Factors Effecting a Loss of Flocculation Activity of Polyacrylamide Solutions: Shear Degradation, Cation Complexation, and Solution Aging

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Synopsis

Polyacrylamide and poly(acrylamide-co-acrylic acid) flocculant solutions were subjected to shear degradation in a rotating cone instrument. At constant shear rate, shear degradation was minimized (highest limiting intrinsic viscosity) by the use of a lower solution concentration and high ionic strength of the polymer solution. Resistance to shear degradation also increased with increasing anionic character of the polyacrylamide. Sheared polymers showed reduced performance as flocculants of coal preparation plant tailings, their major commercial application in the U.K. Partially anionic polyacrylamide solutions were completely inactivated in the presence of certain multivalent cations. Aluminium, iron$_{\mathrm{III}}$, lead, copper, and zinc ions formed complexes with the carboxyl groups on the polymer, resulting in zero flocculation activity. Nonionic polyacrylamides were unaffected. Viscosity–aging of polyacrylamide solutions was observed over a period of several months, but was insufficient to affect the flocculation activity. In the presence of 3% ethanol or methanol, no aging was observed in solutions stored for over a year.

INTRODUCTION

The major market for polyacrylamide flocculants in Britain is in the treatment of coal preparation plant tailings. These tailings consist of a suspension of fine clay particles in water, resulting from a breakdown into fines of the lumps of shale brought up with the coal as run-of-mine material. Polyacrylamide flocculants are used to effect rapid solid–liquid separation to facilitate recycling of the water in the washery, and disposal of the solids. Commercially, the type of polyacrylamide used to treat tailings is chosen from a range of nonionic polyacrylamides and anionic products (where a percentage of the amide groups has been converted to carboxyl groups). Cationic polyacrylamides are not normally used, because of their higher cost and the lower molecular weights available. The most successful polymer type, producing a rapid solids sedimentation rate, good supernatant clarity, and good dewaterability of the thickened tailings, is a very high molecular weight, moderately anionic (30–50% carboxyl groups) polyacrylamide.[1]

The sedimentation rate obtained with flocculated tailings is strongly dependent on the molecular size of the polymer. This implies that any reduction in molecular size will adversely affect flocculation performance. One established cause of molecular weight reduction is shear degradation,[2] which may be expected to occur in practice as the polymer solution is pumped around the

coal preparation plant. Some shear degradation is probably inevitable; however, it is possible to minimize this by an understanding of the effects of shear rate, shear time, concentration, polymer type, and ionic strength. (The latter affects the "goodness" of the solvent.)

The complexation of some multivalent cations with the carboxyl groups on anionic polyacrylamides was observed some time ago,[3] and has frequently been used to explain the binding of anionic flocculants to negatively charged particles (the "salt-link" mechanism), where the cations are absorbed onto the surface of the particles.[4] However, the implications of the presence of these cations in solution with the polyacrylamide alone, in the absence of particles, have not been detailed. In practice, flocculant solutions are prepared using recycled clarified water and the dissolved salt content of this water is very high (~ 10 g 1^{-1}) because of soluble minerals in the run-of-mine material.

The aging of polyacrylamide solutions has been a subject of some controversy. Some authors, e.g., Narkis and Rebhun,[5] have proposed a disaggregation of entangled polyacrylamide molecules during aging, a process observed by changes in the viscosity of the solution. Recent work by Kulicke and co-workers [6-8] has confirmed this view of the disappearance of aggregates. Other workers have presented evidence for a chemical aging, involving the production of free radicals from traces of persulphate left over from the polymerization initiation reaction.[9,10]

EXPERIMENTAL

Polyacrylamides

Polyacrylamide flocculant samples were kindly supplied by Allied Colloids Ltd., Low Moor, Bradford, BD12 OJZ, United Kingdom. The percentage anionic charge was supplied by the manufacturer. Solutions were prepared in glass-distilled water to a stock concentration of 0.1% w/v by shaking for 30 s and allowing the solution to stand. Solutions were normally fully active as flocculants within 1 h.[1] The stock solution was diluted to 0.01% w/v before flocculation tests ensure better mixing.

Viscometry

Viscometry measurements were made in a suspended level capillary viscometer. All measurements were made in $1M$ $NaNO_3$, since commercial "nonionic" polymers are often only nominally nonionic and a small percentage of the amide groups may be hydrolyzed. The temperature was $30°C$.[11] Prior to viscosity measurements, all solutions were filtered through a sintered glass disk (no. 1 pore size) to remove small particles. It was observed that solutions filtered through a clean sinter gave lower capillary flow times; this was attributed to a reduction in concentration due to adsorption of some of the polyacrylamide onto the sinter. Harrington and Zimm[12] observed an anomalous plugging of sintered glass discs by high molecular weight polymers, due to the multiple adsorption sites provided by the very high surface area. Therefore, glass sinters were routinely "presaturated" with the solution of interest until a constant viscometer flow time was obtained. Adsorbed polymer could be removed by soaking the sinter in Decon 90.

Kaolin Suspension

A standard kaolin suspension was prepared at 5% w/v in distilled water with 0.2% analytical grade sodium chloride. Kaolin was grade E clay supplied by English China Clays Ltd., St. Austell, Cornwall (20% particles < 2 μm). The suspension was always left overnight to equilibrate.

