Abdel-Zaher M. ABOUZEID[*], Ahmed A.S. SEIFELNASSR[**]

POLYMERIC FLOCCULATION OF PHOSPHATE SLIMES

This paper reports the investigation of the flocculation of phosphate slimes by a series of synthetic flocculants of a wide range of charge density both anionic and cationic in nature. The extent of flocculation was determined by the measurements of the settling rate, sediment volume and supernatant clarity. The effect of the polymer molecular weight on the flocculation performance has been also investigated. The effect of pH and solids content of the suspension on the performance of certain selected polymers are reported. In this investigation, Abu-Tartur (the largest phosphate deposit in Egypt) phosphate slimes were treated with polymeric flocculants to study the above effects. In the system examined, flocculation was largely controlled by polymer molecular weight and the charge carried by the suspended particles and polymer molecules.

INTRODUCTION

In the past, the mineral processing industry has not been too seriously hindered by the awkward colloidal minerals. Where water and space were readily available, slimes were simply dumped in settling lagoons. At present, however, the situation is sharply changing and the environmental issues are seriously increasing. The falling grades of ore minerals result in bringing new processing problems and making the wastage of values in slimes less justifiable and multiply the tonnage of ores to be treated. Also, the pollution of streams by turbid or toxic effluents and the landscape by unsightly and potentially dangerous tips and sludge lagoons, are becoming irritating problems in mining societies throughout the world (Ahmed and Seifalnassr 1994).

The technological problems associated with colloidal minerals generally fall into one of the following categories: 1) securing effective dispersion before separation processes, 2) solid–liquid separation, for one of the following purposes: a) clarification of waste water for discharge to a water-course, b) clarification of plant water for recycling, c) recovery of the solids as saleable products, d) extraction of waste solids in a firm enough state for disposal as land-fill.

Phosphate slimes are the example of a colloidal system of interest today. Among the engineering studies dealing with phosphate slimes, some approaches involve the modification of slimes (Benedek, Hamielec 1994). Several approaches involve adding a polymeric floccu-

[*] Faculty of Engineering, Cairo University, Egypt.
[**] Faculty of Petroleum and Mining, Suez Canal University, Egypt.

lant, others involve inter-mixing sand with the slime with or without flocculant (Browell and Oxford 1977; Gregory 1978). These methods improved the early stages of dewatering as well as improving the final effective slime volume in some cases.

The inorganic salts such as lime, alum and ferric sulfate have long been used as commercial coagulants in the clarification of water. However, these salts do not work well when the fraction of colloidal particles in the suspension is low (Hogg 1980). The natural organic flocculants such as starch, gum, and gelatin–glue mixtures have been used for treatment of colliery effluents (Kitchener 1969) and phosphate slimes (Browell and Oxford 1977; Gregory 1978). The main disadvantage of the natural flocculants is that these are more susceptible to biological attack (Ahmed and Seifalnassr 1994). Even more effective are the polyacrylamide flocculants which flocculate very dilute mineral pulps under neutral, acid and, alkaline condition (Kitchener 1978). Moreover, with these flocculants particles flocs settle rapidly, leaving a clear supernatant layer.

Phosphate is one of the main commodities produced in Egypt, in which large tonnages are beneficiated with wet processes. The main unit operations involved for processing phosphate ores are size reduction, screening, washing, and flotation. The phosphate ore is slurred hydraulically and pumped to a dressing plant, where the fines (slimes) are removed and disposed by pumping them to large impoundments. The immediate problem with phosphate slimes relate to their disposal which is associated with very large volumes and poor dewatering characteristics. This poses possible environmental problems and delays the reclamation of the affected land for many years. To eliminate those problems, slime slurries must be concentrated to an average density of 30 weight percent solids or more.

In mining and benefaction of Abu-Tartur phosphate ore in Egypt, a huge amount of slimes of 80 mm particle size will be produced and considered as waste product. These slimes, will be pumped to large impoundments, thus result in wasting a substantial amount of water. The district in which that phosphate mine (Abu-Tartur) lies, is suffering from lack of water resources as a result of being in the middle of the Western Desert. The water source there is mainly underground water, which is limited and requires pumping to surface. Hence, conserving and recycling used water is essential. Recently, an attempt (Onoda et. al 1980) was made to use cement dust to coagulate these slimes. This attempt indicated that about 50 kg of cement dust per one ton of slimes is an optimum dosage for reasonable flocculation, which is too much, and the produced supernatant was highly alkaline (pH = 12). The objective of this work is to examine the flocculation of phosphate slimes using a series of polyacrylamide flocculants and the variables involved in their usage.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The polymers used in this study were high molecular weight, water-soluble polymers, generally known as polyacrylamides. They were of different molecular weights

