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Efficiency of Polyacrylamide Polymers in Settling Aggregate Mining Tail Water

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Abstract: *Water reuse and recycling systems in aggregate mining operations require assisted flocculation to meet in-process and environmental quality standards. Determination of the most efficient and effective flocculant is a crucial step in the process, affected by both polymer and suspension characteristics. This paper presents the results of studies on the behaviour of aggregate tail water from Vega Minerals Quarry amended with a range of polyacrylamide (PAM) flocculants. The tail water was highly turbid with ~ 37 g solid L^{-1}. Particle distribution favoured the clay range, but there was an influential amount of larger particles. Settling rate increased with increasing concentration for all polymers, being greatest for the high charged, high molecular weight anionic PAM. Optimum rates were not achieved for the concentration range used. However, the anionic polymers showed significantly faster settling rates than the cationic and non-ionic polymers. Turbidity was responsive to increasing polymer concentration, showing an inverse relationship compared to settling rate. The lowest reduction in turbidity was measured for DF 2468 (cationic PAM) at 10 mg L^{-1}. Stabilisation effects were observed for the anionic PAMs at doses greater than 4 mg L^{-1}, with the lower charged PAM showing overall lower turbidity. The low charged, lower molecular weight anionic PAM is recommended for treatment of these tail waters.*

Keywords: *Polyacrylamide (PAM), Flocculation, Tail water, Turbidity*

1. Introduction

Open pit mining and aggregate processing operations produces large quantities of waste tailings, composed mainly of fine and colloidal particles. In Trinidad and Tobago, standard treatment of these tailings involves the use of sequenced, connected retention ponds, from which water is either recycled or released back into natural surface water bodies. As the industry strives to improve efficiency in recovery of aggregates with improved processing equipment, a greater demand is placed on tail water treatment. Mpofu et al. (2004) indicated that the impoundment of these voluminous tailings is cumbersome and cost ineffective. Additionally, the ability to recover and recycle process water trapped in impounded tailings is crucial during the dry season (February – May). Secondly, reducing the quantity and improving the quality of tail water is related to meeting local environmental standards.

Polymer assisted flocculation, which involves the addition of chemicals that facilitate particle coagulation and increase sedimentation, has been used for solid-liquid separation in industrial and wastewater treatment processes (Mason et al., 2005; Dihang et al., 2008; Kirwan, 2009). Mason et al. (2005) stated that polymers can range in charge type (cationic, anionic, or neutral/ non-ionic), charge density and molecular weight. Polyacrylamides (PAMs) are the most widely and common type of polymeric flocculant employed to flocculate colloidal particles (Nasser and James, 2006). The literature presents various inferences on the comparative performance of different polymer types. Nasser and James (2006) showed greater floc size and faster settling rates for anionic versus cationic PAMs, whilst Besra et al. (2006) in their studies on kaolin suspensions found that the non-ionic PAM was the most effective in improving settling rates. Differences in flocculation mechanism have been suggested as the main reason for differences in behaviour (Seybold, 1994).

However, this assertion does not explain the inverse effects seen for different studies. The variance alludes to the influence of other flocculant and suspension properties including, polymer molecular weight and charge density, and physicochemical and mineralogical properties respectively. Nasser and James (2006) reported that the maximum settling rates of flocs produced by cationic and anionic PAMs decreased with increasing charge density and molecular weight. Liard (1997) demonstrated that the efficiency of anionic PAM for clay flocculation varies with mineralogy (kaolinite > illite > quartz). In addition, the efficiency of the anionic

PAM has been shown to be greater under acidic pH (Deng et al., 2006).

The effectiveness of the flocculation process depends on both the nature of the flocculant as well as suspension properties. The process is rather complex which limits the applicability of flocculation studies using standard suspensions. Yan et al. (2004) lamented that flocculation optimisation practices in industries are still reliant to a large extent on trial and error. Dihang et al. (2008) drew attention to the fact that the vast majority of studies on coagulation and flocculation focused on clay suspensions of uniform physicochemical and mineralogical makeup; kaolin and/or smectite. Contrastingly, this work investigated flocculation of natural aggregate mining tailings with unknown character. It aimed at determining the best polymer for increasing sedimentation.

