part in a flocculation mechanism with suspended particles.

Removal of sediment cannot take place (a) in the absence of suspended matter - which excludes the crucial step in the flocculation of suspended particles —sediment; (b) in the absence of some agitation - which produces floc-forming collisions between particles and particle and sediment.

Investigations of many other mud-flocculant interactions showed that various other flocculants could be used instead of the proprietary material 'Zimmite' - some more, some less effective. A technique for determining optimum dosage for maximum sediment removal has been devised.

4. A cursory examination on the influence of readily available coagulants on the performance of flocculants as mud removers had been made. It shows that, in some cases, removal is improved, whereas in other performance deteriorates.

5. Investigations into the performance of combinations of flocculants as mud removers showed that floc size (the index of effectiveness) was influenced favourably or adversely, depending on the choice of flocculants and order of addition. The reasons for these effects have been suggested.

PART II

ELECTROCHEMICAL PROPERTIES OF POLYMERIC FLOCCULANTS

7. INTRODUCTION

In the foreword to this thesis, it was explained that the investigation had diverged into two different aspects of surface phenomena involving polyelectrolytes. In Part I the mechanism of the colloidal interaction of organic polymer flocculants with Thames River mud was covered. The second part is devoted to the influence of polymeric flocculants on the electro-chemical behaviour of a cupro-nickel alloy.

In brief, certain polymeric flocculants have been found to inhibit corrosion of copper and nickel alloys in neutral saline waters. However, corrosion has been the subject of much practical and theoretical investigation and there is a great deal of literature on the topic. Related to corrosion studies are the investigations into corrosion protection, the literature of which reaches equal proportions. Therefore, in the present thesis, it has been necessary to confine the background detail on this phenomenon to specific circumstances and deal only with aspects closely relevant to the problem of corrosion of condenser tubes in neutral aqueous environments, and to inhibition of this particular corrosion mechanism by what has been widely referred to previously as 'adsorption inhibition'(99).

7.1 Factors determining corrosion in condenser systems

Cooling waters passing through industrial condenser systems vary considerably in composition, from very pure distilled waters to saline waters equivalent to full-strength sea water. In general, if fresh water is used, no serious corrosion problems are likely to arise, and such waters need the use of only 70/30 brass, Admiralty brass (70/29/1) or copper for condenser tubes. If the water is brackish, the alloys used are usually aluminium brass (76/22/2) or cupro-nickels of either 10% or

30% nickel. If the water contains a high proportion of dissolved solids (> 2,000 p.p.m.), aluminium brass or a cupro-nickel alloy is used to reduce the risk of impingement attack, frequently found with copper or ordinary brasses; copper and 70/30 brass only have moderate resistance to rapidly moving sea water. Cupro-nickel alloys also have relatively poor resistance to impingement attack unless they contain a small proportion of iron and manganese - usually 1.0% of each. The presence of iron contributes to the development of a protective film(100), and examination of the protective films on brasses used in the presence of iron-containing components in the system reveals a surface film rich in iron which gives better service than brass in the absence of iron. In recent years, ferrous sulphate has sometimes been added to cooling water to achieve the same effect(101), although the mechanism is not understood.(102)

Water boxes of condenser systems are usually made of cast-iron, and, if unprotected, provide a measure of 'sacrificial' cathodic protection for the tubes. This is undesirable, of course, as the life of the water boxes is also important. However, the problem is overcome by cathodic protection using sacrificial anodes which provide protection for water boxes, tube plates and tube ends - although the protection does not extend more than a few inches down the tubes.(103)

Perhaps the most important factor in condenser tube corrosion is the state of the water itself. Water from many sources, such as the tidal reaches of the River Thames (e.g. West Thurrock) is often highly polluted by industrial and domestic sewage effluent. The oxidation of organic matter reduces the dissolved oxygen level substantially and sometimes there is no detectable oxygen in the water at all; these are conditions under which sulphate-reducing bacteria thrive and produce highly corrosive H_2S(104). Under these conditions protective oxide films cannot survive or be maintained. There is a great deal of inconsistency in the results of corrosion studies in polluted water, but one significant fact that emerges is the dependence of the behaviour of condenser tubes on their previous history. Tubes which have been exposed initially to clean water, and have had the opportunity to form continuous protective films, have better corrosion resistance in service, even though it may be in highly polluted waters. Also, allowing tubes to remain in contact with stagnant waters increases the incidence of corrosion.

Waters containing suspended matter are particularly corrosive, especially if the particles are abrasive or if they are allowed to remain in contact with the tubes. Abrasive action can result in appreciable thinning of the tubes in service, and no doubt can promote failure through pitting attack. Another factor which may result in enhanced corrosion of tubes is cleaning, which may be either mechanical or chemical. Chemically, 5-10% hydrochloric acid (containing an inhibitor for Fe attack) is used to dissolve corrosion products from the tubes, which are then rinsed, washed with alkali and rinsed again. This can lead to the entrenchment of cuprous chloride in the pits and activation of corrosion sites. Mechanical cleaning, although no risk of directly enhancing corrosion rates arises, involves forcing 'bullets' (bristle or nylon brushes) down the tube or employing the Taprogge system - considered by some experts to be the most effective way of dealing with condenser tube corrosion, though no mention is made of the effect on 'thinning' of condenser tubes.

Fundamentally, the resistance to corrosion is greatly dependent on the properties of the oxide layer on the tube surface, irrespective of the environmental conditions.(166)

7.2 Corrosion of cupro-nickel condenser tubes in polluted estuarine waters

The river water used for cooling purposes at West Thurrock is estuarine and has a salinity of up to two thirds that of sea water and a suspended solids content of up to 500 p.p.m. In addition, the dissolved oxygen content is low (10% of saturation level). In order to combat the aggressive nature of the water, 70/30 cupro-nickel alloy, containing 1% each of iron and manganese, was selected to give a maximum service life.

When the generating sets were first brought into service at West Thurrock, the problem of corrosion of the cupro-nickel tubes arose and caused concern, particularly after river water had been allowed to remain stagnant in the condenser for relatively long periods of time. About this time the material 'Zimmite' came to the attention of the C.E.G.B. and was subjected to both plant and laboratory trials The results of both series of tests showed that very small quantities (1-2 p.p.m.) of Zimmite were effective in removing mud; elimination of the cause of corrosion, i.e. mud sediment in contact with the tubes, was attributed to this. The reports of the work carried out at the time suggested that mud containing appreciable quantities of sulphur was responsible for sulphide attack on the surface of the condenser tubes. However, the reports did not include analysis of the corrosion products, but they are reproduced in Table 7.1.

Table 7.1 <u>Typical analysis of corrosion products taken from condenser tubes at West Thurrock prior to treatment with Zimmite</u>

Component	Analysis % w/w
Copper (CuO)	27.14
Nickel (NiO)	5.62
Iron (Fe_2O_3)	23.07
Calcium (CaO)	5.28
Sulphate (SO_4)	1.71
Sulphide (S)	0.20
Silica (SiO_2)	11.31
Organic component	25.33

The analysis shows that very little sulphide is detectable in the corrosion products and calculation shows that if sulphides are formed of copper and nickel, a reasonable level would be in the order of 13% w/w. Nor does the colour of the corrosion products (green-blue to brown) indicate the presence of copper and nickel sulphides which are both black. 'Green staining' is found on copper in waters containing carbon dioxide and is a basic copper carbonate.(106)

This information is not compatible with the theory that sulphur or sulphur-bearing compounds are responsible for corrosion(105). Examination of condenser tubes shows that corrosion is found predominantly on the lower half of the surface of the tubes and, in fact, some tubes showed a well defined horizontal demarcation line along the tube length, above which there was considerably less corrosion.

The earlier investigations also revealed that aerating the system drastically reduced the appearance of corrosion, as did exclusion of suspended matter from the polluted waters (although the O_2 level remained low).

Two equally important factors are, firstly, the intermittent operation of the condenser system (i.e. water was only circulated twelve hours a day; the rest of the time water remained static in the tubes); secondly, polymer treatment was restricted to 10 minutes per day (initially one hour) during normal cooling water flow, although the mud was in contact under both dynamic and static conditions for the rest of the time. Nevertheless the corrosion of the tubes was reduced drastically, even when the Taprogge system was not in use.(105)

Unfortunately, no meaningful conclusions can be drawn from the situation at West Thurrock on the long-term effectiveness of Zimmite addition to cooling water, as the Taprogge system has been in continuous operation for some years now. The Taprogge system very effectively removes corrosion products and mud deposits from condenser units and therefore obscures any observation that might be made on the effects of Zimmite on corrosion. The above information leads to the conclusion that the principal source of corrosion attack under these conditions is the 'differential aeration corrosion'. During shutdown, suspended particles (clay minerals and silica containing 4-10% organic matter) settle in the lower half of the condenser tubes. The oxygen level is low, but not zero and the thin layer of mud is sufficient to exclude oxygen availability at the lower surface; oxygen is consumed continuously by the organic matter in the mud. However, the upper surface of the tube has a greater availability of oxygen than the lower surface and in the presence of even small quantities of electrolyte (i.e. NaCl) offers ideal conditions for a galvanic action between the two electrochemically different surface environments. The area with excess oxygen is the cathode, where reduction of oxygen readily takes place and the area deplete in oxygen is the anode, which corrodes by one of the two processes of metal dissolution as M^{z+} or the formation of insoluble compounds. The well defined demarcation sometimes observed between the two areas is good evidence for this mechanism. Replacing the river cooling water with town-main water also reduces corrosion, as do aeration of the water or filtering out suspended matter. In some tubes, particularly if the condenser is not completely full of water (sometimes the case if outlet valves are not throttled back) water can remain static even during flow of cooling water. In addition, poor hydrodynamic design can give regions of very low flow rate. Both conditions can allow differential aeration cells to continue, irrespective of the conditions elsewhere in the condenser system.

Plant trials at West Thurrock showed that corrosion could be eliminated, although the reason was assumed to be the periodic removal of quantities of mud, and elimination of mud sedimentation. At the time, the inhibition of the corrosion process by the polymer was not considered and no reports of corrosion inhibition as such by the material were found in the literature.

During the course of the investigation into mud polymer interactions, particularly during experiments with the rotating cupro-nickel disc to obtain deposits (Section 2.2), it was observed that the presence of small quantities of polymer appreciably reduced the 'tarnishing' of the specimens. The preliminary investigations into the phenomenon are discussed in greater detail in Section 8.1.

7.3 Corrosion in neutral aqueous environments

No general theory of corrosion exists and each corrosion mechanism depends on factors governing the system. However, from a thermodynamic viewpoint, all corrosion processes can be considered as a loss in free energy, ΔG during the spontaneous progress of a metastable state to a stable state. No account is taken in the above of the kinetics of the corrosion process as this factor is generally governed not by the thermodynamic state of the metal, but by environmental conditions.

Corrosion, as distinct from 'tarnishing' is an electrochemical process involving, at some stage, the transfer of electrons between the metal and the corroding species.

In the particular case under examination, differential aeration on a chemically and physically uniform surface results in generation of electric current between the two areas. If atmospheric oxygen is available at a metal surface immersed in an electrolyte solution, the following reaction is possible.

$$O_2\ (\text{ads}) + 2\ H_2O + 4e \longrightarrow 4OH^-$$

The reaction may be represented in the equation

$$E = E^o + \frac{RT}{ZF} \text{Ln} \frac{[\text{oxidised state}]^2}{[\text{reduced state}]^4}$$

$$\therefore E_{O/OH^-} = E^o_{O/OH^-} + \frac{0.059}{4} \log \frac{O_2}{[OH^-]^4} \text{ volts}$$

at 25°C on the normal hydrogen scale where E^o is the standard electrode potential, R the gas constant, T the absolute temperature, Z the valency change, F the Faraday constant and [ ] the activities of the oxidised and reduced species.

Under equilibrium conditions, $[O_2] = P_{O_2} = 0.2$ atmospheres; but in regions where P_{O_2} is less, then E_{O/OH^-} has a lower value and the overall driving force ΔE is expressed

$$\Delta E = \frac{\log [O_2]\ (\text{equilibrium})}{[O_2]\ (\text{depleted})}$$

The potential difference between the two areas provides the driving force for the electrochemical mechanism of corrosion.

In neutral salt solutions, corrosion proceeds only if a cathodic reaction is possible which consumes the electrons produced by the anodic reaction - the dissolution of metal. The two most common cathodic reactions are (a) reduction of hydrogen ions to gaseous hydrogen and (b) reduction of dissolved oxygen - adsorbed at the electrode surface - to hydroxyl ions.