and of a wide range of charge density, both cationic and anionic in nature. Also a non-ionic polymer was included. These were kindly supplied by Allied Colloids Limited, Bradford, UK. The phosphate slime was prepared by crushing a representative sample from Abu Tartur phosphate mine to 2 mm, then wet attritioned at 1:2 solid to liquid ratio for 10 minutes. The 80 μm fraction was separated by wet classification. The weight of slime was found to be 20% of the initial head sample. The chemical analysis of slime showed that it contains 15% P_2O_5, 21.4% CaO, 4.4% Fe_2O_3, 2.7% MgO and 50.4 % as insoluble residue. The slimes have an average density of 2.4 g/cm^3. Particle size analysis of that phosphate slime indicated that 70% of the solids have particle sizes of less than 38 μm. All experiments were conducted in distilled water unless otherwise stated.

Methods

Flocculation procedure consisted of making up suspensions of slime solids to be flocculated in graduated cylinders and allowing to stand for 30 minutes. Polymeric flocculant dosage was added as solutions of certain concentration. The cylinders were then inverted ten times through 180°. The rate of settling of solids was measured by observing the time taken for them to fall a standard distance. Degree of the supernatant clarity was determined by measuring the turbidity of samples of supernatant taken after 30 min of the experiment start using Orbeco-Hellige series 965 Digital Direct Reading Turbidimeter. Sediment volume was measured 30 min after flocculation start using the graduation on the cylinders. Using the above techniques, studies were undertaken to assess the performance of a range of polymers of varying charge type and density, the effect of the molecular weight of a polymer on its performance, the performance of selected flocculants related to surface charge of suspended solids and the performance of selected polymers in suspensions of varying solid content.

