Clarification of colliery effluents using modified starch and synthetic polymer

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Received 17 September 1998; accepted 16 October 1999

During mining and beneficiation of many minerals, including energy minerals, particulates become suspended in wastewaters. Often associated with these particles are organic and inorganic trace contaminants. Before reuse of discharge of these waters, the suspended particulates and related contaminants must be removed. The work described here is a detailed comparative study of the flocculation of coal washery effluent slurry with modified starch and a synthetic polymer under controlled conditions of pH and flocculant concentration. The degree of flocculation of the system was evaluated by the residual turbidity measurements of the settled suspensions. Results show that the flocculating reagents can significantly contribute to the existence of low settling rates at high supernatant clarity often observed in some coal washery effluent treatment by flocculation and sedimentation method. High supernatant clarify were obtained at pH above 7 for the modified starch and above pH 9 for the synthetic polymer. Optimum polymer dosage which maximized the degree of slurry flocculation was found to be about 65 ppm and 0.4 ppm for the modified starch and synthetic polymer respectively. Both flocculants gave good clarification but the synthetic polymer was much more effective. The study further reveals that in some slurry-polymer systems, fast settling corresponds to high Sediment Volume whereas in others the opposite applies. It is concluded that for proper design and operation of such treatment facilities, this phenomenon should be taken into consideration.

The processing of coal of high commercial quality requires wet cleaning. In areas where there is limited water supply (such as in arid areas), the demand for large volume of water for treating minerals requires efficient recovery of water for reuse. On the other hand, where water supply does not constitute a problem, the disposal of the slurry into stream will obviously generate environmental pollution. Most importantly, in big coal mining cities like Enugu in Nigeria where there is high demand for drinking water due to ever-increasing population, recycling of water to plants is a must. Moreover, in a washing plant, discharge of the effluent is continuous which would require an uninterrupted water supply in order to maintain continuous production of washed coal, since continuous use of the same used water without clarification would lead to ever-increasing impurities and decreasing efficiency of coal washery operations. The quest for solutions to these problems necessitates clarification and dewatering of industrial slurry.

Both natural and synthetic polymeric flocculants have been used for clarification processes\textsuperscript{1}. These natural polymers have the advantage of being non-toxic whereas some synthetic polymers may be toxic\textsuperscript{2}. There are other observed problems associated with the use of both natural and synthetic polymers in flocculation including low floc (particle) density, low settling rate, low supernatant clarity and poor filtrability of the resultant sludge\textsuperscript{3}. A knowledge of natural polymeric flocculant adsorption on black-water solids and its effect on flocculation is relevant in the resolution of some of these problems through proper design and operation of coal-washery treatment facilities. Synthetic flocculant adsorption on blackwater constituents has been studied by several investigators including Mirville and Hogg\textsuperscript{4}. It was established that polymer adsorption is dominated by the presence of coal particles in blackwater which can consume about ten times as much polymer per square centimeter of surface compared to other constituents. This implies that the presence of coal fines leads to high reagent consumption which is economically undesirable.

Although the use of starch-based flocculants in the treatment of coal washery effluent pulps has been practised for sometime and researched quite extensively, but the use of synthetic polymers seems to be more widespread because small amounts of the
Synthetic polymers are not readily available, metal presence of metals. Furthermore, in areas where synthetic polymers are not readily available, metal cations are still been exclusively used as coagulants. In general, metal cations are always present in coal-washery effluent treatment systems either added deliberately during flocculation or invariably present in the particulates.

A lot of work has been done on modifying starches for use as flocculants or flocculant aids, and the chemistry of starches is reasonably well understood and these can be found elsewhere. Starch, when oxidized will result in increased flocculation power.

The work described here aims to compare the effectiveness of polymeric flocculants in 'blackwater' clarification.