(a) $2H^+ + 2e \rightarrow 2H(ads) \rightarrow H_2(g)$

(b) $O_2\ (ads) + 2H_2O + 4e \rightarrow 4OH^-$

Differential aeration on the same metal surface permits only the second reaction, the reduction of dissolved oxygen, to take place. Removal of all the dissolved oxygen from the system halts the corrosion process as the system becomes thermodynamically stable. Under these circumstances, the kinetics of the corrosion reaction are controlled by the rate of diffusion of oxygen to the cathodic sites. If there is an external source of e.m.f., then the cathodic reaction could be the evolution of hydrogen gas in the absence of oxygen. Other cathodic processes do occur, but they are not relevant to this discussion.(107)

The actual corrosion of a metal occurs at anodic sites where the basic reaction is

$$M \rightarrow M^{z+} + ze$$

and is the essence of the spontaneous corrosion process. However, after the first step of loss of metal ions from the lattice, the fate of the species M^{z+} is dependent on the environment and the following types of reactions are possible:

(a) formation of dissolved metallic salts

$M \rightarrow M^{z+}\ (aq.) + ze$

(b) formation of metal hydroxide

$M + z\,H_2O \rightarrow M(OH)_z + zH^+ + ze$

(c) formation of anionic species

$M + zH_2O \rightarrow MO^{z-} + 2zH^+ + ze$

(d) formation of metal oxide

$2M + zH_2O \rightarrow M_2O_z + 2zH^+ + 2ze$

Figure 7.1 illustrates the corrosion mechanism diagrammatically. At point p the current generated by the dissolution of metal is exactly balanced by the current consumed during the cathodic reduction process. The corrosion rate is proportional to the 'corrosion current' and the

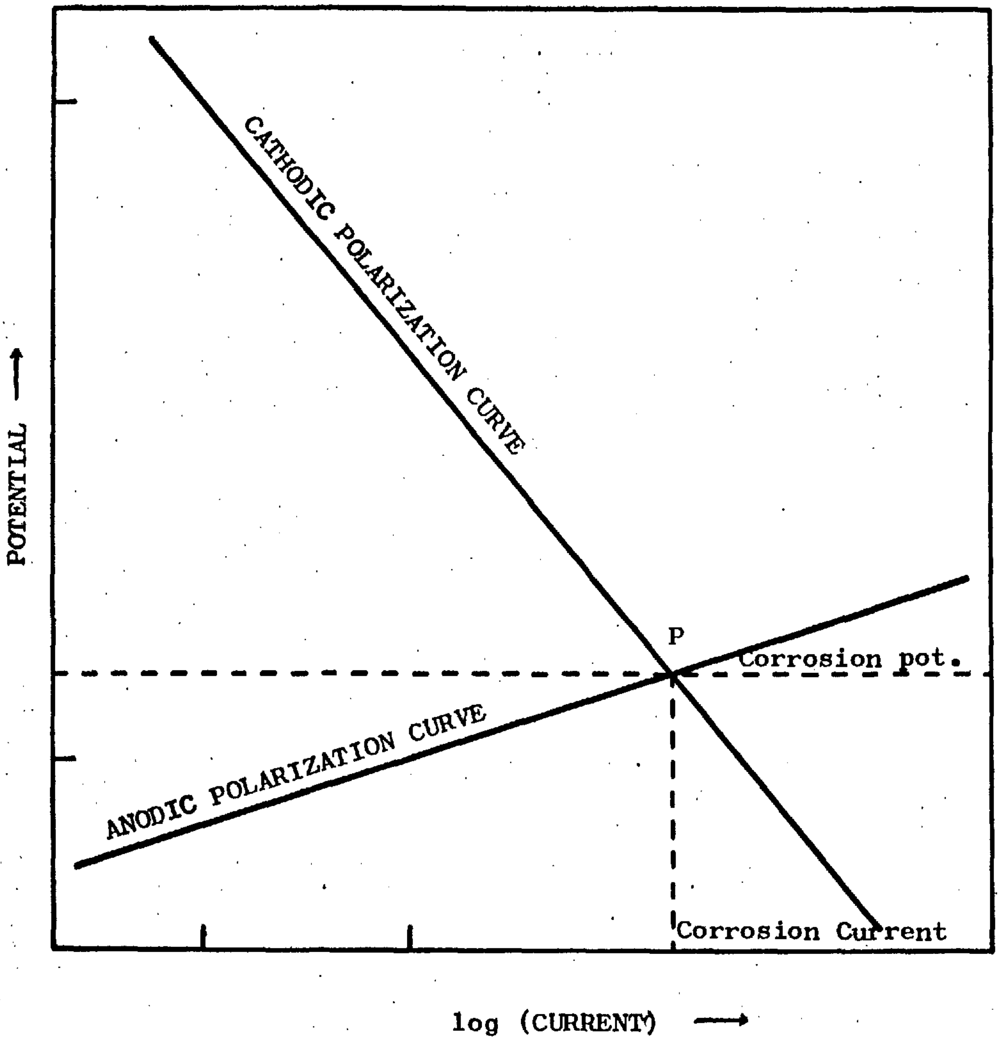


Fig. 7.1 Diagrammatic representation of corrosion process where anodic reaction polarizes slowly: P, corrosion potential.

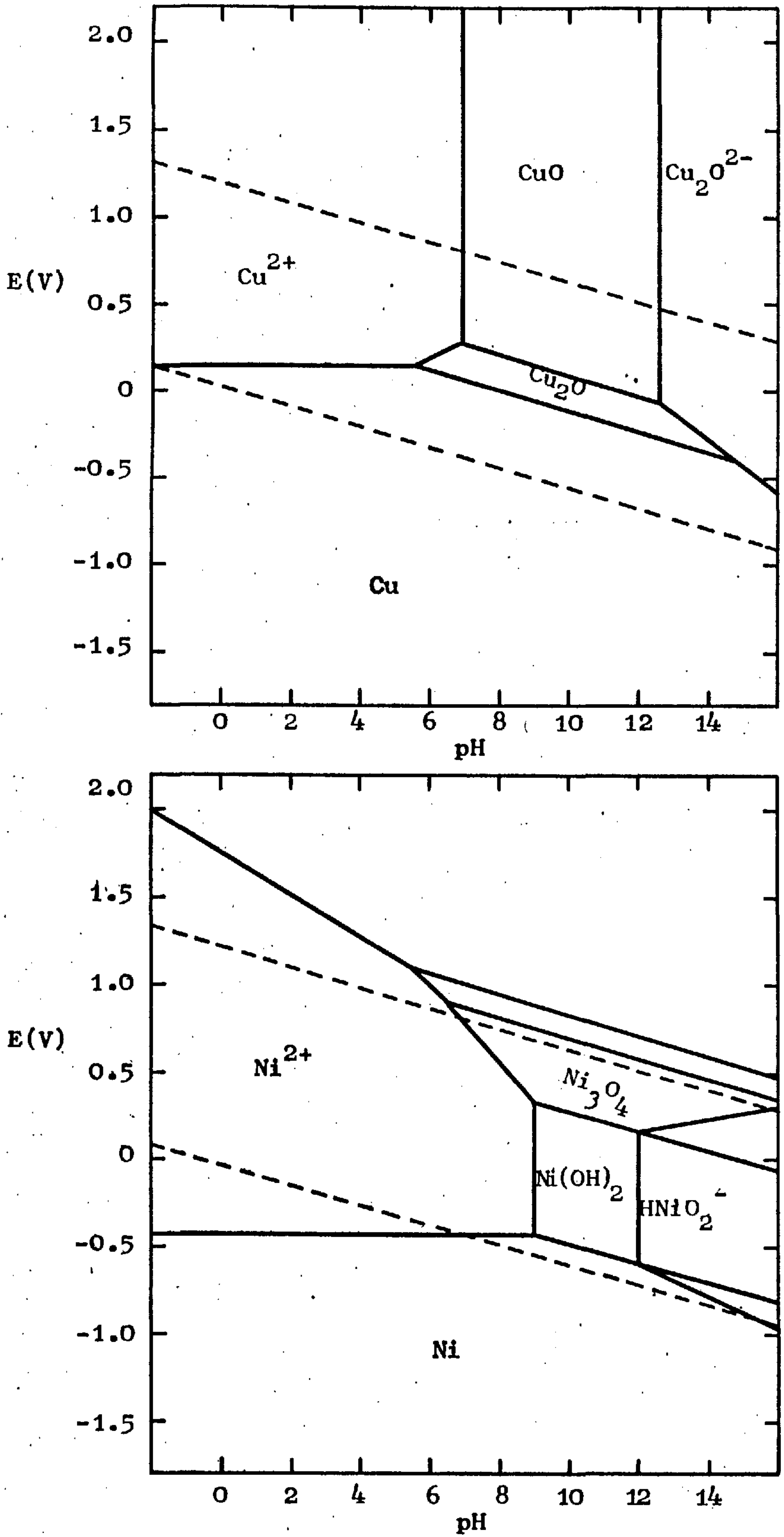


Fig. 7.2 Pourbaix diagrams; potential pH equilibrium diagrams for the systems Cu - H_2O and Ni - H_2O at 25°C.

potential at which it proceeds is the 'corrosion potential'.

The corrosion product is greatly dependent on the particular thermodynamic conditions of the system; such thermodynamic data can be expressed in a graphical form devised by Pourbaix(108). Pourbaix diagrams are essentially isothermal phase diagrams which represent metal ion-oxide equilibria with potential and pH as co-ordinates. The interpretation is that stable corrosion products (e.g. MO) exist only within a limited region of thermodynamic stability. The curves for copper and nickel are reproduced in Figure 7.2. Areas of corrosion, passivation and immunity are shown.

Superimposed on the diagrams are oxygen and hydrogen lines representing the two equilibria

$$4\ OH^- \rightleftharpoons O_{2(1\ atms)} + 2H_2O + 4e$$

$$\tfrac{1}{2}\ H_{2(1atms)} \rightleftharpoons H^+ + e$$

The oxygen line represents the potentials above which oxygen will evolve from an immersed electrode. The hydrogen line represents the potentials below which hydrogen is evolved. The region between defines the domain of water stability. However, in neutral solutions, passivity depends on the electrical and mechanical properties of the solid product and the degree of adhesion to the anodic metal.(163) In oxygen-containing aqueous solutions film growth is attributed to combination of cuprous ions passing outwards and dissolved oxygen which has undergone dissociation at the outer surface passing inwards; i.e.

$$\tfrac{1}{2}\ O_2 + 2e \longrightarrow O^{2-}$$

$$Cu \longrightarrow Cu^+ + e$$

$$2Cu^+ + O^{2-} \longrightarrow Cu_2O$$

In neutral solutions containing chloride, copper forms a cuprous oxide layer with chloride inclusions(109). The chloride ion is said to be particularly 'aggressive' because of its relatively small size and its high polarizability 'producing more soluble anodic reaction products.'(110)

An increase in the level of dissolved solids usually means an increase in the corrosion rate as the aqueous phase has increased conductivity which results in an increase of the electrochemical reactions.

During normal water flow through condensers, the naturally formed oxide is sufficiently protective, but does not resist the galvanic action of differential aeration.

Investigations into the corrosion of copper in aqueous solutions have shown three different rate processes which have been categorized as initial (5 - 60 sec.), intermediate (2 - 10 min) and long term (10 - 40 min) corrosion periods.(111) The following mechanism was postulated:

$$2\ Cu + O_2 + H^+ \rightarrow 2\ Cu^+ + HO_2^-$$

$$2\ Cu^+ + HO_2^- + 2\ Cu \rightarrow 2\ Cu_2O + H^+$$

In the initial corrosion process, first order dependence on oxygen concentration was found, whereas in the second the reaction followed the parabolic rate law, in which the slow step is the diffusion of Cu^+ ions through the corrosion products. The long term corrosion rate is dependent on the logarithm of the corrosion time, suggesting that the slow step in the reaction is a function of a process or surface, the nature of which is changing with time.

Under conditions where the metal surface is undergoing passivation at some point through build up of corrosion products, other areas can undergo severe pitting. The cause is the reduction in size of the anode when compared to the cathode, resulting in intensified attack. If passivation (build up of impermeable corrosion products) is uniform then pitting is minimised or eliminated. Corrosion of alloys is complicated by individual behaviour of the component metals. Nickel is alloyed with copper to produce an alloy with a high resistance to sea water and impingement attack. A modified protective oxide film is responsible for the improved corrosion resistance.(100)

7.4 Prevention of corrosion by inhibitors

Generally, corrosion of metals can be greatly reduced, if not eliminated, by either thermodynamic or kinetic methods.

Briefly, corrosion prevention is achieved thermodynamically by (1) alloying a metal with other metals, so that the nobility of the alloy is increased and the spontaneity of the corrosion reaction is reduced, or (2) by applying cathodic protection in the form of an opposing electrical gradient which prevents metal ions from leaving the metal lattice by imposing a thermodynamic restraint.(112) Both techniques are widely used wherever circumstances permit although, of course, in most industrial systems cost and efficiency must always be considered in selecting and maintaining materials.(113)

Kinetic methods, which are of more relevance to the present study depend on direct interference with one or more electrochemical processes occurring at anodic or cathodic sites somewhere on the corroding surface. This is achieved by reducing the corrosion activity of the environment or establishing a protective film between a corrodible material and its environment.

Considering the reduction of the corrosion activity of the environment in neutral solutions, the most common cathodic species are hydrogen ions and dissolved oxygen: cathodic reactions involving H^+ or O_2(ads) can both be poisoned; and in the case of dissolved O_2 it can be removed chemically. The aggressive nature of the hydrogen ion is reduced by polarizing cathodic sites with adsorbed hydrogen; the presence of traces of arsenic in the metal prevents the reaction

$$2\ H(ads) \longrightarrow H_2(gas)$$

and this stifles the reaction

$$H^+ + e \longrightarrow H(ads)$$

However, it suffers from the disadvantage that arsenic is poisonous (to humans) and causes 'hydrogen cracking' - i.e. migration of hydrogen into the metal lattice and rupture of the metal(114). Both intergranular and mixed inter/trans granular cracking have been attributed to this phenomenon.(164) The reduction of oxygen can be prevented by excluding dissolved oxygen by the addition of reducing agents (e.g. hydrazine or sulphite). Although this method is usual for closed systems (e.g. boiler waters) it is not very practicable in flowing systems which contain large quantities of oxygen, e.g. cooling waters.

The kinetic method most pertinent to this investigation is the use of inhibitors - particularly water-soluble organic compounds. Inhibitors are classified into two types of 'filming' or 'adsorption' inhibitors, although recent investigation shows that certain materials depend on both properties.(115)

Restricting the discussion to aqueous environments, it is relevant to mention certain inorganic inhibitors and their postulated mechanisms. Filming inhibitors create a barrier between the metal and the adjacent fluid and isolate the corroding metal. There are two mechanisms. In the first, the inhibitor causes the corrosion current to exceed the passivating current density and as a result, there is a build up of an adherent passivating oxide film. Such inhibitors (e.g. CrO_4^{2-}) were once thought to be effective solely because of their oxidising properties (a comparison of the effectiveness of the ions TcO_4^{2-} and CrO_4^{2-} shows a considerable difference), but this is now no longer tenable: the effects on the kinetics of the passivation process are specific to each ion and not necessarily dependent on their own reduction.(116) To be effective, most inhibiting XO_4^{n-} ions require the presence of oxygen in the electrolyte. The extent of inhibition is also governed by the internal polarity of the species. This implies that modification of an unprotective oxide film by incorporation of the inhibiting species into pores in the oxide is responsible for inhibition. Materials which passivate anodic areas are classified as anodic inhibitors.

In the second mechanism, the inhibitor (e.g. HCO_3^-, PO_4^{3-}) causes the formation of a corrosion product on cathodic areas and thus stifles the cathodic process. They are classified as cathodic inhibitors. Their mechanism of restraint on the corrosion process can be determined experimentally by their influence on the cathodic and anodic polarization curves of metals in the respective environments(117). The classification is by no means well defined and some inhibitors interfere with both anodic and cathodic processes(118).