Tailings

Tailings samples were from Parkside Colliery, Lancashire (Western Area N.C.B.). The solids content varied between 4 and 8% w/v; the pH was between 7 and 8. Particle size analysis (Coulter Counter model TAII) showed that 70% of the particles were smaller than 5 μm and 35% smaller than 2 μm. The major mineral constituents were silica and the clay minerals kaolinite and illite. The total dissolved solids content of the tailings was high ($\sim$ 10 g L^{-1}) due to continuous recycling of the washery water and a buildup of soluble salts from the mine. The principle ions present were sodium, chloride, calcium, magnesium, and sulfate. These salts produced a small degree of coagulation of the clay particles and a measureable solids sedimentation rate ($\sim$ 0.05 cm min^{-1}).

Flocculation Test Methods

The sedimentation rate test was used as the most appropriate flocculation test method for tailings, since rapid solids separation is the most important criterion in tailings thickening; supernatant clarity, floc volume, and floc dewaterability are of lesser importance. Tailings were flocculated in a stoppered 500 mL measuring cylinder, using five complete inversions after addition of the polymer solution.

Liquid Shear Apparatus

The apparatus used to subject polymer solutions to a known and reproducible shear rate was a workshop design,[13] consisting of a stationary cup containing a rotating cone. The speed of rotation and the gap between the stationary and rotating members could both be varied. The polymer solution was fed into the base of the cup by a low speed Watson-Marlow peristaltic pump, and the sheared polymer solution withdrawn from the top of the apparatus. The solution residence time in the apparatus was of the order of 3 s. The action of the peristaltic pump alone caused no detectable change in the solution intrinsic viscosity.

RESULTS AND DISCUSSION

Shear Degradation of Polyacrylamides

Figure 1 shows the effect of shear time and shear rate on the intrinsic viscosity of a nonionic polyacrylamide. The shear time was varied by the number of times the solution was passed through the liquid shear apparatus. Shear rates were selected in the range which might be produced by pumping operations.[14,15] Figure 1 shows that the polymer is degraded according to the
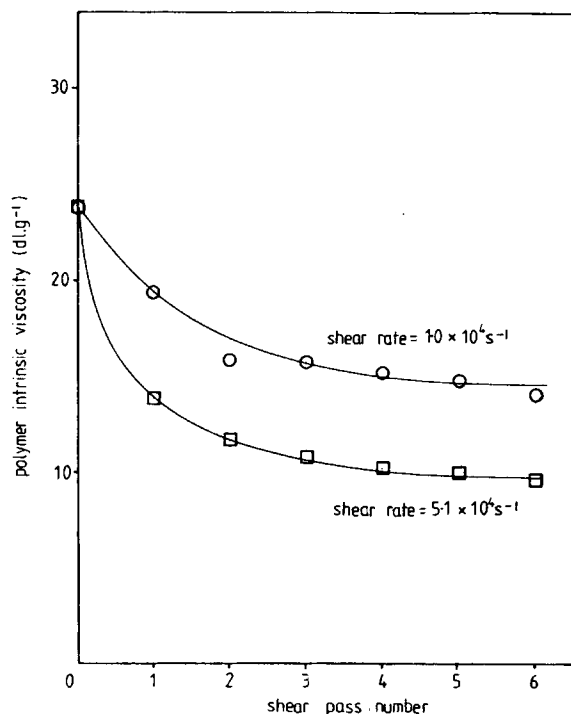
Fig. 1.   Shear degradation of a nonionic polyacrylamide by repeated passes through the shear test apparatus. Polymer concentration = 0.1% w/v in distilled water.

well-established pattern of a rapid decrease in intrinsic viscosity (IV), as the number of passes through the apparatus is increased, towards a constant, limiting the value of IV. As expected, the limiting value is lower for the higher shear rate.

The effect of solution concentration is shown in Figure 2, using a 20% anionic polyacrylamide. (Experimental results showed a similar effect for a 50% anionic polymer and a nonionic polyacrylamide.) Only two concentrations were used, 0.1 and 0.04% w/v. After shearing of the solutions in water, sodium nitrate was added to the sheared polymer solutions in order to eliminate the polyelectrolyte effect before determining the intrinsic viscosity. A solution concentration in excess of 0.1% w/v was not used because the polymer is extremely viscous and difficult to handle. A solution concentration below 0.04% was not used because of the difficulty in accurately measuring the viscosity of a dilute solution. It is evident that the higher concentration solution is degraded more. This is probably because, at a constant shear rate, the higher concentration solution is subjected to a higher shear stress, since it has a higher viscosity. These results are consistent with the general agreement in the literature[2,16] that polymer degradation increases with concentration at constant shear rate. The relationship between degradation and concentration at constant shear stress has given rise to conflicting opinions.[2] However, this is of limited relevance to the present work. The shear rate is fixed by the conditions on the plant.
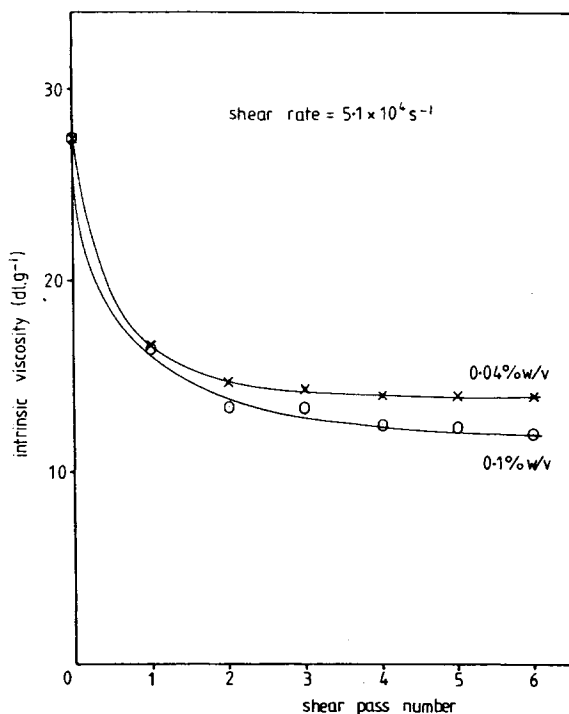
Fig. 2. Molecular degradation of a 20% anionic polyacrylamide in distilled water, by repeated passes through the shear test apparatus. Shear rate = 5.1×10^4 s^{-1}.