**Experimental Procedure**

**Materials**

The coal washery effluent slurry used in this work was collected from Obwetti Coal Preparation Plant, Nigerian Coal Corporation, Enugu, Nigeria. The sample with an initial pH value of 4.6 was collected directly as it came out of the washery prior to the flocculant addition point. It contained 3% solids by weight. Mineralogical analysis of the solids in the slurry showed that the constituents are predominantly fine coal, clays (mostly kaolinite), quartz, pyrite and titania. A wet screening analysis of a sample of the suspended solids showed that 90% of it was finer than 200 mesh (75 μm) Tyler Sieve.

The flocculants used in the tests were modified starch (charged, oxidized starch) and PRAESTOL, a synthetic polymer (an anionic-polyacrylamide) with an approximate average molecular weight of six million. The starch was extracted from cassava tubers, dried to a constant weight in an oven between 50°C and 100°C and ground to a powder. The oxidized flocculant starch solution was prepared by chloridizing 4% (w/v) starch suspension with 2.5% (w/v) calcium hypochlorite. The mixture was then rigorously agitated using a propeller type stirrer for about 15 min at 1500 rpm and then diluted with an equal volume of water to give 0.5% oxidized starch flocculant. Solutions of other concentrations were similarly prepared. The charged oxidized starch flocculant solution was prepared by electrolyzing the oxidized starch solution. Aluminium rods were used as the electrodes. The solution was gently stirred using a propeller type stirrer at 500 rpm throughout the charging process (0.1-0.2 dc) and the voltage across the electrodes was measured. The charging processing produced a white gelatinous substance.

**Fig. 1—Flocculation performance as a function of pH with (a) modified cassava starch and (b) synthetic polymer**

*Synthetic polymers are very efficient. Cationic polymers are effective flocculants for the particles found in 'blackwater'. These reagents are not very attractive because they produce small floc size and consequently low settling rates lead to low thickener capacity. Anionic polymers alone are not used in the flocculation of coal-washery slurries because at neutral pH the majority of the particles found in 'blackwater' are negatively charged and as a result electrostatic interaction prevents the adsorption of the polymeric anion. Indeed, it has been reported that anionic polymers are poor flocculants for 'pure' clay in pure water. In the presence of inorganic cations such as Mg$$^{2+}$$, Al$$^{3+}$$ and Fe$$^{3+}$$, anionic polymers are quite effective flocculants. Also, starch-based and non-ionic synthetic polymers perform best in the presence of metal ions. Furthermore, in areas where synthetic polymers are not readily available, metal*
which is the effective charged oxidized starch flocculant which was then used in subsequent experiments.

Other materials used in this work were NaOH, H$_2$SO$_4$, HCl, phenol and were reagent grade chemicals supplied by the Fisher Scientific Company and distilled water. NaOH and HCl solutions were used for pH adjustment, while H$_2$SO$_4$ and phenol were used for the preparation of samples for spectrophotometric determination of starch concentration. Distilled water was used in the preparation of the reagent solutions.

**Methods**

Samples were taken from the stock 'blackwater' slurry kept mechanically agitated. For the tests, 240 cm$^3$ samples of the agitated slurry were placed in 500 cm$^3$ beakers. The samples were treated with the modified starch flocculant or with the synthetic polymer flocculant to produce total volumes of 250 cm$^3$ containing the desired polymer concentrations ranging from 2-160 ppm (dry solids basis) for the modified starch and from 0.15-1.5 ppm (dry solids basis) for the synthetic polymers. The pH was then adjusted to the desired value ranging from pH 5-12. Mixing was carried out using two 500 cm$^3$ beakers by transferring the sample from one beaker to the other. This mixing method was found to yield reproducible results. The sample was then transferred to a 500 cm$^3$ measuring glass cylinder to which a millimeter scale had been attached on the side and the sample was allowed to sediment. The settling curve of the flocs formed was then monitored by timing the rate of descent of the mudline (interface between the supernatant liquid and the suspension) with time. The constant settling rate values were calculated from the approximately linear portion of the curve coinciding with the uniform terminal velocity of the flocs.