In any inhibition process, if the mechanism is the impediment of an electrochemical process by a material barrier, there must be at some stage an adsorption step, but in most cases it is not rate-determining. Inhibition by organic molecules is generally considered in terms of adsorbed layers. Such layers themselves may be physical barriers to material transport, adsorbing indiscriminately, and inhibitors are known which function in this manner. However, for other systems it appears that inhibition depends on chemisorption of material. The relative effectiveness of different structural isomers rules out inhibition purely by physical adsorption.(165)

There are numerous examples of corrosion inhibition by organic materials, many of them put successfully to industrial use.(119,120) However, the mechanisms are not clear-cut and many are considered to be effective as a combined result of chemically and physically adsorbed barriers. Other systems are known in which adsorption onto a metal surface is likely, but inhibition occurs only in the presence of oxygen, which again suggests that modification of non-protective oxide layers is responsible, not the inhibitor itself forming a physical barrier by adsorption.(121) Other systems are known in which the presence of an adsorbed layer of oxygen at the solid - liquid interface reduces the inhibitive effectiveness of amines by impeding the process of chemisorption.(162) It has been proposed that the early stage of adsorption of organic molecules is strongly influenced by the charge on the double layer of the metal and prior adsorption of suitable anions (e.g. Cl^-) encourages adsorption of certain molecules (e.g. amines). Such adsorption is supposed to be governed by the polarizability of the molecule, charge density and configuration. Studies of adsorption inhibitors of the dissolution of Zn in acid have indicated adsorption into the electrical double layer adjacent to the electrode; presumably the only type of adsorption responsible is electrostatic. Some organic inhibitors have a marked influence on anodic and cathodic polarization curves; similar to xanthates used in froth flotation thiourea bonds strongly to a metal by indiscriminate electron sharing with metal atoms on the surface. In consequence, they tend to interfere with both anodic and cathodic processes. The interference is suggested to result from 'isolation of the metal from the solvating water molecules of the electrolyte',(122). Nitrogen and oxygen compounds, e.g. amines and aldehydes, are often less effective then sulphur-containing inhibitors, and are less strongly adsorbed. They tend to adsorb onto higher energy adsorption sites at growth edges, dislocations, etc. The effect on the cathodic areas results from overlap of the molecule onto adjacent areas; ~~and~~ this interferes with both the anodic and cathodic corrosion mechanisms.

Use of materials known as 'water-displacing agents' in conjunction with organic inhibitors has been patented. Esters of glycols and polyglycols have been used (molecular weight 3×10^2 to 1.5×10^3), the mechanism being the exclusion of water molecules from the metal surface by greater adsorbability(123). However, it does not seem possible to differentiate between 'water displacement' and physical adsorption barriers.

Electrochemists place great emphasis on the similarity of the processes of corrosion, electro-polishing and electro-deposition, and indeed, this idea is borne out in practice. In particular, the addition of organic compounds (brighteners) to plating baths is significant. The materials are frequently organic compounds containing charged groups based on nitrogen or sulphur, e.g. amines or proteins. The mechanism proposed is that the additives inhibit crystallographic growth, either by adsorbing specifically at growth edges, or by non-specific adsorption over the whole surface, either process reducing the differences in activity between various sites on the metal.(124) In some cases, the formation of an insoluble compound at a solid - liquid interface of species normally soluble in bulk solution cannot be excluded. Adsorption of a substance into the electrical double layer at an interface can drastically effect its solvation characteristics.(126)

7.5 Aims of the investigation

During the early stages of the investigation, it became apparent that Zimmite had corrosion-inhibition properties on copper alloy in neutral salt solutions. A literature search was carried out to find information on organic corrosion inhibitors of similar chemical type. However, no such information was discovered and no mention was made of similar materials acting as corrosion inhibitors in the standard reference sources dealing specifically with inhibitors.(119, 120)

The only mention of polyacrylamide being used in connection with the protection of metals was a patent specifying the use of comparatively large quantities of the polymer (5 g/l) during the electrochemical formation of oxide films; no explanation of a mechanism was offered.(127) As it is used/as an additive in an electrochemical process, it cannot be considered as a corrosion inhibitor of the type added to a corroding environment.

However, the search did reveal that 'organic colloids' (e.g. gelatin) have been used as restrainers during acid pickling or inhibitors in acid solution (e.g. starch, albumen, agar-agar).(125) These materials are macromolecules of high molecular weight, which are surface active and readily adsorb on metal or oxide surfaces. The mechanism of protective action is not clear cut and chemisorbed or physically adsorbed barriers are both considered in explaining the restraint of metal dissolution. Such inhibitors are postulated to be initially chemisorbed and then followed by a slower physical adsorption process. The above observations were carried out in acid solution; at neutral pH values, the presence of an oxide layer may completely alter the character of the adsorption mechanism. Some of the materials used to inhibit corrosion are also used in solid - liquid separation as flocculants (e.g. gelatin, polyvinyl alcohol, gum tragacanth), their high adsorbability on mineral surfaces and high molecular weight again being responsible. Organic colloids, presumably, can function as adsorption inhibitors of the type that retard metal ion transfer by the presence of physically or chemically adsorbed layers on the metal surface.

In view of the lack of information on corrosion inhibition by high molecular weight synthetic polymers and the possibility that Zimmite might be effective as a corrosion inhibitor in its own right and not just as a remover of the cause of corrosion, a programme of research was devised to establish the following:

(1) The mechanism of action of Zimmite as a corrosion inhibitor of cupro-nickel in saline waters;

(2) whether the property is common to other high molecular weight polymeric flocculants;

(3) whether the inhibition stifles sufficiently to be of practical value, the type of corrosion encountered at West Thurrock generating station.

8. CORROSION AND INHIBITION OF CUPRO-NICKEL

The following tests were used in establishing the mechanism of corrosion of condenser tubes and in observing effects of inhibition during laboratory tests.

8.1 Static corrosion tests

Some doubt had arisen concerning the nature of attack at West Thurrock. The high 'free sulphide' content of the mud (reported to vary between 0.3 to 8.5%(105)) was considered to be responsible for corrosion. The presence of sulphide is a direct result of the action of sulphate-reducing bacteria often found in polluted waters of low oxygen content. Evidence suggested that sulphide attack was not responsible for the major attack on the tubes, although some small contribution cannot be excluded (Table 7.1). Tests were designed to establish the mechanism of corrosion and examine corrosion products.

Specimens of cupro-nickel were cut from actual condenser tubes (obtained from West Thurrock) and subjected to the effects of differential aeration cells under both aerobic and anaerobic conditions. Differential aeration was achieved by allowing mud to settle on part of the metal surface and leaving the rest exposed, the whole specimen being already totally immersed in river water. The metal was used both as obtained (after degreasing), and also after cleaning in 10% hydrochloric acid to remove the dull oxide film. Anaerobic conditions were obtained by using a closed system to exclude air; any traces of oxygen were consumed by the organic matter of the mud. Aerobic conditions were obtained by exposing the surface of the supernatant liquid to the atmosphere - the mud restricts access of oxygen to the unexposed surface. Table 8.1 gives the results of inspection of the samples after 24 days immersion.

The tests show that specimens subjected to aerobic conditions corroded appreciably (deposit attack) whereas specimens under anaerobic conditions suffered little or no corrosion(128). (Oxidation of mud soon reduces the O_2 level to zero and inhibits the cathodic reaction). Tests on the green corrosion product showed no sign of

H_2S evolution with acid, and the material is probably a basic carbonate with a small quantity of basic chloride included.

Another series of tests was carried out to establish if the 'aggressive' nature of the mud was really significant in determining the characteristics of corrosion. Suspensions of inactive clay, etc., in river water were prepared and again arranged so that sediment formed on part of the cupro-nickel specimen, while other areas remained exposed. Some tests were left open to the atmosphere (aerobic conditions); others were made anaerobic by flushing with nitrogen and leaving in closed containers. The specimens were degreased before testing but not acid-cleaned. Table 8.2 shows the results. Even in the absence of active organic components, all the aerobic specimens suffered from deposit attack of the same form found in the presence of mud; anaerobic specimens remained unattacked.

Specimens of cupro-nickel placed at this time in the River Thames at West Thurrock (principally aimed at obtaining mud deposits) suffered from severe corrosion and were covered with green corrosion products similar to 'green stain', a common corrosion product found on copper in contact with waters containing appreciable amounts of carbon dioxide.(106) Qualitative analysis revealed that sulphide was not detectable - strong evidence for excluding sulphide attack(129). Very little chloride and sulphate were detected, but substantial amounts of carbon dioxide were present. Quantitative analysis showed that the corrosion product contained about 33% copper and 11% nickel - close to the 70/30 ratio of the original metal. An appreciable quantity of intractable residue remained - probably clay minerals and silica. Although no further detailed examination of the corrosion product was made, it is reasonable to conclude that it was a mixture of basic carbonates. It seems, therefore, that this information, in combination with that presented in Table 7.1, is good evidence for the theory that condenser tube corrosion at West Thurrock is due principally to galvanic attack resulting from differential aeration cells set up during overnight shut-down.

8.2 Observations on corrosion inhibition

During attempts to obtain deposits of river mud under both turbulent and laminar hydrodynamic flow, it was noticeable that the incidence of corrosion of specimens was irregular. Although the full significance of the observations was not appreciated at the time, they did lead to further investigations of the inhibitive action of Zimmite on cupro-nickel in estuarine waters.

A rig simulating the passage of cooling water through a cupro-nickelcondenser tube (turbulent flow) was described in Section 2.2. Tests were designed to show interactions between polymer and deposited mud. However, examination of the results of the tests (Table 2.1) showed that not only did aeration eliminate corrosion - a result of the absence of differential aeration - but so did the presence of Zimmite, even though 'aggressive' mud remained in contact with the tube for 12 hours each day. Although the tests were designed to be anaerobic, some oxygen entered the system through the pump and the level was sufficient to maintain the cathodic reaction of the differential aeration cell. These observations confirmed the laboratory and plant trials carried out at West Thurrock(105), although the inhibitive action of Zimmite was not considered at the time.

Further information concerning this unsuspected property was obtained during attempts to obtain deposition under controlled hydrodynamic conditions (laminar flow) on the apparatus described in Section 2.2. At the time, deposition of mud was thought to take place as primary and secondary deposits. In fact, the primary deposit was due to the incipient corrosion of the cupro-nickel discs - again reduced or eliminated in the presence of Zimmite. The tenacious primary deposit that formed in the absence of polymer was readily soluble in dilute acids, but the loosely adherent secondary deposit (mud) remained unaffected. The results of the tests are included in Table 2.2.

Examination of these results and the conclusion that Zimmite could be responsible for inhibition led to other qualitative tests designed to study the effect of Zimmite on cupro-nickel in a system selected to produce rapid corrosion. The tests took the form of partial immersion of coupons in beakers containing 0.2M NaCl. Some were treated with varying concentrations of Zimmite, others were left untreated. Tests were also extended to other metals, namely, mild steel, brass and copper. The degree of corrosion was estimated by inspection after several days' immersion. The results are included in Table 8.3.

The results of the tests (with the exception of those on mild steel) showed unequivocally that small quantities of Zimmite had a significant influence on the extent of the corrosion of the specimen. Untreated specimens followed the normal corrosion pattern for such tests.(130)

8.3 Dynamic corrosion tests

Once it had been established that Zimmite was potentially a corrosion inhibitor, tests were designed to show this effect conclusively during experiments simulating flow of water through condenser tubes. The apparatus described in Section 2.2 was used without modification and tubes were subjected to intermittent flow of suspensions of mud in Thames River water. Two apparatuses were used and comparative results were obtained from Zimmite treated and untreated systems. Table 8.4 lists the qualitative results of the tests.

Tests showed that Zimmite-treated suspensions (flocculated) did not result in corrosion of condenser tubes. However, no corrosion was observed on tubes previously treated with Zimmite by immersion in dilute solutions, even though no polymer was present in the suspension which was not destabilized by flocculation. The different surface condition of treated and untreated tubes after prolonged contact with mud is illustrated in Plate 8.1.

The tests confirmed the hypothesis that Zimmite added to the corrosion medium acted as a corrosion inhibitor; these led to the investigation of the electrochemical behaviour of cupro-nickel in the presence of Zimmite, in order to establish the mechanism. This investigation is discussed in the following Section.

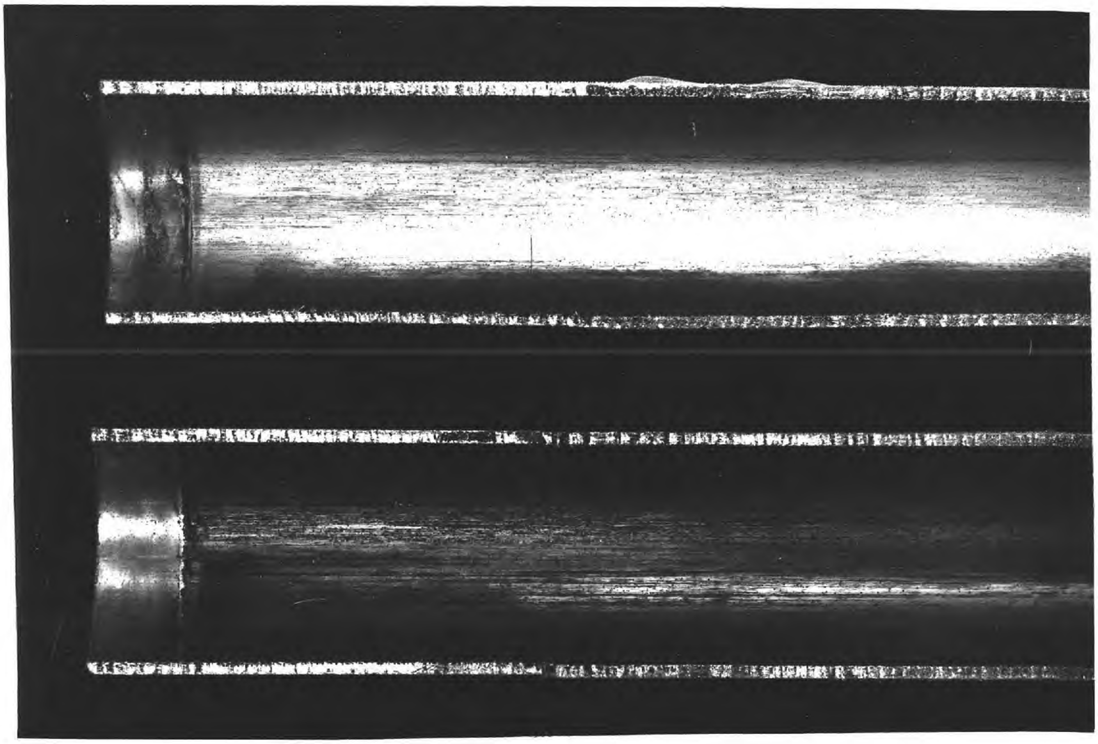


Plate 8.1 Sectioned condenser tubes after contact with simulated cooling water - 14 days intermittent flow. Upper tube treated with Zimmite; lower tube untreated.