RESULTS AND DISCUSSION

Effect of polymer properties

Cationic charge density. In this investigation the phosphate slime (10% wt. solids) at its natural pH 6.87 was treated with a number of polymers varying in their cationic character. The settling rate, the turbidity of supernatants, and the sediment volume were used as measures of flocculation efficiency. The results of these investigations are set out in Figures 1a to 1c. Those figures demonstrate that the low cationic-content polymer (5% cationic) is the most effective in terms of settling rate, supernatant clarity and sediment volume. On the other hand the polymer with high cationic character was found to be the least effective. Also, with all tested polymer flocculants, it is obvious that the degree of flocculation is improved by increasing the polymer concentration. However, both the supernatant turbidity and sediment volume are levelled beyond flocculant concentrations more than about 50 ppm. The cationic polymer is expected to function primarily through the charge mechanism (Ogorman and Kitchener 1974). In this type
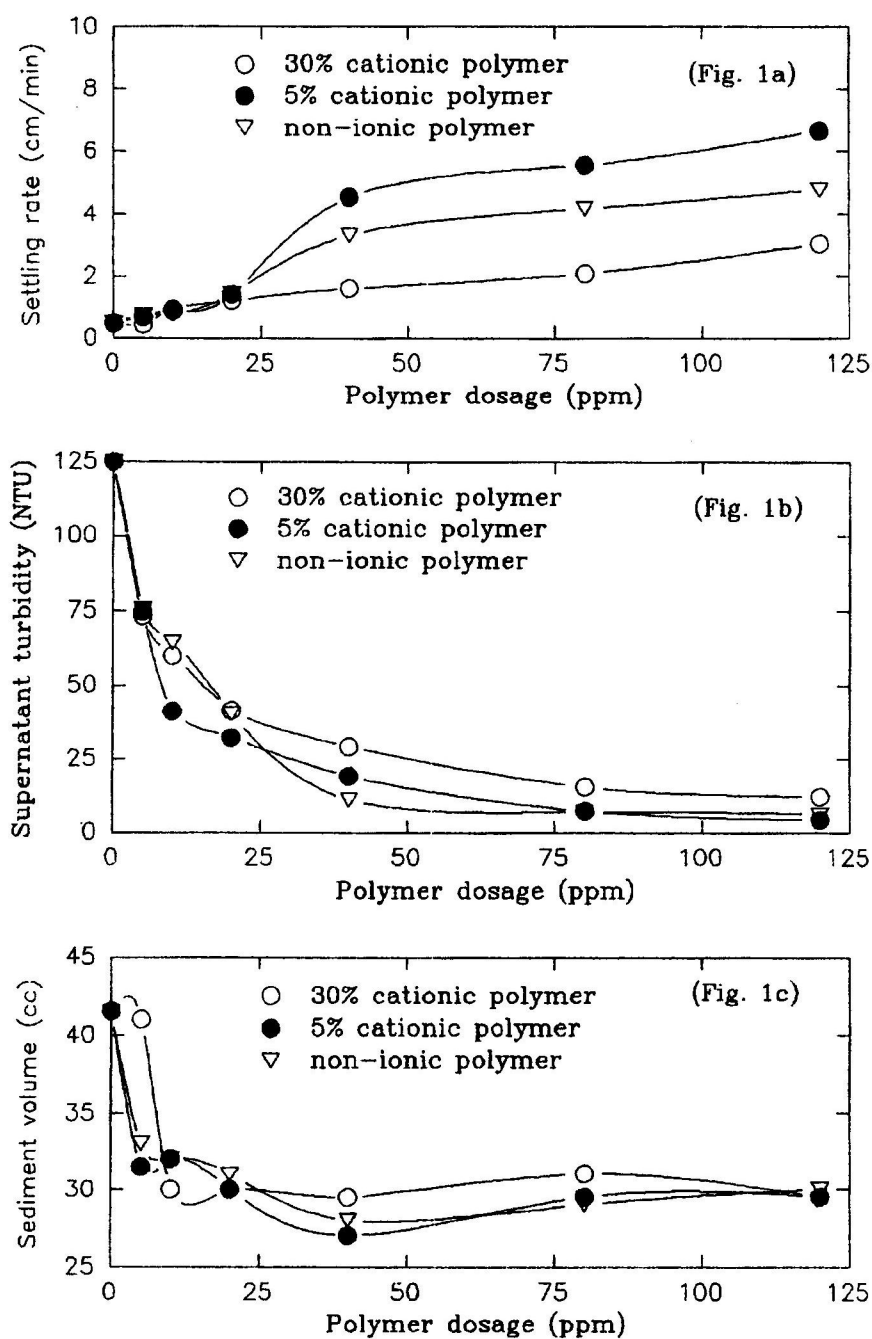
Fig. 1. Effect of cationic charge density of the polymer on the flocculation performance
of phosphate slime (10% of solids, pH = 6.87)
a – settling rate, b – supernatant turbidity, c – sediment volume

of flocculation mechanism, small molecules of polymers are adsorbed electrostatically to give positively charged patches on the slime particle surfaces. These patches can then interact, again electrostatically, with bare, negatively charged regions on the surfaces of other particles. The greatest clarities (lowest supernatant turbidity) and settling rates and lowest sediment volumes were obtained with low cationic charge density polymer with declining effectiveness as the charge was increased. This may be due to the fact that the phosphate slime is composed mainly of positively charged minerals such as calcite and dolomite. Also, the clayey minerals which represent about 30% of slime solids may exhibit a resultant positively charged surface at the given slime pH = 6.87 since the point of zero charge of clays is about pH = 7.4 (Osborne 1974). Another explanation for the low flocculation efficiency by increasing the cationic charge density, is the interchange repulsion of similar charged molecules of the polymer.