Polyacrylamide solutions prepared on a commercial scale are often dissolved in recycled plant water of very high ionic strength. The ionic strength of a typical sample of coal preparation plant water was calculated to be 0.087. Unfortunately, some of the ions present in coal preparation plant water form complexes with anionic polyacrylamides, making it impossible to determine the intrinsic viscosity of the solution even in the presence of strong salt solution (see the following section). Therefore, the ionic strength of poly-acrylamide solutions was varied using an "indifferent" electrolyte, sodium nitrate, which does not form complexes with polyacrylamides.[3] Solutions of a 30% anionic polyacrylamide dissolved in water and in various concentrations of sodium nitrate solution were repeatedly passed through the liquid shear apparatus. The sodium nitrate concentration was then increased in all cases to $1M$ to facilitate viscosity measurements. The data shown in Figure 3 indicate that the polymer dissolved in water only is most susceptible to degradation, and increasing resistance to degradation is encountered up to $1M$ NaNO$_3$.

An anionic polymer in distilled water has an extended conformation due to the polyelectrolyte effect. In strong salt solution, the polymer is in the form of a compact coil. Strong salt solution is therefore a poorer solvent for an anionic polyacrylamide. Some workers have reported greater polymer degradation in a poor solvent,[17] but others[18,19] have presented conflicting results, showing that the extent of chain degradation increased for greater polymer chain expansion. The present results are in accordance with the latter authors.
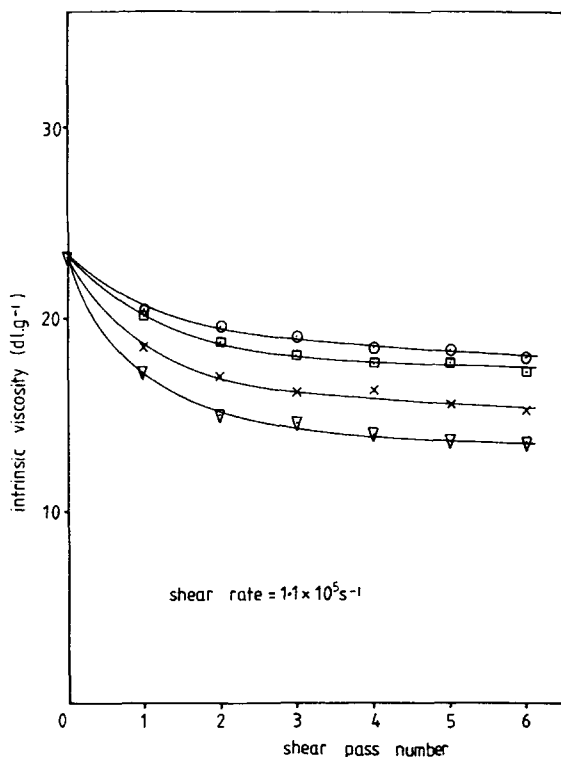
Fig. 3. Influence of solvent on shear degradation of a 30% anionic polyacrylamide. Polymer concentration = 0.1% w/v, shear rate = 1.1×10^5 s^{-1}. (○) $1M$ NaNO$_3$; (□) $0.1M$ NaNO$_3$; (×) $0.01M$ NaNO$_3$; (▽) water.

Polymer coil dimensions may also be varied by varying the anionicity of a polymer of fixed intrinsic viscosity. The results illustrated in Figure 4 show the shear degradation of a series of polymers of varying anionicity produced by hydrolysis of the same parent nonionic polyacrylamide, and therefore having approximately the same intrinsic viscosities when dissolved in $1M$ NaNO$_3$. The polymers were subjected to shear degradation when dissolved in distilled water, and sodium nitrate was added subsequently in order to determine the intrinsic viscosity. Unexpectedly, the more highly ionic polymers were degraded less than those of lower anionicity. These results are difficult to reconcile with the previous results, since the more anionic polymers are subject to a higher shear stress at the same shear rate. It is curious that the extended conformation of the anionic polymer protects it from molecular breakage more than the coiled conformation of the nonionic polymer, whereas the same anionic polymer in strong salt solution, where it is coiled, becomes more susceptible to damage.