Table 8.1 Results of differential aeration tests on cupro-nickel specimens in Thames River water containing mud.

Specimen preparation	Test conditions	Observations on inspection
degreased: acid cleaned	aerobic	Severe corrosion: red stain under centre of mud deposit green at edges: both soluble in acid: exposed area untouched.
degreased	aerobic	
degreased: acid cleaned	anaerobic	slight staining of acid cleaned specimen; otherwise no corrosion
degreased	anaerobic	

Table 8.2 Results of differential aeration tests employing 'inactive' sediment.

Sediment	Test conditions	Observations
kaolin	aerobic	severe corrosion beneath sediment, as for Table 8.1.
silica	aerobic	
alumina	aerobic	
kaolin	anaerobic	no corrosion
silica	anaerobic	
alumina	anaerobic	

Table 8.3 Qualitative results of corrosion tests on partially immersed specimens (4 days immersion) in 0.2 M NaCl

Specimen	Dose (Zimmite)	Observations
cupro-nickel	-	rapid tarnish, developing to severe attack, 'green stain'.
" "	10 p.p.m.	slow tarnish developing to mild attack after 4 days
" "	20 p.p.m.	uniform slow tarnish: small areas of localised attack
copper	-	rapid tarnishing developing to severe attack
"	20 p.p.m.	uniform tarnish developing slowly: localised areas of attack developing
brass (70/30)	-	rapid tarnishing developing to severe attack
" "	20 p.p.m.	uniform tarnish film developing slowly: small localised areas
mild steel	-	rapid rusting of specimen: loose adherent film
" "	20 p.p.m.	rapid rusting, but film more adherent than above

Table 8.4 Effect of Zimmite on condenser tube under simulated condenser conditions. Thames River mud and water, 12 hrs on, 12 hrs off. 14 days flow time.

Specimen preparation	Suspension	Observations of sectioned tube
degreased: acid cleaned	T.R. mud and water anaerobic	corrosion of lower half of tube: red scale loosely adherent acid soluble
" "	T.R. mud and water aerobic	uniform tarnish film: no corrosion
" "	T.R. mud Zimmite (50 p.p.m.) anaerobic	" "
" " immersed in Zimmite (20 p.p.m.) for 2 hours	T.R. mud and water anaerobic	" "

9. ELECTROCHEMICAL INVESTIGATIONS AND ELECTRON MICROSCOPY

9.1 Introduction

The techniques for the electrochemical investigation of electrode processes are well established and methods of assessing the corrosion of metals and alloys and evaluating the role of inhibitors from thermodynamic and kinetic stand points have been established (despite earlier criticism of their validity)(131).

In particular, potentiostatic and potentiodynamic methods provide useful information concerning the change in kinetics of the electrode processes and the reactions taking place at the electrode surface.(132)(133) The thermodynamic interpretation of electrochemical data, and the prediction of conditions of immunity, passivation or corrosion for a system has been dealt with by Pourbaix.(108)

Measurements of surface capacity and resistance of electrodes immersed in electrolyte combined with examination of corroding and inhibited specimen surfaces have been used in this investigation to supplement the information gained from potentiometric studies.

9.2 Potentiostatic and potentiokinetic studies

Cupro-nickel sheet of the same composition as the condenser tubes (68% Cu, 30% Ni, 1% Mn, 1% Fe) was used to prepare specimens for potentiometric studies. A 500 ml 'Quickfit' demountable reaction vessel was adopted as the corrosion test cell (Fig. 9.1). The five membered top allowed the installation of the specimen electrode assembly, a Luggin capillary for the reference electrode, platinum counter-electrode, degassing tube and gas exit. A magnetic stirrer was used to stir the solutions.

The test electrode assembly consisted of a rectangular piece of cupro-nickel sheet (1.5 x 2 cm) mounted in a 'Quickfit' extension tube and sealed with 'Plasticene'. Unwanted areas of the electrode were blocked by spraying with a quick-drying aerosol lacquer. Cleaning the electrodes before mounting and spraying with lacquer was carried out firstly by degreasing in benzene, then immersing in detergent ('RBS 25') and placing in an ultrasonic bath, and lastly immersing in 10% sulphuric acid for three minutes. However, each specimen was subjected to cathodic

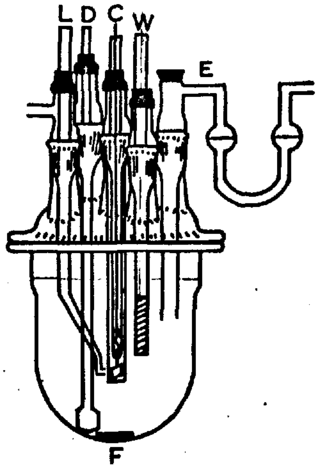


Fig. 9.1 Corrosion test cell. (W) - cupro-nickel electrode; (C) - Pt electrode; (L) - Luggin capillary; (D) - gas inlet; (E) - gas outlet; (F) - stirrer .

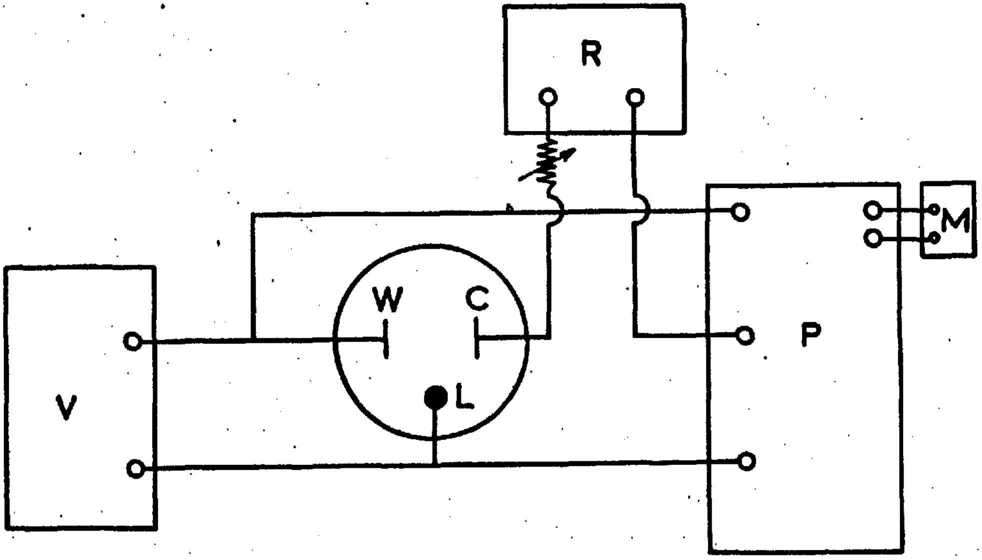


Fig. 9.2 Corrosion cell and electrical assembly. (W) - cupro-nickel electrode; (C) - Pt counter electrode; (L) - calomel reference electrode; (V) - valve volmeter; (P)- potentiostat; (R) - chart recorder; (M) - ammeter.

polarization to the point of hydrogen evolution for one minute before any measurements were made on it. This technique is reported to reduce any oxides to the metal on the electrode surface(134); it does, in fact, produce a uniform hydrophilic surface and is probably the nearest to a chemically clean surface that conditions allow (short of ultra-high vacuum evaporated film techniques). In practice, condenser tubes are likely to be covered with an air-formed oxide film which under mild conditions (e.g. unpolluted river water) is sufficient to maintain corrosion rates at an acceptable level.

In order to simulate practical conditions as closely as possible, for the majority of the tests 0.2 M NaCl, containing 10% of oxygen saturation, was used as the electrolyte. This condition is frequently encountered in the estuarine waters at West Thurrock. For differential aeration to be maintained, an appreciable level of oxygen is required for the cathodic process to persist, i.e. $O_2 + 4H^+ + 4e \rightarrow 2H_2O$; as stated before, the rate of the corrosion process (excluding any restraint imposed by corrosion products) is governed by the oxygen level at the cathode, or, more correctly, the rate of diffusion of oxygen to the cathodic sites. If there is an excessive amount of oxygen present, then film repair is rapid and the formation of insoluble corrosion products is a self-passivating process. However, at low concentration of oxygen, film repair after film breakdown is a slow process and the oxide formed is not always passivating(135). Studies have been made on the effects of chloride and other halide ions on oxide-covered aluminium(110). Results have shown that chloride ions become included at certain locations in the oxide film which create additional current carriers and lower the ionic resistance of the film. Oxide films formed on copper in the presence of chloride also incorporate chloride ions into the lattice, which presumably lowers ionic resistance in the same way, as aluminium without influencing the overall electrical resistance. In addition, if oxygen diffusion through the oxide is restricted (i.e. at very low concentrations) a likely condition at low potentials, metal dissolution without passive film formation predominates, and metal ions pass from the lattice into the aqueous phase as hydrated M^{z+} ions.

The diagrammatic arrangement of the apparatus and circuit is shown in Fig. 9.2. Potentiodynamic measurements were carried out by manually changing the potential by small regular increments at 30 second intervals. The potential was maintained by a potentiostat relative to the standard calomel electrode (SCE) (with an accuracy of ± 2mV). A saturated calomel reference electrode was used in all the experiments and voltages were measured with a Philips high impedance valve voltmeter and current with a multirange Model 100A Taylor meter (sensitivity 10μA f.s.d.)

Polarization curves between ± 1500mV (SCE) were obtained for cupronickel in 0.2 M sodium chloride, in the presence and absence of oxygen and in the presence and absence of various quantities of Zimmite (Figs. 9.3 and 9.4).

A shift in the breakaway potential - the point at which there is a marked increase in current density with a small increase in potential (point P Fig. 9.3) in the presence of oxygen and Zimmite was observed. In the absence of oxygen (Fig. 9.4) the influence of polymer on the anodic processes was relatively slight but still apparent. At slightly higher anodic potentials, the presence of Zimmite made no difference to the polarization curves, which coincided at a point referred to as the 'restitution potential'. A marked difference was also observed in the physical appearance of corrosion products that formed on the surface of the test electrodes; specimens corroding in the absence of polymer gave a layer of oxide that was coarse grained when examined microscopically, had little mechanical strength and did not adhere to the metal surface, but corrosion products formed at similar potentials in the presence of Zimmite were relatively fine grained, tenacious and resisted mechanical abrasion.

Similar effects were observed with some other high molecular weight polymers of similar composition on polarization curves carried out under similar conditions (Table 9.1)

Table 9.1 Qualitative effect of polymeric flocculants on anodic polarization curve for Cu/Ni in 0.2 M NaCl (10% of O_2 saturation)

Flocculant	Effect as inhibitor
Zimmite	active
Superfloc 20	active
Separan AP30	inactive
Separan NP20	active
Powda^floc	inactive
Tylose 400p	inactive

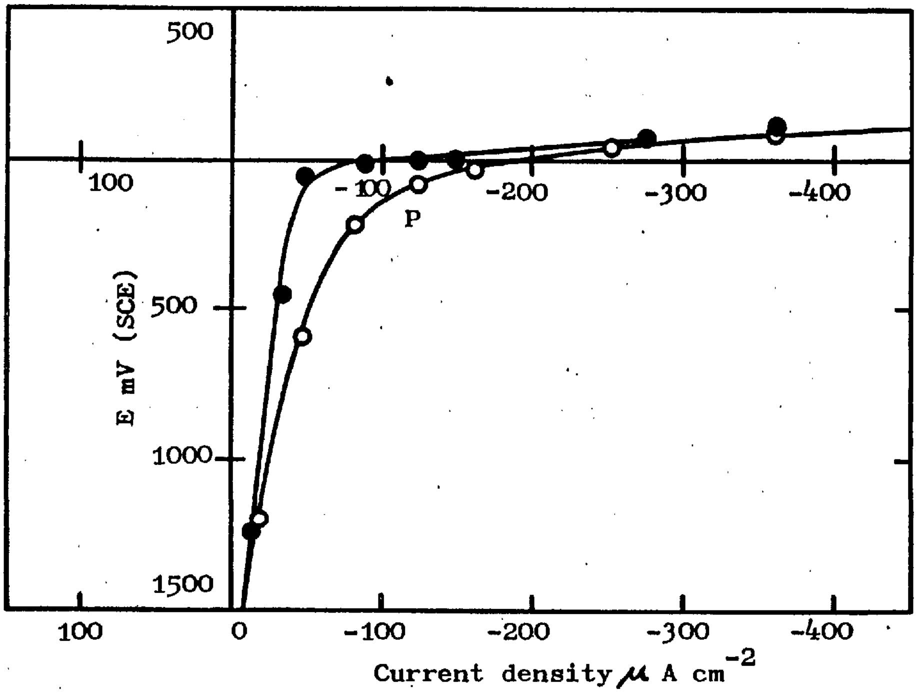


Fig. 9.3 Polarization curve for Cu/Ni in 0.2 M NaCl (10% O_2 saturation); o, in absence of polymer; ●, in presence of polymer (20 p.p.m. Zimmite)

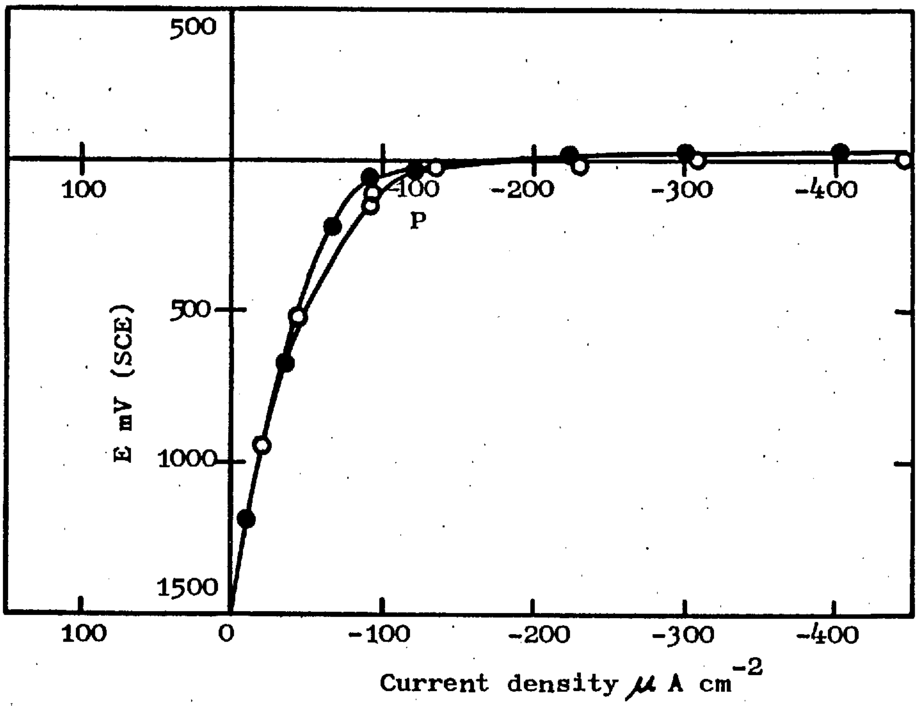


Fig. 9.4 Polarization curve for Cu/Ni in 0.2 M NaCl (de-oxygenated); o, in absence of polymer; ●, in presence of polymer (20 p.p.m. Zimmite)

It is conventional to plot such data on a semi-logarithmic scale with respect to the current. The curves show a considerable reduction in current density at small anodic potentials in the presence of Zimmite (Fig. 9.5) after relatively short immersion times.