Anionic charge density. The results of numerous flocculation tests conducted with a series of polymers varying in their anionic charge density is summarized in Figures 2a–2c. These figures show that all the flocculation parameters are improved with increased polymer dosage up to certain limit after which the settling properties deteriorate. As far as the rate of settling of suspended solids is concerned, a very different picture emerged. The slowest settling solids were produced when the phosphate slime was treated with a highly anionic flocculant. This also applied to both supernatant turbidity and sediment volume. The most effective flocculant was found to be that of moderately anionic charge density. This observation may be accounted for by accepting that the orientation of polymer molecules at the particle surface depends to a large extent upon the intensity of interaction between the polymer and the particle surface (Pradip et. al 1980). Thus highly charged polymer molecules may be completely adsorbed on oppositely charged surfaces in a conformation which tends to collapse rapidly on the surface, and are unlikely to cause bridging. Less highly charged polymers are adsorbed in a conformation in which lengths or loops of the polymer chain extend out into solution, creating conditions suitable for bridging. Best flocculation performance should therefore be obtained with polymers which are bonded to the surface at only a few sites. Fortunately, however, since the majority of the particles found in phosphate slime are positively charged at slime natural pH = 6.87, electrostatic interactions will generally enhance the adsorption of the polymeric anion. It is worth to mention here, that the anionic polymer are found (Ogorman and Kitchener 1974) to be very poor flocculants for pure clays in pure water. However, in the presence of quite appreciable amounts of calcium or other multivalent cations as in the case of phosphate slime, where these reagents were found to be more effective flocculants for phosphate slimes. Moreover, the results presented in Figs. 1a–c and 2a–c indicate the non-ionic polymer is also more efficient flocculant for phosphate slime than those flocculants having higher cationic or anionic charge density. This again can be attributed to the presence of metal ions in phosphate slimes. Presumably, the non-ionic polymer function primarily through the bridging mechanism (Sadowski and Laskowski 1980), adsorption being controlled by hydrogen bonding of the amide groups to the hydroxylated solid surfaces.
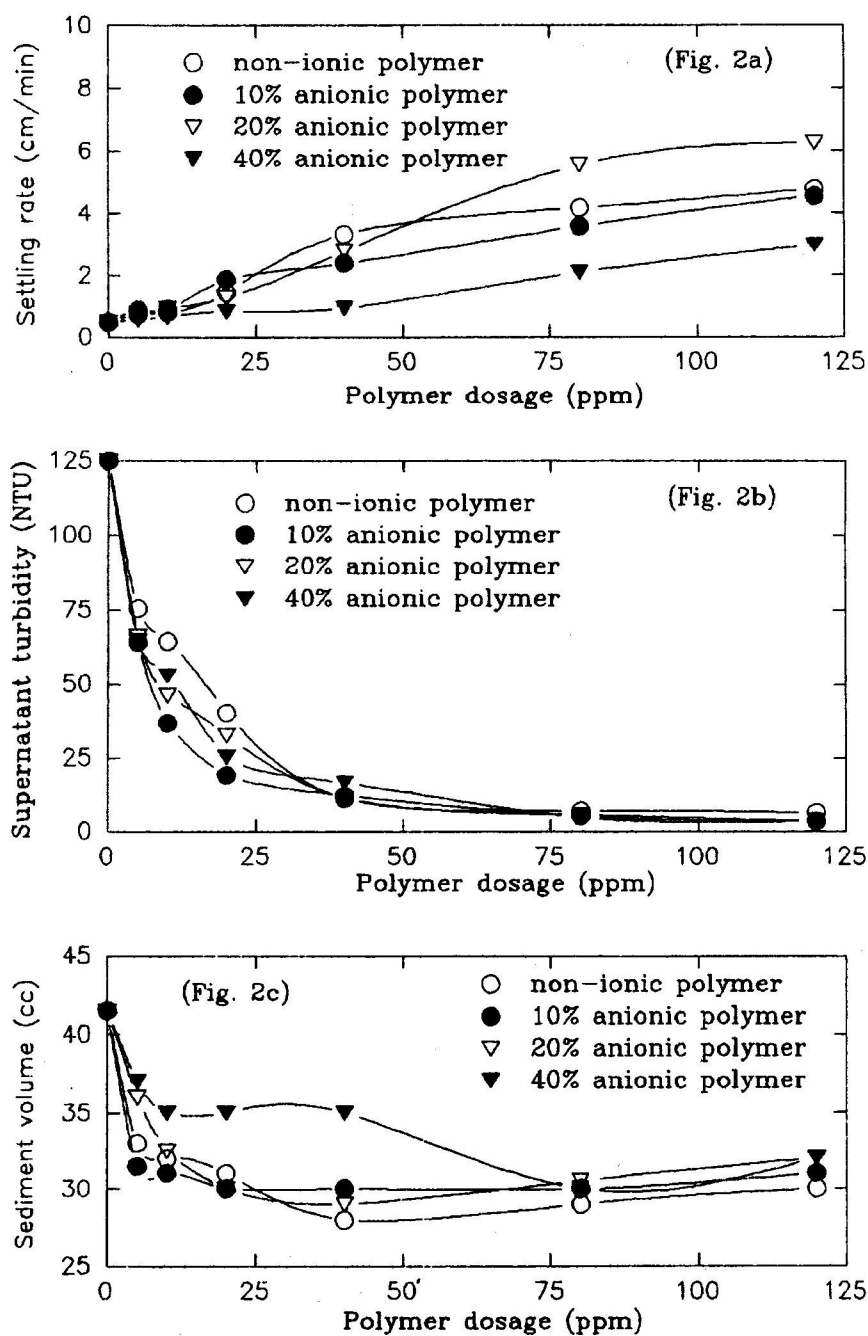
Fig. 2. Effect of anionic charge density of the polymer on the flocculation performance
of phosphate slime (10% of solids, pH = 6.87)
a – settling rate, b – supernatant turbidity, c – sediment volume