2. Materials and Methods

2.1 Materials

The aggregate tail water sample used in the experiments was taken from the sedimentation tank at Vega Minerals Ltd., Valencia, Trinidad and Tobago. The water treatment system consisted of a sedimentation tank followed by a series of four connected retention ponds. Representative samples were collected (grab) and transferred to the laboratory in 20L buckets and discharged to a stirring tank (150L). Prior to the characterisation and flocculation tests, the composite aggregate slurry was stirred to obtain a homogenous suspension.

Total suspended solids, turbidity, pH, EC, alkalinity and hardness of the tail water were determined according to standard methods (SMEWW, 2005). A gravimetric analysis was used for determining suspended solids. Turbidity was measured via the Nephelometric method, using a turbidimeter (DRT-100B). Tailings hardness was determined by titration. Particle size distribution was determined by the hydrometer methods, described by Gee and Or (2002) and cation exchange capacity of the solids by the unbuffered salt extraction method (Sumner and Miller, 1996). pH and EC were measured with a multimeter (Eijkelkamp 18.28).

Four locally available PAM polymers varying in type, molecular weight and charge density were used in the flocculation tests (see Table 1). They consisted of a high molecular weight non-ionic polymer, a high molecular weight cationic and anionic polymer, both having high charge densities and a low molecular weight anionic polymer with low charge density. For each polymer, a homogenous stock solution (0.1 %) was prepared using distilled water according to Sabah and Cengiz (2004) and Besra et al. (2006).

Table 1. Characteristics of the polymers provided by Ashland Trinidad and Tobago Ltd.

Polymer	Symbol	Ionic Type	Molecular Weight g mol^{-1}	Charge Density %
DREWFLOC 260	DF260	Anionic	(Low)†	(Low)
AMERFLOC 2300	AF2300	Non-ionic	16 -18 × 10^6 (High)	0
AMERFLOC 2270	AF2270	Anionic	16-18 × 10^6 (High)	30 (Medium)
DREWFLOC 2468	DF2468	Cationic	11 × 10^6 (High)	60 (High)

† Supplier could only indicate that the values were low

3.1 Methods

The flocculation tests were conducted by placing 1000 ml of the aggregate tail water (~ 3.71 % solids) into a 1,000 ml beaker and mixing for 2 min at 150 rpm to ensure complete dispersion. The PAM was added by pipette during stirring to bring the PAM concentration in the beaker to 0 (control), 1, 2, 5 and 10 mg L^{-1}. Stirring stopped 1 min after PAM addition. The suspension was quickly transferred to a 1,000 ml graduated cylinder and further agitated 10 times with a perforated stirrer. The height of the slurry and water interval as a function of time was used to calculate the settling rate of the flocculated suspension. Flocculation was performed at suspension pH, at 20°C. Fitzpatrick et al. (2004), using a range of temperatures from 6-29°C indicated that flocculation was slowed at low temperatures, and floccule destabilisation increased with increasing temperature.

Following settling to a standard height (25 cm from surface), an aliquot of the supernatant (between 10 -15 cm from the surface) was extracted and used for turbidity measurement. All flocculation tests were repeated in triplicate.

Effects of PAM type and concentration on settling rate and turbidity were statistically analysed by the general linear model (GLM) ANOVA procedure, with mean separation using least significant difference (LSD) at $\alpha = 0.05$.

3. Results and Discussion

3.1 Characterisation of Aggregate Tail Water

Particle size distribution of the tail water is illustrated in Figure 1. According to the ISSS Classification, clay size particles (<2 µm) account for 54 % of the particles, whilst particles of silt (2-20 µm) and sand (20-2000 µm) amounted to 34 and 12 %, respectively. The results are consistent with soil survey data for the Piarco series (Brown and Bally, 1966). Eudoxie (2010) identified kaolinite and illite as the dominant minerals in the clay fraction, whilst quartz was representative of the larger particle sizes.