The above experiments showed unambiguously that the presence of a high molecular weight polymer flocculant influenced the anodic and cathodic behaviour of Cu-Ni electrodes in 0.2M NaCl containing 10% oxygen saturation to the extent of causing significant inhibition of the corrosion process. The theory that a physico-chemically adsorbed barrier film was solely responsible for restraining the process by restricting diffusion of current carrying species was untenable because polyacrylamide gels are known to permit the diffusion of relatively small organic species through their structure. The dependence on the presence of oxygen indicated passivation through modified film growth. Therefore, it became necessary to investigate the mechanism further and to compare other flocculants as inhibitors. As the inhibition process was not instantaneous, it was decided to adopt the technique of holding the specimen at a predetermined potential and observing changes in current characteristics with time. This method has been used successfully in observing the inter-crystalline corrosion of stainless steels in electrolyte solutions(131). Any change in current density is accepted as being directly proportional to a change in corrosion rate. Although all corrosion measurements were carried out in the laboratory, it is reasonable to extrapolate laboratory conditions to those in practice. A reasonable estimation of change in corrosion rate can be made without investigating more about the system than the electrochemical phenomena(166).

If the premise that passivation through modified film growth is correct, it should indicate the nature of films formed during corrosion and during inhibition.

In order to assess the approximate potentials likely to be found between anodic and cathodic areas during corrosion, a simple laboratory cell was set up to measure the potential difference between two cupro-nickel specimens, one immersed in aerated 0.2M NaCl and the other in deaerated 0.2M NaCl. The difference in potential was found to be about 90 mV. This was equated with the potential that arises in practice in condenser tubes between the oxygen-excess and oxygen-depleted areas. This potential difference was found to be within the anodic region where the polarization curve was influenced by the presence of Zimmite.

The static potential was chosen to be -150 mV (SCE) as this was within the range of effectiveness of the inhibitor near the corrosion potential, and not too close to the restitution potential - the point where polarization curves of inhibited and uninhibited specimens coincide. As inhibition was mainly associated with the anodic portion of the polarization curve (although as mentioned, there was a slight shift of the cathodic curve (Fig. 9.3)), tests were confined to anodic polarization conditions. The effect of polymer added to the cell on the cathodic curves was instantaneous, indicating a fundamental difference in mechanism. Complete inhibition was not instantaneous upon adding the inhibitor during anodic polarization but took many minutes (about 40) to achieve a current density of about 15% of the original value (Fig. 9.6). A number of different types of flocculant were tried and the degree of inhibition after a defined contact time is shown in Table 9.2. The time - current curves for effective flocculation are all of the same type as Fig. 9.6.

During the tests, several observations were made which proved valuable in establishing the mechanism of inhibition by high molecular weight polymers. Experiments showed that:

1. Polarization resistance curves remained unchanged if partially inhibited specimens were transferred to polymer-free solutions of otherwise identical composition (Fig. 9.7) i.e. once adsorbed, the polymer remained effective, although no longer present in the bulk of the solution.
2. The rate of corrosion inhibition was dependent on the concentration of polymer (Fig. 9.8)
3. Specimens allowed to corrode initially without restraint could subsequently be inhibited by polymer, although

Table 9.2 Effect of polymeric flocculants on corrosion rate of Cu/Ni in 0.2 M NaCl, 10% of O_2 saturation, potential -150mV (SCE) (type of flocculant listed in Appendix I)

Flocculant (20 p.p.m.)	Contact Time (minutes)	% Inhibition of initial corrosion rate
Zimmite	35	80
Separan NP20	30	75
Separan C-90	25	90
Separan C-120	25	95
Separan AP-30	100	0
UCAR C-149	40	85
Superfloc 20	30	70
Wisproflok P	50	88
Tylose MH4000 P	50	0
Tylose C1000	40	0
Polyflok PX	40	70
Powdaflok	80	0
Floccotan	45	75
Wisprofloc 20	150	0
Starch phosphate	100	0
Polyflok 209P	120	0
Tragaflok	95	0
Nalco 600	25	90

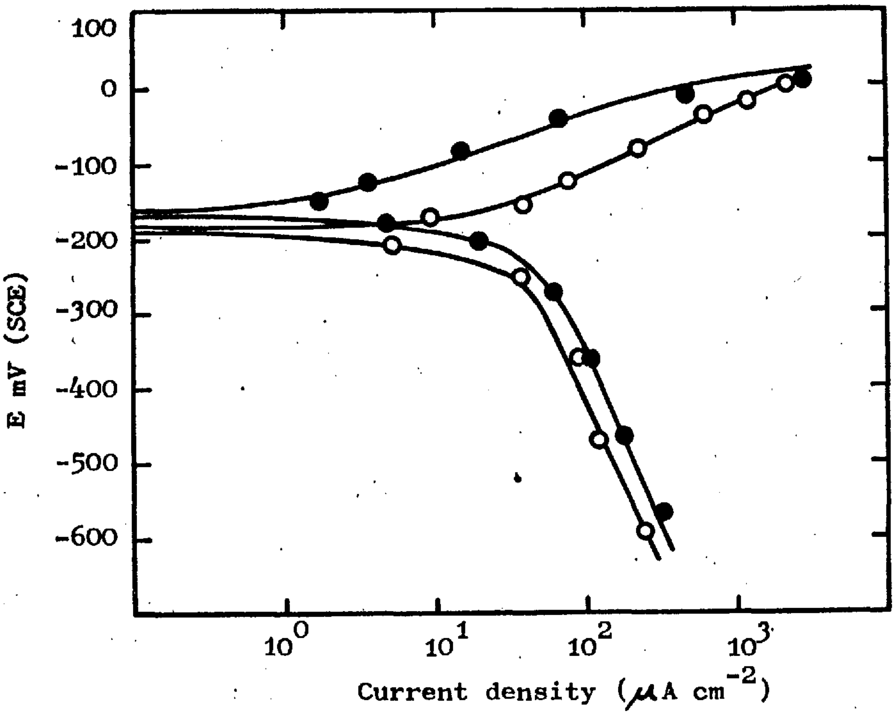


Fig. 9.5 Polarization curve for Cu/Ni in 0.2 M NaCl (10% O_2 sat) o, in absence of polymer; •, in presence of polymer (20 p.p.m. Zimmite)

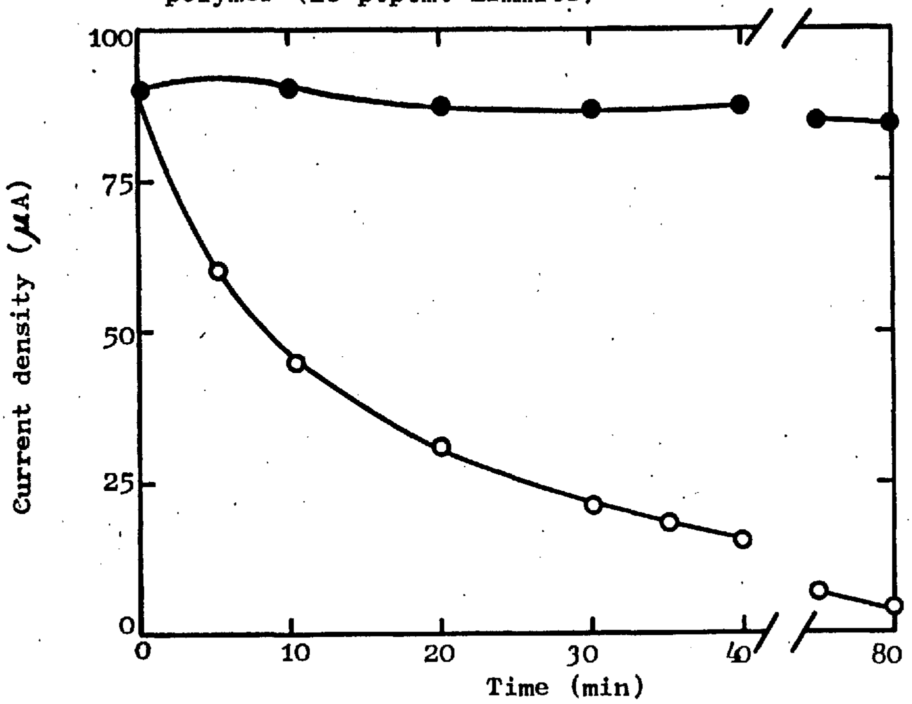


Fig. 9.6 Typical graph of current variation with time for Cu/Ni electrode in 0.2 M NaCl at a fixed potential of -150 mV (SCE) - 10% O_2 saturation: •, freely corroding specimen; o, polymer inhibited specimen (20 p.p.m. Zimmite)

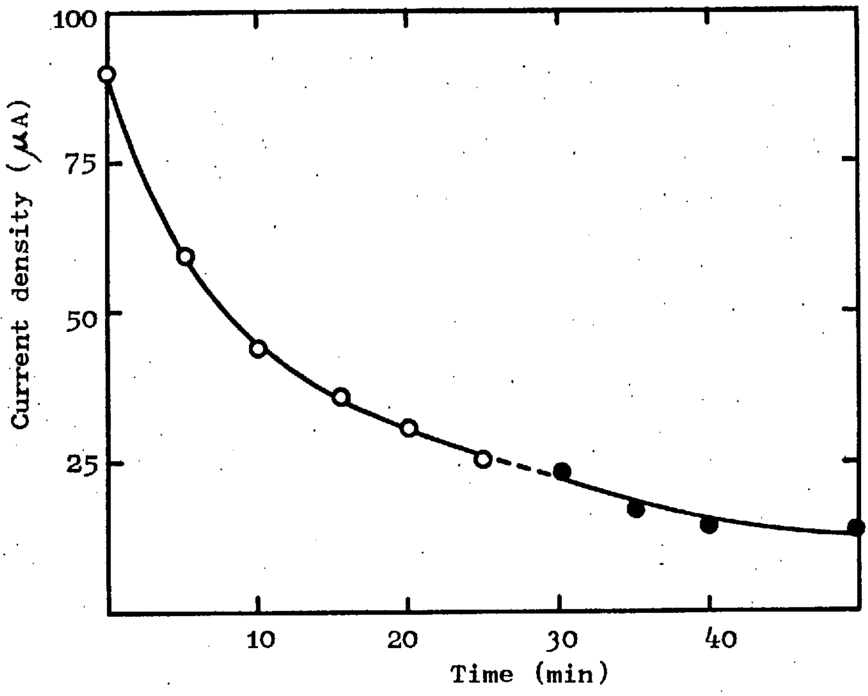


Fig. 9.7 Graph of current variation with time for Cu/Ni in 0.2 M Na Cl at a fixed potential of -150mV (SCE); 10% O_2 saturation: o, in presence of polymer (20 p.p.m. Zimmite); ●, transferred to polymer-free electrolyte.

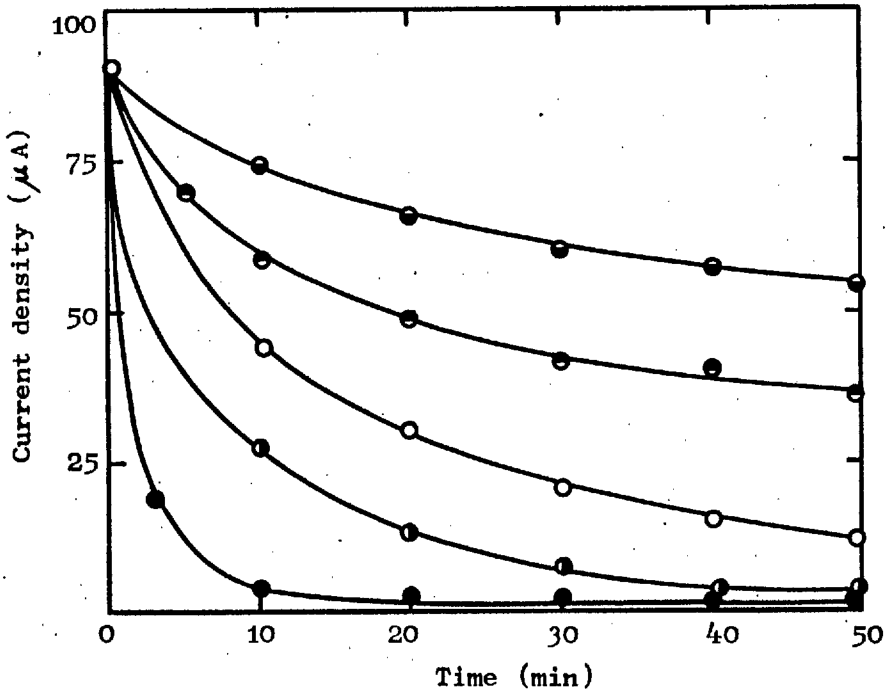


Fig. 9.8 Variation of current with time for Cu/Ni in 0.2 M NaCl at fixed potential of -150mV (SCE) 10% O_2 saturation: ◐ , 1 p.p.m. Zimmite; ●, 10 p.p.m. Zimmite; o, 20 p.p.m. Zimmite; ◑, 40 p.p.m. Zimmite; ●, 80 p.p.m. Zimmite.