The reduction in intrinsic viscosity of the sheared polyacrylamide samples caused a reduction in flocculation activity with tailings (Table I). The sedimentation rate of flocculated tailings was strongly dependent on the intrinsic viscosity of the polyacrylamide used; Figure 5 shows the relationship between sedimentation rate and log (polymer intrinsic viscosity) for flocculated tail-
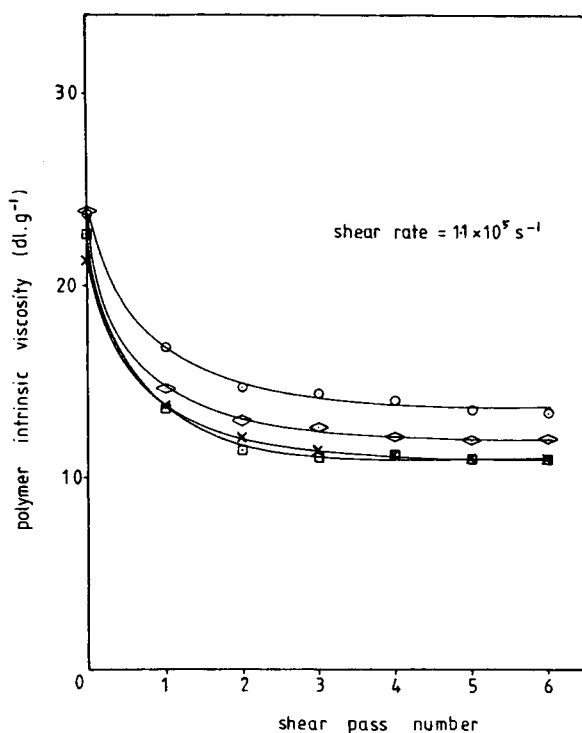
Fig. 4. Effect of polyacrylamide percentage anionic charge on shear degradation. 0.1% w/v aqueous solution, shear rate = 1.1×10^5 s^{-1}. Polymer samples prepared by controlled hydrolysis of a single, nonionic parent material. Anionic charge (%): (○) 32; (◇) 26; (□) 14; (×) 7.

TABLE I
Reduction in Tailings Flocculation Activity
of Sheared Polymer Solutions[a]

Polymer	Anionic charge	Sedimentation rate using unsheared polymer	Sedimentation rate using sheared polymer	Activity as percentage of original rate
A	7.4	2.23	0.48	21%
B	13.5	3.34	0.65	19%
C	25.7	7.11	1.93	27%
D	31.8	7.90	2.94	37%

[a] Dosage = 0.08 mg/g tailings solids.

ings. Even though the polyacrylamides varied in anionic charge between 0 and 100%, the correlation was strong ($r = 0.94$).

In contrast, the sedimentation behavior of flocculated kaolin was found to be only weakly dependent on the polymer intrinsic viscosity ($r = 0.33$), the polymer charge being of greater importance (Fig. 6). Hence, sheared polyacrylamide solutions showed little change in activity with the kaolin suspension.
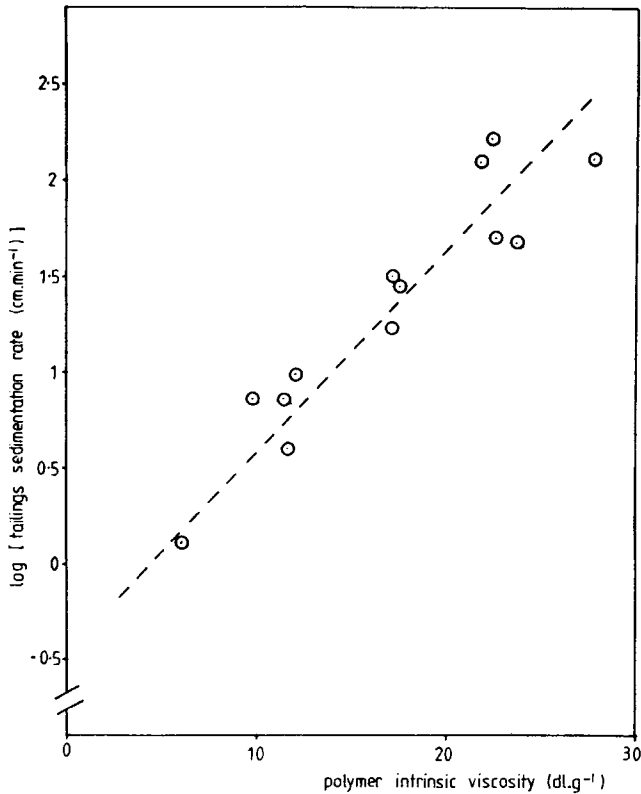
Fig. 5. Dependence of flocculated tailings sedimentation rate on the intrinsic viscosity of the polyacrylamide. Polyacrylamides of various anionic charges (0–100%). Polymer addition = 0.4 mg/g solids.

Inactivation of Anionic Polyacrylamides by Complex Formation

A range of cations which might possibly occur in the water used commercially to prepare a flocculant solution were tested for their effect on the solution activity. All cations were used as the nitrate salt, to avoid the formation of cation–chloro complexes.[3] The polymer solution was taken as 100% active if it produced the same tailings sedimentation rate in the presence of the cation as in its absence. 0% activity was recorded if the sedimentation rate was identical to that of untreated tailings.

A solution of a nonionic polyacrylamide (0.02% w/v) was completely unaffected by the presence of up to $0.1M$ sodium, potassium, calcium, magnesium, copper, zinc, lead, aluminium, and iron$_{III}$ ions. In contrast, the activity of a 0.02% w/v solution of a 30% anionic polyacrylamide was severely affected by several of these species. (No attempt was made to control the pH in these experiments, since the cation concentration was low in most cases and any buffering substances could have introduced further complexation problems).