Molecular Weight. For this study, 10% anionic polymers of different molecular weights were used. The results are shown in Figure 3a–c. It is clear that the higher molecular weight polymer (larger polymer chain) are more effective as flocculants. It should be pointed out that the effective size of polymer coil in the solution is probably the key factor (Thomas and Leslie 1980). The coil size depends not only on molecular weight but also on the charge density on the polymer chain. A charged polymer chain may have a larger coil than one with a larger molecular weight but with no charge.

From the previous results, it can be concluded that the most effective polymer flocculants are 5% cationic, 20% anionic and the very high molecular weight (10% anionic) polymers. Therefore, these flocculants were selected for the subsequent investigations.

Effect of Solids Concentration in Slurries

The phosphate slime slurries were prepared to yield several percent solids, ranging from 2.5 wt% to 20 wt%. The selected polymeric flocculants were employed at a dosage of 100 ppm. Figure 4a–c shows that the selected polymers behave in a similar way with respect to the variations in the solids content of phosphate slime. It is obvious that the percentage solids has a marked effect on all flocculation parameters including settling rate supernatant turbidity and sediment volume. The settling rate was declined dramatically with increasing the solids content up to about 10 wt% solids after which no change was observed. With respect to the supernatant turbidity, it was not affected by solids content in the range of 2.5–15 wt%. At higher solids content the supernatant turbidity was increased markedly. The sediment volume was increased with increasing the solids content. The percentage solids in a suspension determines the number of interparticle collisions. Therefore, the stability of the flocs increases with increasing pulp density which results in slower settling rate and higher turbidity of the supernatants. Another explanation of this is that the loose ends of the adsorbed polymer molecules have a greater chance of becoming adsorbed on their own mineral particles, and the total amount of bridging in the system is decreased.