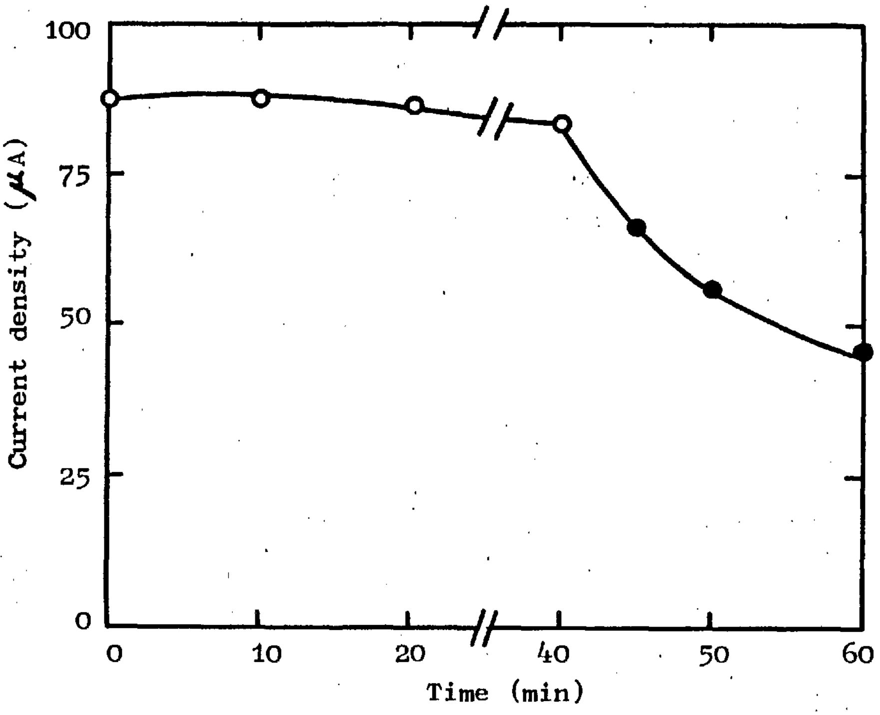


Fig. 9.9 Variation of current with time for Cu/Ni in 0.2 M NaCl at a fixed potential of -150mV (SCE); 10% O_2 saturation. o, freely corroding; ●, the same system polymer added after 40 min (20 p.p.m. Zimmite)

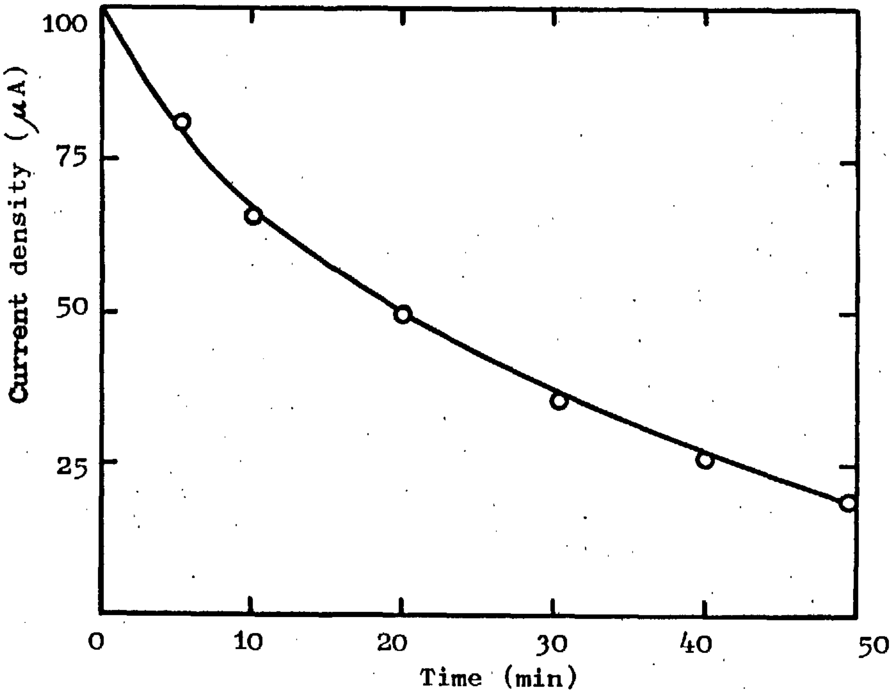


Fig. 9.10 Variation of current with time for Cu in 0.2 M NaCl at a fixed potential of -150mV (SCE) 10% O_2 saturation in presence of polymer (20 p.p.m. Zimmite)

the rate of inhibition was significantly lower than for inhibition of chemically clean surfaces (Fig. 9.9)

4. Inhibition of the anodic process under a constant potential was found to be pH-dependent. No inhibition was observed at low pH and the rate of inhibition appeared to be enhanced at slightly alkaline pH values (Table 9.3).

Table 9.3 Effect of pH change on inhibition characteristics of Zimmite (Cu/Ni in 0.2M NaCl 10% of O_2 sat -15mV SCE)

pH	Effectiveness
1.5	ineffective
2.9	ineffective
5.1	effective
7.5	effective
10.2	effective
13.1	ineffective

5. Inhibited specimens, if washed with diluted acid and rinsed, lost their inhibition (i.e. corrosion rates increased to initial values), but soon followed the expected behaviour of decreasing current density values when re-immersed in electrolyte containing polymer.
6. Inhibition of corrosion of pure copper was also observed by the same techniques (Fig. 9.10).

9.3 Capacitance and resistance measurements

In an inhibition process involving a restraint of the kinetics of an electrode process, the mechanism is either a depression of the corrosive activity of the electrolyte or the establishment of a physically or chemisorbed barrier at the electrode solution interface.

The mechanism of inhibition by polyacrylamide could not be assumed to depend on the reduction of the activity of the corrosivity of sodium chloride or the restriction of diffusion of oxygen to the electrode surface; in fact, polarization measurements indicated an increased diffusion rate. It therefore became necessary to consider the formation of adsorbed layers of polyacrylamide or oxide, or both, on to the electrode surface.

Measurement of changes in capacitance, C, and resistance, R, with time have been used to study the chemical and physical adsorption of inhibitors(136) and also changes in the physical properties of oxides immersed in electrolytes(156).

Briefly, an adsorbed film is made the dielectric of a parallel plate condenser and any changes in the properties of this film during a corrosion process etc., can be measured as changes in capacitance and resistance. The technique used here to measure C and R with time was that developed by Isaacs and Leach(156). (Use of apparatus made available by H.G. Masterson, C.E.R.L., Leatherhead). Electrode preparation was similar to that described in section 9.1. Measurements were carried out in 0.2M NaCl solution, either under freely corroding conditions, or in the presence of inhibitors.

The capacitance and resistance curves for inhibited and corroding specimens are shown in Fig. 9.11.

Earlier measurements were carried out in sodium sulphate solution in the absence of oxygen; the dependence on the presence of oxygen for successful inhibition had not then been realised.

Changes in capacitance have been used by some workers to calculate the degree of surface coverage F from the simple relationship(136)

$$F = \frac{C_1 - C_2}{C_2} \times 100\%$$

where C_1 is the capacitance in the presence of an adsorbed film and C_2 is the capacitance of the film free surface.

This relationship seems of doubtful significance for several reasons. Firstly, idealised monolayer coverage of one type, i.e. either

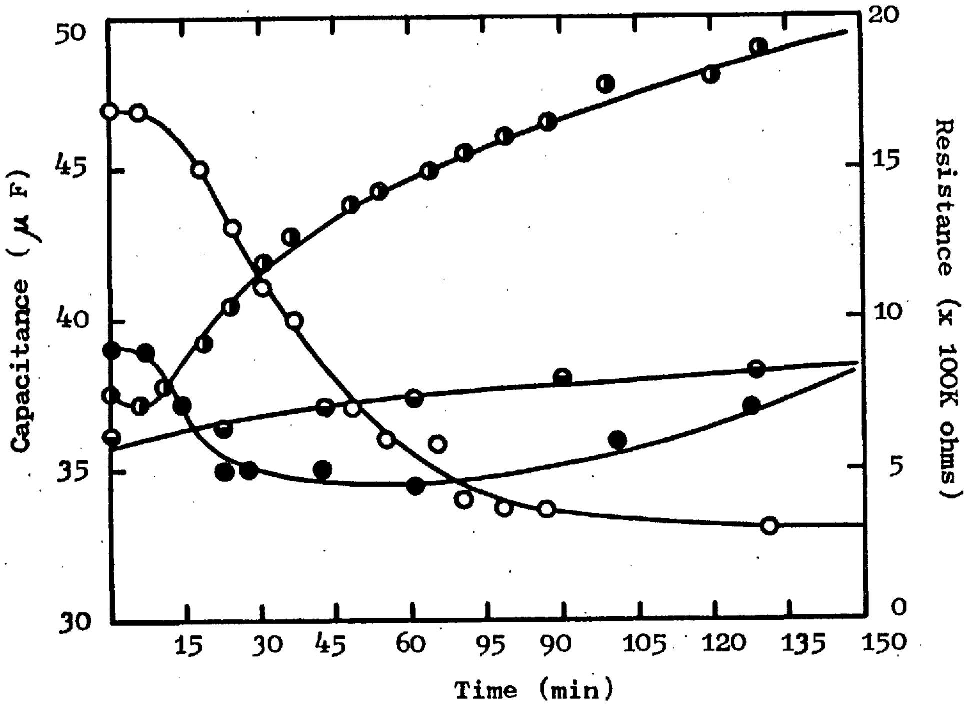


Fig. 9.11 Variation of capacitance and resistance with time for Cu/Ni in 0.2 M NaCl - 10% O_2 saturation

- o Capacitance in presence of polymer (20 p.p.m.)
- ● Capacitance in absence of polymer
- ◐ Resistance in presence of polymer (20 p.p.m.)
- ◐ Resistance in absence of polymer

physical or chemical must be assumed. Secondly, it is essential to know the dielectric constants of physically and chemically adsorbed material and also the mechanism and structure of adsorbed multilayers.

No quantitative deductions were made because of the lack of information on the dielectric properties of oxide formed on alloys or the adsorbed polymer. The results served only to demonstrate an increase in the resistance of the surface film (either modified oxide or adsorbed polymer) during its growth.

9.4 Electron Microscopy

The data obtained from polarization studies and capacitance and resistance measurements strongly suggested that inhibition was dependent on the formation of an oxide film, the structure of which was altered to become passivating in the presence of polymeric flocculants. Examination of inhibited and corroded surfaces by electron microscopy was considered a technique suitable for examining the difference in morphology or topography of the oxide surfaces. Published work has shown the presence of pores in certain oxide surfaces, particularly during anodic dissolution processes in which the nature of the pore determines the extent and rate of metal dissolution.(137)

Initially, electron diffraction by a single crystal of copper was employed. The aim was to observe a change in the well-defined scattering pattern given by a single crystal which might indicate the presence of adsorbed polymer layers. It was realised, however, that low atomic weight species (e.g. C,O,N) could not influence the electron beam significantly, although multilayers of adsorbed organic compounds might have an additive effect. The diffraction pattern obtained was predominantly that of a single copper crystal but which had superimposed on it a diffuse pattern which could have been either copper oxide or adsorbed layers of organic material (estimated thickness about 5A). Although the specimen was prepared by immersion of a single crystal of copper in deaerated polyacrylamide solutions, the possibility of oxide formation cannot be excluded, and was probably responsible for the diffuse pattern.

In investigating the structure of oxide layers on metals, it is usual to examine the oxide films by direct transmission after removing from the metal substrate. Unfortunately, this technique involves skilful manipulation of specimens and suffers from the disadvantage that such treatment might completely change its physical structure, particularly in the case of an alloy which undergoes preferential loss of less noble ions from the lattice - thereby establishing a concentration gradient within the oxide film.

Another method is to make a replica of the metal or metal oxide surface and examine it by transmission after suitable shadowing. This technique was adopted although it can be criticised on the grounds that in specimen preparation, such as the drying stage, the surface might change its physical form. However, specimens withdrawn from the polarization cell, during polarization resistance experiments, and dried with acetone, then replaced, continued their course where they left off, indicating a persistence in relevant surface structure and properties.

The technique employed was to withdraw the specimens from the polarization cell, rinse with acetone to dry and then take 'Formvar' replicas. After stripping the replicas from the specimen surface, it was necessary to dissolve any adherent oxide in 10% H_2SO_4 before drying and shadowing with carbon and gold. Non-adherent oxide was frequently removed from corroded electrodes, but never from inhibited specimens. This method gave satisfactory replicas that were not obscured by the presence of opaque copper and nickel corrosion products. The electron-micrographs of inhibited and corroding specimens are shown in Plate 9.1. a &b (Electron microscope made available by A.B. Pressland, Department of Chemical Engineering, Imperial College). There is seen to be a marked difference in surface topography; b, the inhibited specimen shows fairly uniformly distributed round projections with flat surfaces, whereas the freely corroding specimen is ruptured, fissured and porous. The interpretation of this difference could be the supression of growth of active centres on the inhibited surface.

Other experiments were devised to establish this effect of suppression of growth of active centres. In the early stages of

PLATE 9.1. a

PLATE 9.1. b

PLATE 9.2. a

PLATE 9.2. b

ELECTRON MICROGRAPHS OF CUPRO-NICKEL (X 10,000) oxidation of a metal surface, oxidation commences at nucleation sites randomly distributed over the surface, as shown in Plate 9.2 (a). This is the electron micrograph of a specimen prepared up to and including the cathodic reduction stage and then washed with distilled water containing dissolved oxygen and then dried. Specimen (b) is one which has had a similar treatment, but in the presence of Zimmite at every stage. The suppression of active centres in (b) is marked.