The cation concentration range over which the polymer is inactivated is shown in Figure 7 for lead and copper and Figure 8 for zinc and aluminium.
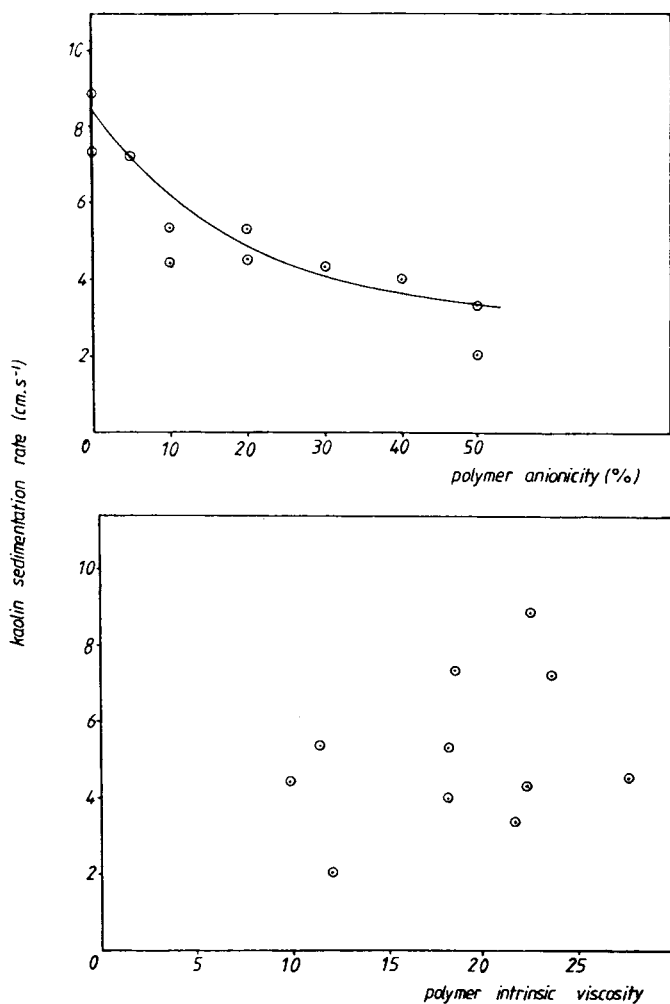
Fig. 6. Molecular characteristics of polyacrylamides influencing flocculation activity with kaolin suspension. Polymer addition = 0.8 μg/g kaolin.

Aluminium is a particularly powerful inactivator of anionic polyacrylamides, and complete inactivation of a 0.02% w/v solution is achieved at an Al^{3+} concentration of only about $10^{-5}M$, equivalent to about 2.7 ppm. $Iron_{III}$ inactivation occurs at a similar concentration. In Figure 9, a series of polyacrylamides of various anionic charges is illustrated. It is apparent that there is a direct relationship between the number of carboxyl groups on the molecule and the concentration of $iron_{III}$ needed to inactivate the flocculant.

Complex formation between a cation and an anionic polyacrylamide is not in itself sufficient to reduce flocculation performance. Sodium and potassium ions do not form complexes with anionic polyacrylamides, but calcium and magnesium ions do,[3] and yet they do not influence the flocculation activity of the polymer. The reason is that calcium and magnesium form 1:1 complexes with carboxyl groups[3] and hence do not affect the polymer conformation, other than by a minor effect on the polyelectrolyte effect. However, a cation
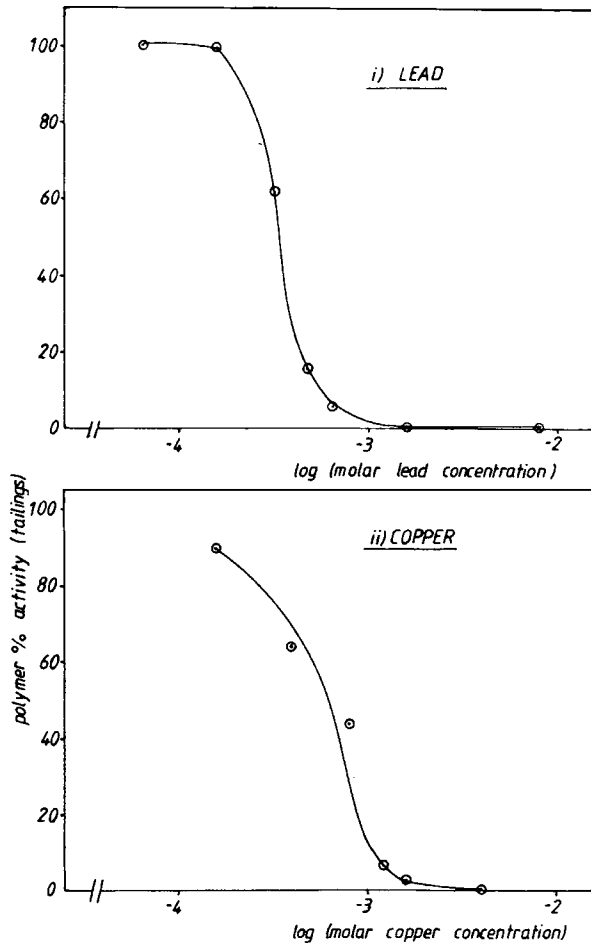
Fig. 7.   Inactivation of a 0.02% w/v solution of a 30% anionic polyacrylamide (IV = 22) by lead and copper ions in solution. Polymer activity in standard tailings flocculation test.