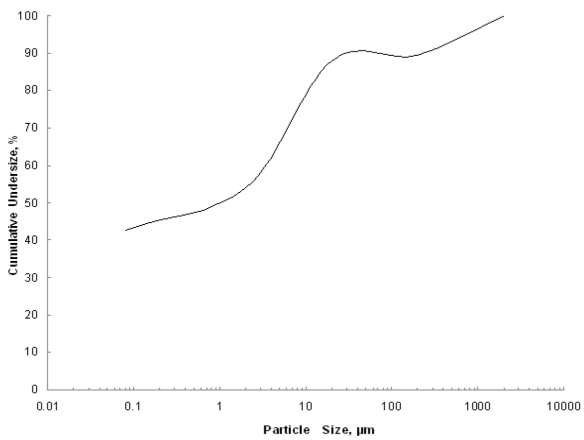

Figure 1. Particle size distribution of aggregate tail water

Table 2 shows the characteristics of the aggregate tail water. At the in-situ pH (5.95) the particles had a CEC of 4.7 cmol^{+} kg^{-1}. The low-moderate charge suggests a predominance of kaolinite versus illite in the aggregate tail water. Sabah and Cengiz (2004) and Nasser and James (2006) both measured zeta potential of kaolinite minerals and showed moderate negative values (approximately -30mV, pH 6). The tail water has a high concentration of suspended particles, which relates to the high turbidity (698 NTU). However, it has very low concentrations of dissolved ions, especially Ca and Mg. This supports the presence of kaolinite and illite, which are devoid of Ca and Mg.

Table 2. Selected properties of the aggregate tail water

Property	Value
Natural pH	5.95
Total suspended soils (g L^{-1})	37.1
Turbidity (NTU)	698
Conductivity (dS m^{-1})	0.08
Alkalinity (mg $CaCO_3$ L^{-1})	2.5
Hardness (mg $CaCO_3$ L^{-1})	10.5
Sand: silt: clay (%)	12:34:54

3.2 Flocculation Tests

The effectiveness of different PAM types in flocculation performance is shown in Figure 2. For all polymers, the settling rate increased with increasing polymer concentration. Sabah and Cengiz (2004) and Besra et al. (2006) both showed similar responses to PAM polymers. In their studies optimal doses were attained, albeit at much higher polymer concentrations. Nasser and James (2006) experimenting on kaolinite suspensions showed an optimal dose of between 12-25 mg L^{-1} cationic polymer.

In their case, the suspension contained a significantly greater proportion of solids. Based on McLaughlin and Bartholomew (2007) assertions that much lower concentrations of PAM were needed for flocculating natural soils, this study evaluated the polymers at relatively low doses. The non-attainment of optimal settling rates across all polymer types (see Figure 2) indicates that equilibrium concentrations were not achieved for any of the polymers. Lower settling rates at low polymer doses is attributed to insufficient polymer available for bridging an appreciable number of particles in the suspension (Mpofu et al., 2004).

The increase in the number of adsorbed polymer and consequent bridging at higher polymer concentration, led to enhanced settling rates. The notable differences in settling rates at all polymer concentrations among the PAM types can be explained in terms of the ionic nature of the polymer as well as the particle distribution and mineralogy of the suspended solids. A similar response was seen for both anionic PAMs with DF 260 showing slightly lower settling rates at all tested concentrations.