Similar experiments were attempted using a Stereoscan electron microscope. This microscope permits direct observation of specimen surfaces without the need to prepare replicas or thin oxide films. It was considered that the difference in pore structure might be revealed by examination of surface topography. The micrographs revealed some difference of surface structure, but the resolution of the microscope was not sufficient to show any distinct change in pore size. The thinness of the films may have been partly responsible for the poor resolution; if the oxide is less than about 1500-2000 A thick, the electron beam penetrates it and does not give a true indication of the nature of the outer surface.

10. DISCUSSION

10.1 Mechanism of inhibition

During normal flow of cooling water, cupro-nickel adequately resists the aggressive nature of saline estuarine waters. However, under static conditions,the alloy is not able to counter the effects of differential aeration cells set up within the tubes. Corrosion resistance is, of course, dependent on the nature of the oxide film formed at the metal-water interface. Thermodynamically, copper is very reactive, but the presence of an oxide film generally imposes an effective restraint on its oxidation.(138) The defect structure of the oxide has a major influence on its ionic diffusion characteristics, influencing the growth of the oxide and its subsequent reactions with its environment.(139) Intermittent flow, as encountered at West Thurrock, is likely to have an activating influence on protective oxide films(138) and makes them susceptible to dissolution through disproportionation and oxidation. In practice, the essential components in the system are alloy, H_2O, O_2, CO_2 and electrolyte. The corrosion products will be a composition of oxides and basic carbonates of the four alloy components. Corrosion studies in the laboratory have been carried out in the absence of CO_2, leaving the metal oxides as the principal solid corrosion product. Studies of the corrosion of copper have shown that the cuprous oxide which forms initially in neutral aerated waters readily adsorbs CO_2, to form a basic carbonate.

The overall composition of oxide on cupro-nickel has been shown by analysis to be equivalent to the composition of the alloy. However, a concentration gradient is established within the film; cuprous oxide (Cu_2O) forms as a thin film on the outside, because of the higher diffusion rate of Cu in the oxide, although it is more noble than Ni(140). In addition, oxides of iron and manganese must be incorporated into the structure. Superimposed on the concentration gradient of the metal oxides is the stoichiometry of the oxide layer. At the oxide-water interface, the oxide is oxygen-rich, resulting from an excess of O^{2-} ions; the converse applies at the oxide-metal interface, where the oxide is metal-rich.(141)

There are numerous theories in the literature on the mechanisms of corrosion inhibition in particular systems. All those involving an adsorption process at some stage require the establishment of an impervious film, either by oxidation of the metal surface to a passivating layer, or the adsorption of the inhibitor by chemical or physical bonding, the compound itself being the barrier to the process. Little reference is made to materials which may change the structure of a corrosion product (and bring about auto-passivation) without themselves being a major physical barrier to material transport. In the case of inhibitors such as SiO_3^{2-}, or HPO_4^{2-}, which are dependent on the presence of oxygen for inhibition, plugging of pores in the oxide film with corresponding metal salts has been suggested.(157) The mechanism of inhibition by colloidal material such as gelatine inhibiting the dissolution of steel in acid, has been attributed to blocking of active sites by physical and chemical adsorption and also the exclusion of the corrosive environment by its displacement.(136)(119) However, a significant piece of work has been recorded in the literature which postulates modification of a corrosion product by an organic colloid to form a passivating layer. This work was carried out by Campbell at the British Non-Ferrous Metals Research Association, around 1950(142). He discovered that inconsistencies in corrosion of copper pipes in tap-water were due to the presence of a colloidal organic inhibitor. Only certain waters had contained this inhibitor, in particular those passing through agricultural land, but not those drawn from deep wells. He postulated that the material (which unfortunately he was unable to identify) was responsible for changing the physical nature of the corrosion products from a coarse, open, structure to a close, fine grained passivating layer. The inhibitor, classified as anodic (possibly humic acid not destroyed by O_2-containing waters) was present only in small amounts (sometimes as little as 1 p.p.m.) but it could be detected polarographically. The work on this topic was discontinued after an alternative procedure for manufacturing the pipes was devised which eliminated corrosion in supply water. A possible similar mechanism might be concerned in the corrosion inhibition of copper and its alloys with benzotriazole(143). Polarization diagrams for the system benzotriazole and copper led to the conclusion that benzotriazole reinforces weak parts of the oxide film and is chemically bonded as a polymeric film to the oxide or metal surface. It is significant that the inhibitive power is 'less clearly defined in the presence of oxygen' though this could be attributed to the competing reactions between oxygen to form cuprous oxide and benzotriazole to form a complex, both of which passivate the metal. It is possible that chemisorption to form an impervious layer of complex and modification of the oxide layer enhancing passivity are both responsible.

The polarization curves obtained in the present work (Figs. 9.3,9.4) are typical for copper-based alloys in electrolyte solutions. In the presence of polymer (20 p.p.m. Zimmite) the curves are modified. The most marked effect is the reduction in current density - interpreted as corrosion rate - of the electrode subject to anodic polarization between +10 - -300mV (SCE), in the presence of 10% O_2 saturation. This effect is sufficient to reduce the corrosion rate of the differential aeration cell established in the condenser tubes to an insignificant level. The slight increase in the cathodic current density in the presence of Zimmite is attributable to either the introduction of small quantities of oxygen or the presence of reducible species in the Zimmite - the polymer itself is not reducible. There is a slight reduction in the anodic polarization curve, in the absence of oxygen, [illegible] between the potentials 0mV and -200mV SCE, indicating a reduction in the rate of dissolution of M^{2+} into solution. This observation means that a contribution to corrosion inhibition by a physically adsorbed polymer film cannot be ruled out. It seems reasonable that an adsorbed polymer layer can restrict loss of metal ions from the lattice, without decreasing reduction of oxygen. The dependence on the presence of oxygen for effective inhibition indicates that modification of the passivating oxide film is principally responsible for inhibition of corrosion - the plugging of pores by polymer does not seem a tenable theory. If the mechanism is solely dependent on a physically or chemically adsorbed barrier, graphs of current v. time (Figs. 9.6-9.9) might be expected to show rapid inhibition within seconds of polymer addition as adsorption of polymers is a rapid process (reported to be 90% complete within 2 seconds(92)). For instance, the adsorption of gelatine on nickel in acid solution involves a rapid increase in film resistance which soon reaches a limiting value(136). However, it took about 40 minutes to reduce the corrosion rate to 90% of the original under a constant potential of -150mV (SCE) at a concentration of 20 p.p.m. Zimmite. Continued maintenance at the preselected potential resulted in a current density which was almost immeasurable with the meter used. The free potential also drifted to a more noble cathodic value, indicating ennoblement of the metal

Table 9.2 shows the pH-dependence of the effectiveness of Zimmite as a corrosion inhibitor. At low pH values (e.g. less than about pH 3 - 3.5) the inhibitor is ineffective, whereas at neutral and slightly alkaline pH values it is effective. At highly alkaline pH values it again becomes ineffective. Flocculation of mineral suspensions at the extreme pH values is still possible (although the effect is reduced, Section 5.4) showing that adsorption of polymer is not prevented at these pH values. Examination of the Pourbaix diagrams for copper and nickel (Fig. 7.2) shows that they are very similar; the areas of passivation, immunity and corrosion almost coincide. In the absence of a Pourbaix diagram for 70/30 Cu - Ni alloy, it has been assumed that the alloy would have similar characteristics. It is highly significant that inhibition of the corrosion corresponds to the pH values at which oxide film formation occurs. In regions where metal dissolution and soluble oxyanion formation is possible, inhibition is virtually ineffective, despite continued adsorption of polymer. This is strong evidence for the theory that modification of the passivating oxide layer is responsible for inhibition. Because of the marked influence of the polymer on the anodic polarization curve it can be classified as an anodic inhibitor.

A number of different types of polymer were assessed as corrosion inhibitors (Table 9.2). It seems likely that the factors governing the adsorption of a polymer on a substrate (e.g. an oxide) govern, in part, the inhibition process.

At neutral pH values, data on the z.p.c. of hydrated metal oxides (i.e. Cu_2O and NiO) suggest that the charge of the oxide is positive, i.e. z.p.c. is at about pH 9-10(146). However, as far as is known, no data are available on the z.p.c. of surface films of mixed oxides. As these sites are anodic growth centres it is likely that the z.p.c. is lower than might otherwise be expected; this is indicated by the poor response of anionic polyacrylamides (e.g. Separan AP30), which have little restraining influence on oxide growth under anodic polarization. Anionic polymers adsorb to a very slight extent on negative mineral or oxide surfaces. Conversely, non-ionic and cationic polyacrylamides are very effective; they readily adsorb on negatively charged oxide surfaces. This can be demonstrated by their ability to flocculate copper hydroxide at alkaline pH (z.p.c. of hydrated $Cu(OH)_2$ $\div 9.4$).

Polyethyleneimines work particularly well as corrosion inhibitors, although they are not particularly good flocculants (being of relatively low mol. wt.). They are positively charged, but readily adsorb and restrain the corrosion process. This is a special case, as polyethyleneimines complex copper ions to form deep blue water-soluble compounds; the adsorption of a complex molecule on a substrate can significantly reduce its solvation characteristics and make it insoluble as a surface film.(126) Evidence for this is the small quantities required to give a degree of inhibition, equivalent to higher concentrations fo non-ionic polyacrylamide. Molecules which do not flocculate negatively charged clay particles do not act as inhibitors, e.g. Tylose MH 4000 (a sodium carboxymethyl cellulose) Polyox (a polyethyleneoxide), Tragaflok (guar gum product). All the effective inhibitor-flocculants were found to be capable of flocculating cuprous hydroxide dispersions.

10.2 Adsorption of polymeric flocculant and influence on oxide growth

Adsorption of polymer of high molecular weight requires a relatively long time to reach equilibrium, although 90% of the amount adsorbed at equilibrium does so within a few seconds(92). The capacitance and resistances v. time curves (Fig. 9.11) show that the capacitance for an inhibited specimen is higher than an uninhibited specimen, although the resistance for each specimen remains the same. The presence of non-ionic organic molecules has been shown to increase the double-layer differential capacitance of a dropping mercury electrode.(147). Therefore, high initial capacitance indicates a 'physically adsorbed' layer of polymer at the metal-solution interface. 'Physically adsorbed' is loosely applied here; bonding will be through hydrogen-bonding to metal oxide, as the metal is hardly likely to be free from oxide at neutral pH in an environment containing oxygen.

The resistance of the inhibited specimen increases as the capacitance decreases - which is equivalent to the build up of a passivating oxide layer. The resistance of the uninhibited specimen increases only slightly, as does the capacity. The latter effect is probably brought about by unrestricted film growth, off-set by an increase in capacitance as a result of hydration of the oxide film(145). It is possible that adsorption of polymer into the double layer at the electrode surface might reduce the activity of the O^{2-} or Cl^- which draw M^{2+} cations from the metal lattice. This could explain the slight effect of the polymer in the absence of oxygen. Once build-up of passive film starts in the presence of polymer - indicated by the increase in film resistance - capacitance decreases, indicating thickening of the oxide layer plus the possible increase in adsorbed polymer resulting from the formation of a continuous oxide film.

The mechanism of crystal growth on electrodes is still speculative, principally because of a lack of experimental data. Some cases of crystal growth have been investigated in which growth of nucleation centres has been shown to be two- or three-dimensional. It has been possible to follow the relationship between rate constants and their concentration and potential dependence.(148) However, in all but a few cases of crystal growth, the relative rates of lattice formation, surface diffusion and formation of lattice growth sites is uncertain. Once formed, growth of a continuous oxide layer is governed by the kinetics of migration of the reacting species. Studies on metals such as copper, nickel and aluminium have shown the existence of a duplex structure of the oxide film.(149) Such films consist of a thin amorphous layer of oxide next to the metal, with an outer porous layer of oxide. The porous layer is subject to considerable mechanical stress, because of the difference in volume between the oxide and metal.(150) Films of up to 10μ have been formed on Cu and found to have far less passivation than much thinner films.(158)

In the case of inhibition by modification of the structure of an oxide, it becomes necessary to consider the effects of an adsorbed molecule on crystal morphology.

Much effort has been devoted to the study of crystal growth and the governing factors. Of particular interest is the influence of impurities on morphology. When sufficient impurity is added to an electroplating solution, it is possible to reduce the size of crystals considerably, e.g. on adding gelatin to $CdSO_4$ and $CuSO_4$ plating baths there is a reduction in grain size from 1 mm to 0.2μ - 1μ (151b) Such additions are known to have marked influence on physical properties such as hardness, resistance and strength,(all of which are increased.) Uniform fine grain size results because the very high critical supersaturation required for growth of crystals in solutions with high impurity content cannot be maintained because the rate of diffusion of metal ions to the crystal decreases - crystals grow to a limiting size and stop. Impurities which modify crystal morphology are not necessarily incorporated into the crystal. The impurities adsorb at high energy sites, blocking growth and creating new nucleation sites, the rate of formation of which increases with increasing impurity level. There can be little doubt that flocculants such as polyacrylamide are capable of increasing nucleation rates during oxide growth and developing a passivating film of small grained oxide which has increased ionic resistance, mechanical strength and adhesion.

Of particular relevance are the studies of the interaction of polyelectrolytes and supersaturated salt solutions. It has been known for some time that high molecular weight polymers (e.g. sodium polyacrylate) in very small quantities (1 p.p.m.) are capable of suppressing crystal growth from supersaturated solutions (e.g. calcium carbonate) and extending the incubation period for such growth by many times.(161) The crystals when they are formed are different in structure from the untreated crystals,(159) but vary in size with the concentration of polymer in the mother liquid; they are smaller in size than normal crystals(151a). The progressive increase in crystal size suggests that orientation of polymer adsorbed on nucleation sites influences the subsequent growth of the crystals; at low concentrations, more segments will be adsorbed per polymer molecular and tend to lie flat on the surface, whereas at higher concentrations fewer segments per molecule are adsorbed and much of the molecule is extended into the solution(152).

The suppression of salt precipitation has been claimed for Zimmite(71), which is said to restrict the deposition of calcium carbonate from solution. Doubtless the polymer adsorbs at high energy sites and restricts growth as well as redistributing growth along other crystal axes. This effect was confirmed during the preparation of thin films of copper hydroxide. Solutionsof equimolar copper sulphate and sodium hydroxide were separated by a dialysis membrane. Sodium hydroxide diffused through the membrane and formed a thin film at the membrane surface in contact with $CuSO_4$ solution. Normal film growth has a 'nodular' structure - this is the term applied to coarse grained film growth observed during calcium carbonate deposition from supply waters containing HCO_3^- - and is very fragile. In the presence of small quantities of polymer (10 p.p.m.) the film has an 'egg shell' structure - this means that it has a finer grain structure and greater mechanical strength. Similar effects have been observed during deposition of carbonate from supply waters - the presence of organic colloids (e.g. egg albumen) imparts a fine grained structure to the deposit(153). Traces of gelatin or organic soil extract have also been shown to inhibit the precipitation of calcium salts from natural waters and impart an apparent degree of hardness higher than the theoretical value(154).