Effect of the Surface Charge of Suspended Solids

In this series of experiments, phosphate slime of 5 wt% solids, at different values of pH, were treated with the previously selected three polymers. The polymers were 5% cationic, 20% anionic and very high molecular weight (10% anionic) polymers. The results of this study are set out in Figure 5a–i. Fig. 5(a, d, g) presents the results of phosphate slime flocculation with 5% cationic polymer. The clarity of the supernatant was improved by increasing the negative charge of solid particles (by increasing the suspension pH). The maximum settling rate was attained at pH near neutral. The sediment volume is increased, probably due to the formation of larger flocs. The results concerning the 20% anionic flocculant are shown in Figure 5b, e, h. The settling rate was improved by increasing the slime pH, while the supernatant clarity deteriorates on both sides of highly acidic and highly alkaline suspension. Figure 5c, f, i shows that the
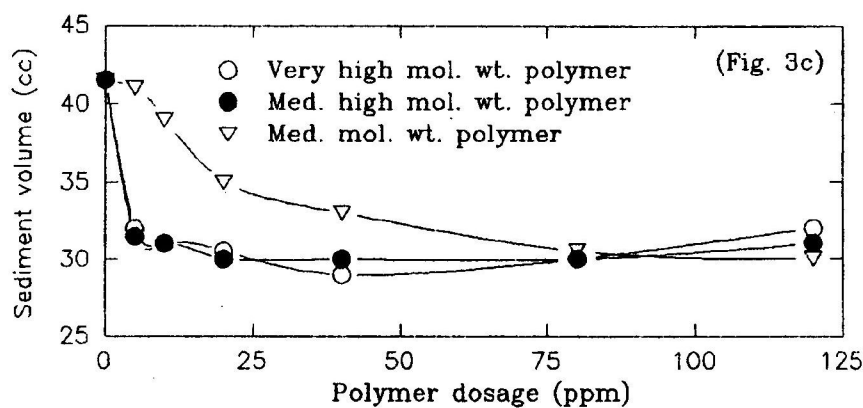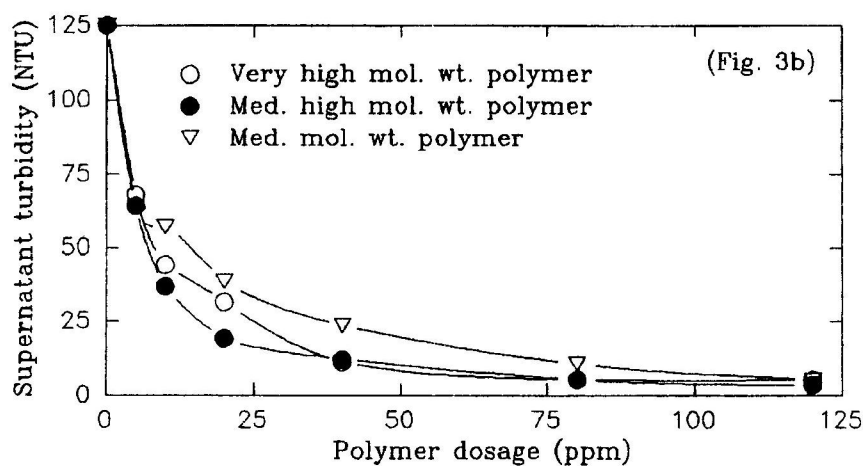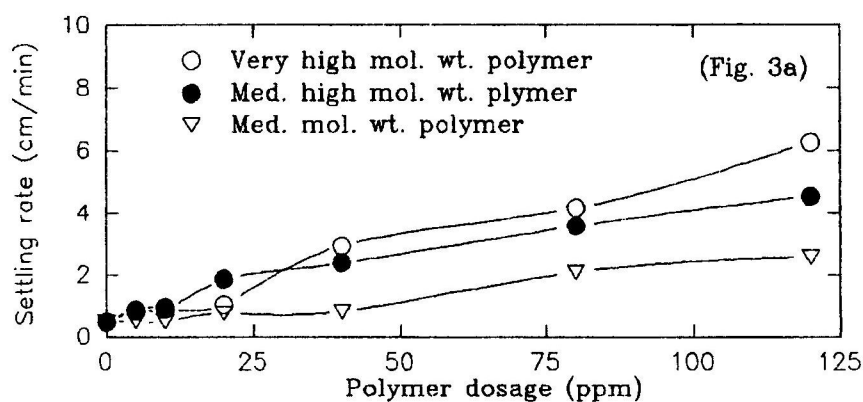
Fig. 3. Effect of polymer molecular weight on the flocculation performance
of phosphate slime (10% of solids, pH = 6.87)
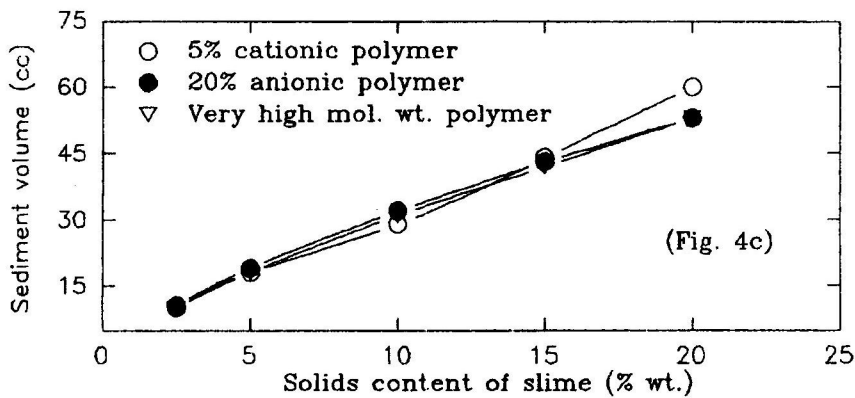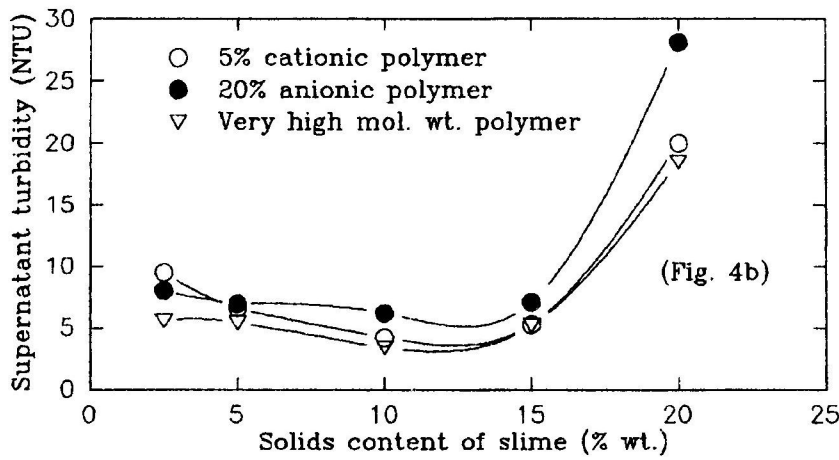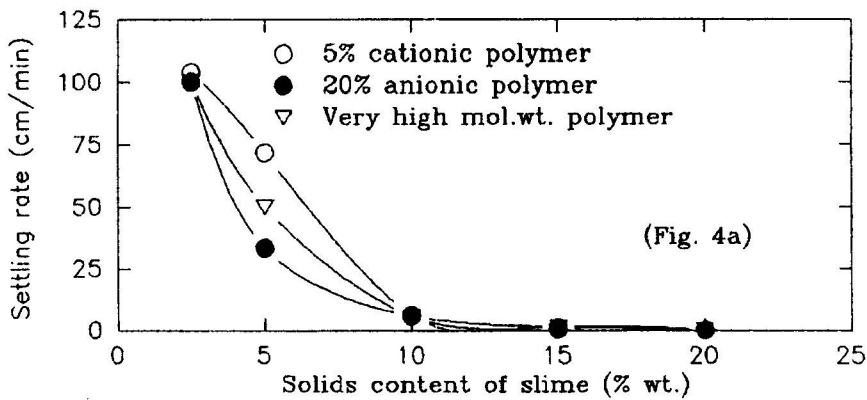a – settling rate, b – supernatant turbidity, c – sediment volume