such as copper forms a chelate by bonding to two carboxyl ligands. Those ligands are much more likely to be on the same molecule than on separate molecules,[20] so that intramolecular bonding occurs, making the conformation of the polymer much more compact. Since the hydrophilic carboxyl groups are now crosslinked by cations in the interior of the molecular coil, the hydrophobic carbon chain becomes orientated on the outside of the molecule (Fig. 10). The property of solubility in water of a macromolecule depends on the presence of a substantial number of polar groups in sterically exposed positions on the molecule. The change in conformation due to extensive chelation results, as expected, in insolubility. Precipitation of flocculant solutions was observed at high cation concentrations. At rather lower concentrations where partial inactivation of the polyacrylamide was observed, the change in conformation was insufficient to result in precipitation, e.g., for iron $_{III}$, the polymer was less than 10% active before turbidity was first detectable.

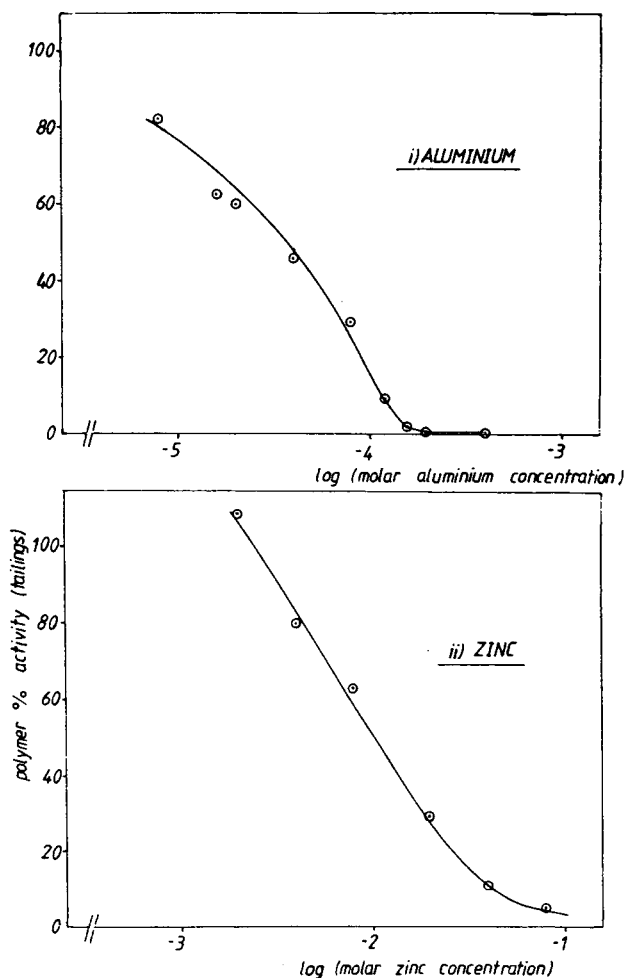Fig. 8. Inactivation of a 0.02% w/v solution of a 30% anionic polyacrylamide (IV = 22) by aluminium and zinc ions in solution. Polymer activity in standard tailings flocculation test.

At low cation concentrations where the degree of complexation is small, only moderate contraction of the polymer chain is involved. The activity of the polyacrylamide solution then depends upon the test suspension. As already noted, the flocculation behavior of tailings is very sensitive to the polymer size, as measured by its intrinsic viscosity (Fig. 5). The flocculation behavior of a kaolin suspension, however, depends primarily on the anionic charge of the polyacrylamide and is only weakly dependent on the intrinsic viscosity (Fig. 6). Therefore, a low degree of cation complexation of a polyacrylamide solution results in a molecule large enough to flocculate kaolin but too small to flocculate tailings efficiently. Figure 11 illustrates how a concentration of $10^{-4}M$ iron$_{III}$, or greater, inactivates both tailings and kaolin flocculation, but below $10^{-4}M$ there is a discrepancy in the polymer activity with the two suspensions.
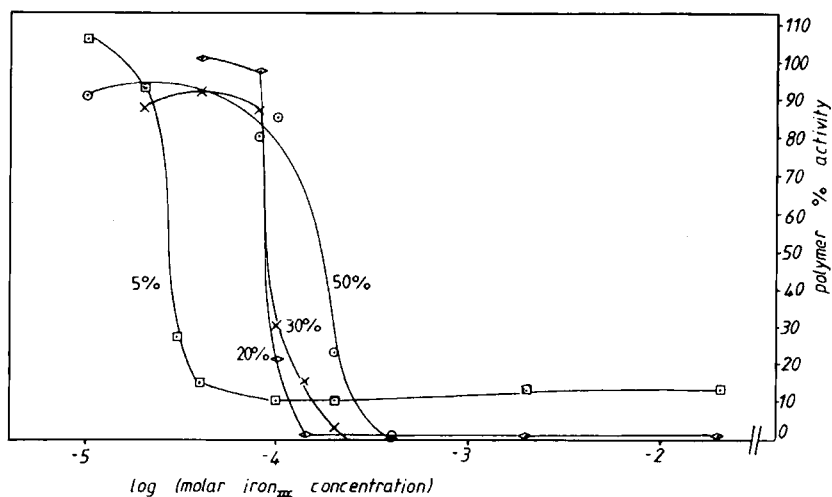
Fig. 9. Inactivation of a series of polyacrylamides of different percentage anionic charges by iron$_{III}$ ions in solution. Polymer concentration = 0.02% w/v; polymer activity in standard tailings flocculation test. Anionic charge (%): (□) 5; (◇) 20; (×) 30; (○) 50.
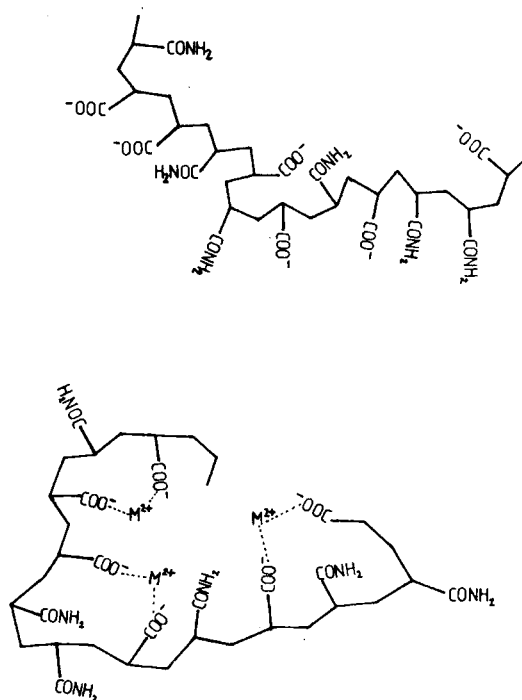