The flocculant performance was also monitored by measurement of the turbidity of the sample before treatment and that of the supernatant using a Hach's model 2100A turbidimeter (a product of Hach Chemical Company, Ames, Iowa, U.S.A.). The percent turbidity was then used as a performance index for the flocculants; low turbidity supernatant corresponding to high percent reduction in sediment density. Tests were first performed on slurries without any flocculant so that the effectiveness of the flocculants could be judged. All tests were conducted at room temperature (25 ± 3°C).

**Results and Discussions**

The effect of pH on the flocculation response of the 'blackwater' is presented in Fig. 1. Preliminary tests indicated that the fine particles in the 'blackwater' samples were not flocculated in the acidic pH range, but a good flocculation performance was observed in the alkaline range. It is noticeable in Fig. 1(a) that turbidity decreases linearly with pH. Also, from the same figure, it can be seen that settling rate decreases with pH and that the minimum turbidity occurs at low settling rates. This indicates that very high supernatant clarity can only be attained at the expense of some reduction in settling rate. From Fig. 1(b), it can be observed that turbidity decreases non-linearly with pH, while settling rate increases with increasing pH, and at about pH 9 there is a sharp drop in the settling rate to low values due to increased repulsion.
(ionic effect) thus indicating again that high supernatant clarity does not correspond to high settling rate. Although starch and PRAESTOL are both non-ionic polymers, the high supernatant clarity shown by the charged starch is probably a result of the bridging action of the long starch chains on the coal particles.

Fig. 2 shows the extent of flocculation as a function of flocculant concentration. The flocculation behaviour of the slurries at the two pH values (pH 9 and 12) was remarkably similar. From the figure, it can be seen that settling rate increases with increasing flocculant concentration while turbidity shows a decreasing tendency. This is an indication that at these pH values, increase in flocculant concentration results in a corresponding increase in supernatant clarity as well as generation of large fast settling flocs. This shows that high supernatant clarity does correspond to high settling rate. However, at about 65 ppm and 0.4 ppm starch and synthetic polymer concentration respectively, the settling rate curve attains a maximum value (16 cm/min and 80 cm/min for starch and synthetic polymer respectively). At higher concentration, larger but fragile flocs could be formed which leave 'haze' resulting in greater turbidity. It should be noted that both flocculants gave good clarification of the 'blackwater' even though the synthetic polymer was much more effective.

The settling rate and turbidity curves (Figs 1 and 2) show that in some cases fast settling correlate with high supernatant clarity (low turbidity) as in Fig. 2 whereas in Fig. 1, high supernatant clarity can only be achieved at low settling rates. The reasons for these observations are not quite obvious. This could however, be due to differences between “free-settling” and “hindered-settling” regimes as well as to the packing nature of the flocs. Large flocs cannot pack as closely as small ones hence they produce more porous sediments and larger volumes.

Conclusions
On the basis of the above results and discussions, the following conclusions can be drawn:

(i) Clarification (i.e. well flocculated system) based on low turbidity was achieved at appreciable low concentration of the synthetic reagent. The concentration at which minimum turbidity was attained did not necessarily correspond to the point of high settling rate.
(ii) The settling rate recorded with synthetic polymer was at least five times greater than as recorded with modified starch. Both flocculants gave good clarification but the synthetic polymer was much more effective (i.e. gave lower turbidity).
(iii) For effective clarification, higher modified starch dosage is required than with synthetic polymer.

Acknowledgements
The authors are grateful to Mr. N. A. Okonkwo of the Nigerian Coal Corporation, Enugu, Mr. R. E. Anumoa of Industrial Chemistry Department of former Anambra State University of Technology, Awka for their interest and help during this study and to Engr. C. A. Nwafor (formerly of Anambra State University of Technology, Enugu) who was involved in some of the tests.

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