Fig. 4. Effect of slime solids content on its flocculation
using 100 ppm dosage of various polymers
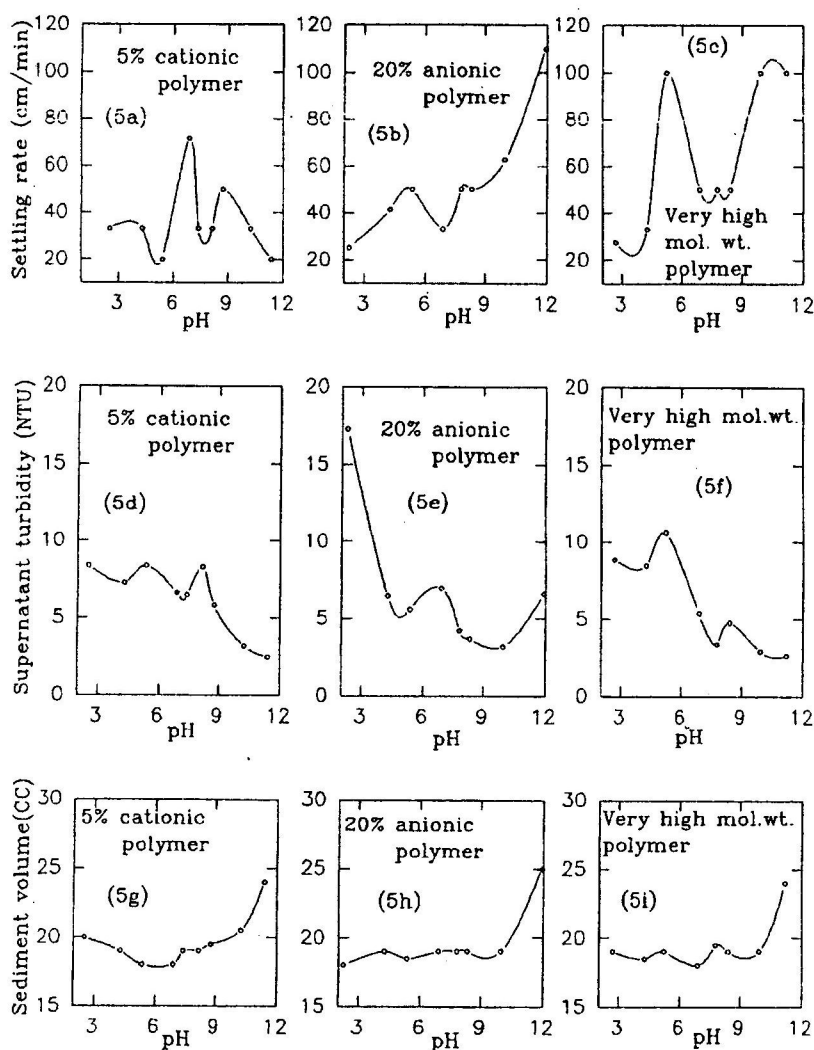a – settling rate, b – supernatant turbidity, c – sediment volume