Fig. 10. Schematic diagram of the change in molecular conformation of an anionic polyacrylamide after complex formation with a divalent cation (M^{2+}).
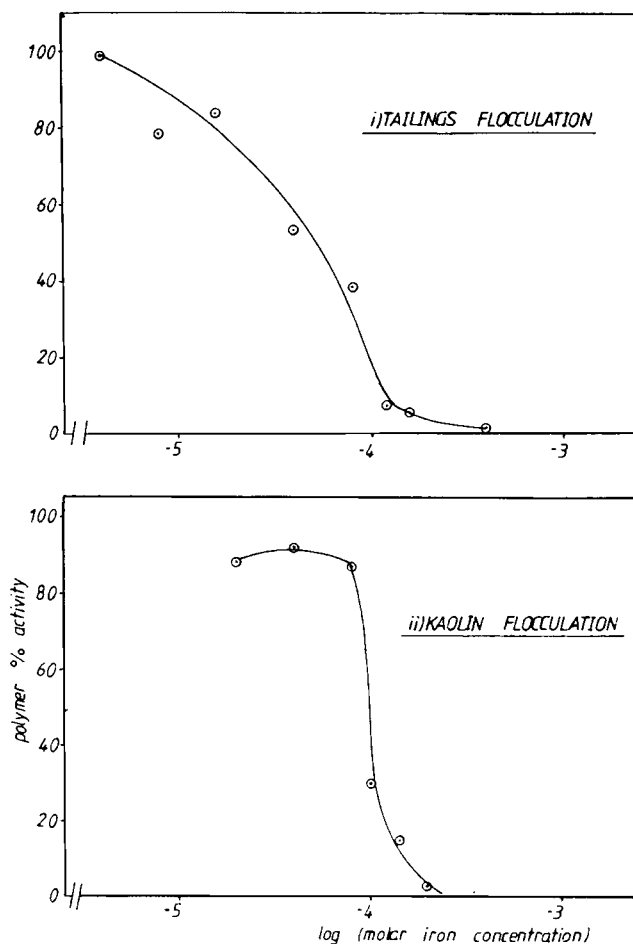
Fig. 11.   Inactivation of a 30% anionic polyacrylamide by iron$_{III}$ ions. Polymer concentration = 0.02% w/v. Polymer flocculation activity with (i) tailings and (ii) kaolin.

Conformational changes resulting from 1:1 complex formation are illustrated by the viscosity data in Figure 12. In the presence of 0.1M magnesium nitrate, the intrinsic viscosity of a 30% anionic polyacrylamide cannot be determined even in the presence of 1M NaNO$_3$, the electrolyte normally used to eliminate the polyelectrolyte effect. This is because the degree of complex formation, and hence the polymer conformation, changes as the Mg^{2+}:polymer ratio varies. It proved impossible to determine the intrinsic viscosity of one commercial flocculant sample because of viscosity data similar to those shown in Figure 12; the presence of calcium or magnesium salts in the sample was suspected.