Good evidence for this theory is found on examining the electron micrograph of the Formvar replicas of electrode surfaces. Plate 9.2

(a) shows a surface covered with growing active centres (the circular areas are projections from the oxide surface) where film growth is spreading laterally in the form of flat plateaux proceeding until they become like the surface in Plate 9.1(a). In this particular case, the oxide first grows outwards and upwards, has little mechanical strength because of internal stress(150) and offers little resistance to the transport of cations or anions through its lattice. It does not passivate the surface and the rate of growth is constant, as indicated by the constant current density recorded at a constant applied potential. Such growth follows a rectilinear equation (i.e. $y = kt$, where y is the thickness, k the proportionality constant and t is time), which is typical of a corrosion mechanism in which the corrosion products do not significantly influence the kinetics of film growth. In comparison, the appearance of raised plateaux in Plate 9.1(b) which have been formed after an equivalent number of coulombs have been consumed as in Plate 9.1(a) indicates that growth of active centres has been suppressed. Minor plateaux can also be observed and could either be (1) nucleation sites suppressed early in growth or (2) fresh active centres, suppressed after redistribution during corrosion of growth from incipient active centres.

This theory is confirmed by the observations on specimens prepared to the cathodic reduction stage and then allowed to come into contact with O_2-containing water. Uninhibited surfaces rapidly form nucleation centres (Plate 9.2(a)) whilst inhibited specimens reveal almost complete suppression of active sites and the formation of a 'two-dimensional' surface film. No detailed analysis for the rate law for the growth and passivation of the surface shown in Fig. 9.1(b) has been made, partly because the oxidation presents difficulties (as the structure of the oxide is unknown) and partly because the mechanism of inhibition is not necessarily solely attributable to auto-passivation by modification of the oxide structure. Experimentally it is difficult to assign a growth law to film build up and frequently the type of growth changes with film thickness(155). The rate of growth may be dependent on (1) rate of cation dissolution from the lattice, (2) rate of anion formation, (3) the rate of dissolution of oxygen to the metal surface. However, the films exhibit an approximately logarithmic relationship, i.e. $W = k_1 \log (k_2 t + 1)$ where W is the decrease in current density and k_1 and k_2 are constants probably dependent on concentration of inhibitor. The isotherm Fig. 9.8 shows the different curves of the same type, obtained at different concentrations of Zimmite; k_1 and k_2 change with concentration - the increase in polymer concentration increases the rate of nucleation of the two dimensional surface film and in the absence of outward growth of oxide passivity is soon established.

Inhibition of corroded surfaces is a slower process (Fig. 9.9). The existing oxide is very porous, which presumably restricts the diffusion of the colloidal polymeric flocculant to the points at which oxide is forming. Once the polymer has access it restricts the incipient type of growth and encourages the formation of close grained impervious films.

Polymers adsorb strongly on oxide surfaces (where bonding is possible) the heats of adsorption can be in the order of 5×10^3 k cal/mole As poisons of crystal growth they are not necessarily incorporated into the oxide layer but, once adsorbed, their influence on the oxide morphology persists even in the absence of polymer in bulk solution (Fig. 9.7); the greater the concentration the greater the nucleation rate and the more rapid is the build up of a fine grained oxide film having high mechanical strength, adhesion and ionic resistance.

11. SUMMARY OF CONCLUSIONS

Investigations into the corrosion inhibition of cupro-nickel by a proprietary mud remover (a polymeric flocculant) have led to the following conclusions:

1. Corrosion of copper and copper-based alloys in neutral saline waters can be inhibited by the presence of small quantities of synthetic polymeric flocculants of high molecular weight.
2. The main effect of the organic polymer - which must have the facility to adsorb on the metal oxide surface - is to modify crystal growth of the oxide and influence the morphology to the extent that a two-dimensional passivating layer is formed.
3. The inhibitors can be classified as 'anodic' because of their influence on anodic polarization curves. Evidence suggests that adsorption of the polymer molecules contributes to inhibition by partial exclusion of the corrosive environment i.e. 'solvent displacement inhibition'.
4. Laboratory tests simulating conditions in condenser tubes, combined with the knowledge of the corrosion mechanism and its inhibition indicate that use of polymeric flocculants could be of practical value in industrial cooling water systems. There is also evidence to suggest that inhibition of corrosion of old tubes could be effected by suitable treatment with polymer.

APPENDIX I

List of flocculants and coagulants tested during investigation; prices quoted were current for November 1966 - (5 tons minimum) ((S) = solid, (L) = Liquid)

Flocculant - name or code number	Manufacturer or Agent in Britain	Chemical type, (manufacturers specification)	Mol. Wt. (x 10^6)	Cost/lb
Zimmite	Zimmite of Europe Ltd., London, S.W.7.	non-ionic polyacrylamide (S)	6	20/-d
Magnafloc R139	(	anionic polymer (S)		8/6d
Magnafloc R140	(Allied Colloids Co. Ltd.,	cationic polymer (S)		8/6d
Magnafloc R155	(Bradford	anionic polymer (S)	12	8/6d
Separan NP10	(	non-ionic polyacrylamide (S)	1	8/6d
Separan NP20	(R.W. Greeff & Co. Ltd.,	non-ionic polyacrylamide (S)	3	13/1¾d
Separan AP30	((Dow Chemical Co.)	anionic polyacrylamide (S)	2-3	9/5¾d
Separan C90	(London, E.C.2.	cationic polyelectrolyte (L)		3/9½d
Separan C120	(	polyethyleneimine: cationic (L)	0.05-0.10	4/7½d
Flocbel FC10	(Float-ore Ltd.,	cationic polyacrylamide (S)		7/9d
Flocbel FC11	(Uxbridge, Middlesex	cationic polyacrylamide (S)		7/9d
Flocbel FC109	(	non-ionic polysaccharide (S)		-/9½d
Sedomax HP	(	anionic vinyl polymer (S)		9/9d
Sedomax F	(I.C.I. Ltd.,	anionic vinyl polymer (L)		-/11½d
Sedomax G	((Chemicals Dept.London North)	anionic vinyl polymer (L)		1/1d

APPENDIX I (cont.)

A.100	(	anionic acrylamide copolymer (S)		8/3d
C.100	(	cationic polyacrylamide copolymer (S)		9/3d
C.110	(	cationic polyacrylamide copolymer (S)		9/3d
CL.40	(B.T.I. Chemicals Ltd., (Bradford	cationic tertiary substituted polyamide (L)		1/11d
CL.80	(	cationic, quarternary substituted polyamide (L)		1/11d
Superfloc 16	(	non-ionic polyacrylamide (S)	3-5	11/3d
Superfloc 20	(Cyanamid of Gt. Britain Ltd.,	non-ionic polyacrylamide (S)	>3-5	11/3d
Aerofloc 550	(London, W.C.2.	polyacrylate (S or L 20% w/v)		6/5d
Tragora 40	(Tragarol Products Ltd.,	mannogalactan (S)		2/2d
Tragora 55	(Hooton, Cheshire	modified mannogalactan (S)		5/7d.
Floccotan	(Forestal Industries ((U.K.) Ltd.	amphoteric tannin derivative (L; 45% w/v)	>0.05	-/9d
Nalco 600	(Nalco Ltd.,	cationic polyelectrolyte (L)		2/6d.
Nalcolyte 670	(London, W.1.	non-ionic polymer (S)	>1.0	12/4d
Nalco 632	(	cationic polymer (L)		3/8d
Tylose MH 4000	(Hoescht Chemicals Ltd.,	methylhydroxyethyl cellulose (S)		5/9½d
Tylose CB4000	(London, S.W.1.	carboxymethyl cellulose (S)		5/11½d
Tylose MH 4000P	(	hydroxyethyl cellulose (S)		5/11½d
Primafloc C3	(Lennig Chemicals Ltd.	cationic polyamine (L; 30% w/v)		3/6½d
Primafloc C5	(London, W.C.1.	cationic polyamine (L; 25% w/v)		2/5d
Primafloc C6	(	cationic polyelectrolyte (L;20% w/v		3/11d
Primafloc C7	(	cationic polymer (S)	> 1	9/5d

APPENDIX I (cont.)

Polyflok PX	((	non-ionic polyacrylamide (L; 10% w/v)	2	1/-d
Polyflok 209P	(The Yorkshire Dyeware and	ethylene oxide condensate (S)	10	8/9d
Powdaflok	(Chemical Co., Ltd., Leeds	starch chloride (S)		-/4½d
Tragaflok	(	pre-gelatinised starch (S)		-/10d
Wisprofloc P	(	cationic starch derivative (S)		2/9d
Wisprofloc 20	(	anionic starch derivative (S)		1/3d
Polymer X-150	(Union Carbide Ltd.,	cationic polymer (L; 28% w/v)		5/3½d
Polyox	(Rickmansworth, Herts	polyethylenoxide (S)		
Gelatine	(	protein (S)		4/5½d
Glue (bone)	(Edward Gorton Ltd.,	protein (S)		1/3d
Glue (hide)	(Warrington	protein (S)		1/7½d
	INORGANIC COAGULANTS			
Aluminium chloride	(Berk Ltd., (London, W.1.	$AlCl_3$ $6H_2O$ (L; 48-52 % w/w)		-/3d
Ferric chloride	(	$FeCl_3$ (L; 38-40 % w/w)		-/3½d

APPENDIX II

Calculation of the statistical end-to-end distance of non-ionic polyacrylamide in aqueous solution.

Symbols	$[\eta]$	intrinsic viscosity in ordinary solvent
	$[\eta]_\Theta$	intrinsic viscosity in Θ solvent
	α_η	expansion factor
	M	molecular weight of polymer
	Φ_o	universal constant 2.87×10^{23} (c.g.s.)
	B	polymer solvent interaction parameter
	$\langle Ro^2 \rangle$	mean square dimension of polymer chain
	$\langle R^2 \rangle^{\frac{1}{2}}$	'real dimension' - root mean square end-to-end distance of polymer chain.
	$\langle So^2 \rangle$	unpeturbed mean square radius of gyration
	$\langle S^2 \rangle$	real unpeturbed mean square radius of gyration.

According to Stockmayer and Fixman

$$[\eta] = [\eta]_\Theta \alpha_\eta^3 \tag{1}$$

$$[\eta] = KM^{\frac{1}{2}} \tag{2}$$

where

$$K = \Phi_o \, A^3 \tag{3}$$

and

$$\alpha_\eta^3 = 1 + 1.55Z \tag{4}$$

A and Z are defined thus

$$A^2 = \langle Ro^2 \rangle \, M^{-1} \tag{5}$$

and

$$Z = \left(\frac{3}{2\pi}\right)^{3/2} BA^{-3} \, M^{\frac{1}{2}} \tag{6}$$

By combining these equations

$$[\eta] = KM^{\frac{1}{2}} + 0.51 \, \Phi_o \, BM^{\frac{1}{2}} \tag{7}$$

dividing through by $M^{\frac{1}{2}}$

$$[\eta] \, M^{\frac{1}{2}} = K + 0.51 \, \Phi_o \, BM^{\frac{1}{2}} \tag{8}$$

A plot of $[\eta]\, M^{-\frac{1}{2}}$ against $M^{\frac{1}{2}}$ gives a straight line of slope $0.51\, \Phi_o B$ and intercept K. By substituting K in equation (3) $\langle Ro^2 \rangle$ can be determined from equation 5: then substituting B into equation (6), Z is determined. This enables α_η to be calculated from equation (4),

but $\langle So^2 \rangle = ((\frac{1}{6})\, \langle Ro^2 \rangle$ (9)

and $\dfrac{\langle S^2 \rangle}{\langle So^2 \rangle} = \alpha_S$ (10)

where $\alpha_S^{\;3} = \alpha_\eta^{\;2.43}$ (11)

The relationship between the number average molecular weight and the intrinsic viscosity at 30°C is reported by Dainton$^{(167)}$ to be

$[\eta] = 6.8 \times 10^{-4}\, M^{0.66}$ (12)

Sakaguchi and Nagase$^{(36)}$ have obtained curves for plots of $[\eta]\, M^{-\frac{1}{2}}$ against $M^{\frac{1}{2}}$ values calculated from equation 12. Values of K (intercept) and B (slope) were obtained.

$K = 3.40 \times 10^{-3}$ (13)

$B = 2.10 \times 10^{-27}$ (14)

From equation (12) when the molecular weight is 6×10^{6} $M^{\frac{1}{2}} \times 10^{-2} = 24.5$ and $[\eta] \times M^{-\frac{1}{2}} \times 10^{-3} = 8.23$. Substituting K and M values into equations (3) and (5):

$\langle Ro^2 \rangle = 1.480 \times 10^{-10}$

$\langle Ro^2 \rangle^{\frac{1}{2}} = 1.217 \times 10^{-5}$ (16)

The dimension of the polymer chain in a theta solvent is 1217 Å. Using the value of $B = 2.10 \times 10^{-27}$ values of Z, α_η and α_S were calculated

$Z = 1.433$ (17)

$\alpha_\eta = 1.466$ (18)

$\alpha_S = 1.363$ (19)

From the above $\langle S^2 \rangle$, $\langle S^2 \rangle^{\frac{1}{2}}$ and $\langle R^2 \rangle^{\frac{1}{2}}$ can be calculated

$$\langle S^2 \rangle = 3.361 \times 10^{-11} \qquad (20)$$

$$\langle S^2 \rangle^{\frac{1}{2}} = 5.797 \times 10^{-6} \qquad (21)$$

$$\langle R^2 \rangle^{\frac{1}{2}} = \frac{\langle S^2 \rangle^{\frac{1}{2}}}{6^{\frac{1}{2}}}$$

$$= 1.420 \times 10^{-5} \qquad (22)$$

Therefore the statistical end-to-end distance of a non-ionic polyacrylamide molecule, molecular weight 6 x 10^6, is calculated to be 1420 A.

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