Fig. 5. Effect of pH on the flocculation performance of phosphate slime
using 100 ppm dosage of various polymers at 5% wt. content of solids
a–c – settling rate, d–f – supernatant turbidity, g–i – sediment volume

polymer of a very high molecular weight (10% anionic) behaves in a similar way to the
5% cationic polymer in relation to slime pH variations. As previously mentioned, ap-
proximately 30% of solids in the phosphate slime are clays. The remaining constituents
of slime are silica, various aluminosilicate minerals, and a variety of phosphate and
carbonate minerals. Therefore, the surface charge on clays (alumina) has the predomi-
nant influence on the flocculation of phosphate slimes. The reported point of zero
charge of alumina is 7.4 (Osborne 1974) and that of phosphate minerals is in the range

of 5.8–6.5 (Vanderhoff 1974), 9.5 for both calcite and dolomite (Wilde and Dexter 1972) and 2 for silica (Osborne 1974). Therefore, the solid surface of that slime exhibits a quite positive charge even at high pH values. Hence the three selected polymers gave the minimum supernatant turbidity (turbidity is a measure of flocculation efficiency), near the neutral pH, which corresponds to the point of zero charge of clays, however, the most efficient flocculant is the 20% anionic polymer.

In order to simulate the conditions that will be applicable to field practice, several flocculation tests were conducted using tap water instead of distilled water. The results are shown in Tables 1, 2.

Table 1. Flocculation of phosphate slime in tap water
(5 wt% solids, 100 ppm of the used polymer pH = 7.01)

Polymer type	Settling rate cm/min	Supernatant turbidity (NTU)	Sediment volume (CC)
5% cationic	50.1	7.6	18
20% anionic	41.63	6.8	19
very high mol. wt	50.1	5.5	19

Table 2. Flocculation of phosphate slime in distilled water
(5 wt%, 100 ppm of the used polymer pH = 6.88)

Polymer type	Settling rate (cm/min)	Supernatant turbidity (NTU)	Sediment volume (CC)
5% cationic	71.76	6.6	18
20% anionic	33.3	7	19
very high mol. wt	50.1	5.4	18

Examining the data presented in Table 1 and Table 2, it can be seen that there is no significant difference between the results obtained by polymer flocculation in distilled or tap water. This may be due to the fact that the pH values of both slimes are very close to each other.

CONCLUSIONS

The conclusions drown from this work are as follows. The cationic flocculant of low charge density was more effective and the anionic flocculants of moderately charge density (20% anionic) were effective flocculants. Surprisingly, non-ionic polyacrylamide polymer is also found to be an efficient flocculant for phosphate slime.

The molecular weight of the polyacrylamide polymers in relation to their perform-ance as flocculants has been described in the paper. It has been confirmed that increas-ing the molecular weight improves the performance of the flocculant. The solids con-centration in the slime has a marked influence on the flocculation. The best performance was achieved at diluted slimes which is very common in practice.

pH determines the flocculating action of polyacrylamide polymers towards phos-phate slime suspensions. The polyacrylamide flocculants function at a concentrations as low as 100 ppm based on solid weight.

The supernatant clarity achieved after flocculation was close or equal to that of do-mestic water. The turbidity of the supernatant ranges from 3-7 NTU while that of do-mestic water range from 4.5 to 6 NTU.

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Badano flokulację drobnych ziarn fosforytowych za pomocą serii syntetycznych kationowych i anionowych flokulantów o zróżnicowanym ładunku elektrycznym. Stopień flokulacji określano przez pomiar szybkości sedymentacji cząstek w wodzie, objętości osadu oraz mętności górnej części zawiesiny. Badano również wpływ ciężaru cząsteczkowego polimeru na przebieg flokulacji. Przedstawiono także wpływ pH i zawartości części stałych w wodnej zawiesinie na działanie wybranych polimerów. Do badań użyto fosforytu z Abu-Tartur (Egipt). W badanym układzie flokulacja była głównie kontrolowana przez ciężar cząsteczkowy polimeru oraz ładunek elektryczny cząstek stałych i ładunek elektryczny polimeru.