Aging of Polyacrylamide Solutions

A solution of 30% anionic polyacrylamide at a concentration of 0.1% w/v was stored in a glass container at room temperature in daylight. A similar
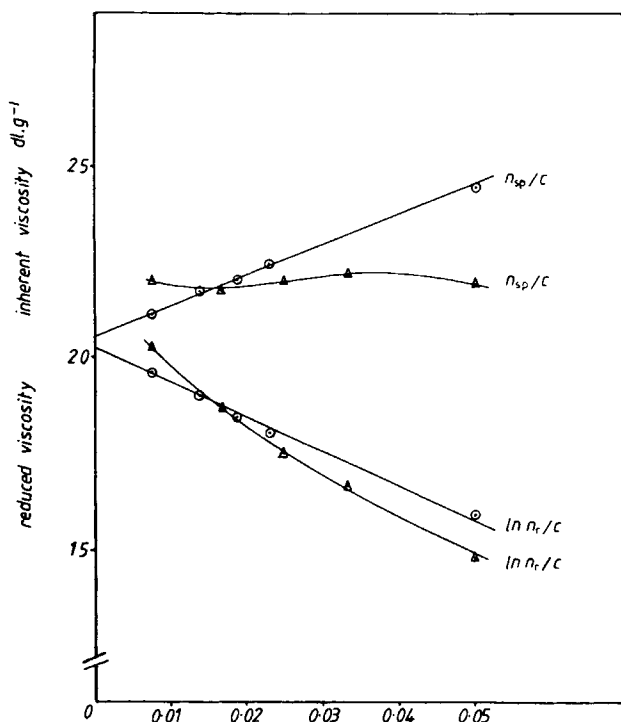
Fig. 12. Changes in reduced viscosity (η_{sp}/c) and inherent viscosity (ln η_r/c) as a function of concentration. 30% anionic polyacrylamide in $1M$ NaNO$_3$, in the presence and absence of 0.1M Mg(NO$_3$)$_2$: (○) $1M$ NaNO$_3$; (△) $1M$ NaNO$_3$ + 0.1M Mg(NO$_3$)$_2$.

solution was prepared using coal preparation plant water. At intervals over a period of several months, the reduced viscosities of these solutions were determined after adding sodium nitrate to a concentration of $1M$. The intrinsic viscosities were not determined because, as noted above, it is impossible to do this if calcium or magnesium ions are present, as is the case with coal preparation plant water.

The viscosity–aging behavior of the two solutions is shown in Figure 13. The initial reduced viscosities of the two solutions are not identical because of divalent cation complex formation in the coal preparation plant water solution. Aging occurs in both solutions and is not markedly faster when salts are present.

No significant change in flocculation activity was observed in the aged polymer solutions. This was probably because (i) the viscosity changes involved were small and (ii) although the same batch of tailings was used during the 3 months' aging, flocculation reproducibility was poor due to temperature fluctuations of several degrees from day to day.

A number of polyacrylamide solutions (nonionic and anionic) were also aged in the presence of 3% alcohol (ethanol or methanol) for periods of over a year. No change in viscosity was observed, in the presence and in the absence of
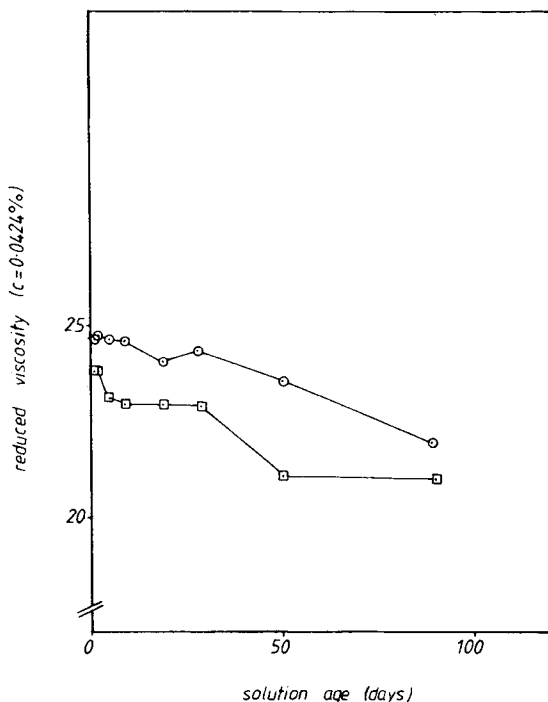
Fig. 13. Reduced viscosity of aqueous polyacrylamide solutions during storage at room temperature, in daylight: (o) distilled water; (□) coal preparation plant water.

dissolved salts. The use of 3% alcohol is often recommended by polymer manufacturers as a "wetting agent" for the dry polymer beads during solution preparation in the laboratory.[21] However, it has also been reported to be a stabilizing agent for polyacrylamide solutions, protecting against molecular degradation due to free radicals.[10,22] It would appear that the viscosity–aging observed in these experiments was due to free-radical attack, preventable by the presence of alcohol.

CONCLUSIONS

1. Shear degradation of polyacrylamide solutions results in a fall in the intrinsic viscosity, which causes a loss of flocculation activity. At a constant shear rate, molecular degradation may be minimized by: (i) minimum time of exposure to shear; (ii) low solution concentration; (iii) high ionic strength of the solution; (iv) high percentage anionic charge of the polyacrylamide.

2. Nonionic polyacrylamides do not form complexes with multivalent cations. The viscosity behavior of anionic polyacrylamides is affected by those cations, e.g., magnesium, which form 1 : 1 complexes with carboxyl groups on the polymer. The polymer chain conformation, solubility, and flocculation activity of anionic polyacrylamides is affected by the following cations, which form 1 : 2 complexes with carboxyl ligands on the polymer: Zn^{2+}, Pb^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}.

3. Viscosity–aging of polyacrylamide solutions, in terms of molecular degradation, was not observed in the presence of a small quantity (3%) of ethanol or methanol in solution. A small reduction in intrinsic viscosity was recorded over several months in the absence of alcohol. This was insufficient to affect the flocculation activity.

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