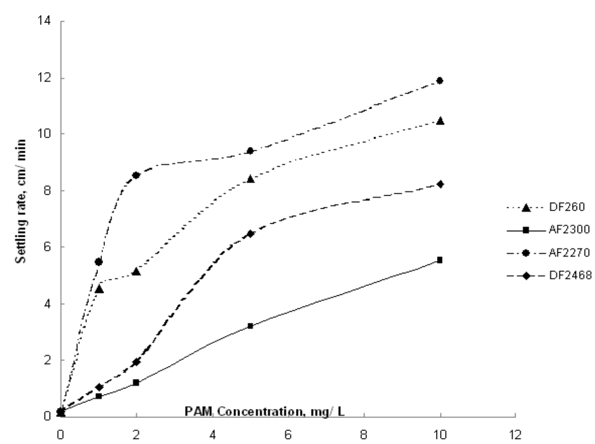

Figure 2. Effects of PAM type and concentration on sedimentation rates of aggregate tail water

Main effects of polymer type showed non-significant differences between the two anionic PAMs (see Table 3). However, when compared to the non-ionic and cationic PAMs, the anionic PAMs showed significantly ($P<0.05$) higher settling rates. Sabah and

Cengiz (2004) used similar PAM types in their study and observed similar patterns. They postulated that the main differences between the low and high molecular weight anionic charged polymers resulted from the latter's ability to produce larger floccules. Nasser and James (2006) argued differently and stated that for anionic polymers, especially in kaolinite dominated suspensions, increasing charge density will reduce the settling rate. However, both authors agreed that increasing molecular weight favours faster settling through larger flocs. In our experiments high molecular weight, high charge density PAM showed the highest settling rate, alluding to a probable stronger influence of molecular weight on flocculation. The cationic PAM had a high molecular weight and charge density, which negatively influenced its flocculation efficiency. Angle et al. (1997) explained that the strong absorption of cationic polymers to the particle surface through electrostatic attraction would prevent effective bridging.

Table 3. Main effect of flocculant on settling rate and turbidity of aggregate tailings

Flocculant	Settling Rate	Turbidity
	cm min^{-1}	NTU
Control	0.17^{d}	625^{a}
DF260	7.16^{a}	156^{d}
AF2300	2.66^{c}	438^{b}
AF2270	8.83^{a}	263^{c}
DF2468	4.44^{b}	177^{cd}

Remarks: Mean values in columns followed by the same letter (superscript) are not statistically different (P < 0.05) according to LSD

Table 3 indicates that AF 2300, the non-ionic PAM had a significantly slower settling rate than all other polymers, although greater than the control. The data conflicts Besra et al. (2006) who showed the greatest settling rate for this PAM type for kaolinite suspensions. Importantly, the concentrations used in their study were approximately 2.5-fold greater. Sabah and Cengiz (2004) in explaining the poor performance of the non-ionic polymer in coal tailing flocculations made reference to the conformation of polymer chains in suspensions, with non-ionic polymers showing low polymer bridging mechanism. All polymer concentrations resulted significantly in faster settling rates (> 10-fold) than the control (see Table 4).

At lower polymer concentrations, settling rates were indifferent. Flocculation rate continued to increase with increasing polymer concentration, implying that for the aggregate tail water a stabilisation range was not attained. Shrestha et al. (2006) showed that the polymer stabilisation range increased with suspension solid content. 10-20 g L^{-1} natural soil suspension eliminated inhibition at 5-10 mg L^{-1} PAM. In our study a maximum of 10 mg L^{-1} PAM was used, which was below the optimal level for a solid content of 37 g L^{-1}. The greatest settling rate was much lower than other studies with similar solid content alluding to the lower than optimal PAM concentrations.

Table 4. Main effect of concentration on settling rate and turbidity of aggregate tailings

Concentration	Settling Rate	Turbidity
mg L^{-1}	cm min^{-1}	NTU
0	0.17^{d}	625^{a}
1	2.95^{c}	421^{b}
2	4.21^{c}	276^{c}
5	6.88^{b}	167^{d}
10	9.04^{a}	171^{d}

Remarks: Mean values in columns followed by the same letter (superscript) are not statistically different (P < 0.05) according to LSD

3.3 Turbidity

Figure 3 shows the suspension clarity for various polymers at increasing concentration. Good agreement was observed with settling rate, although an inverse relationship with concentration was evident. The pattern of steady turbidity reduction with a stabilisation response (< 4 mg L^{-1}) was evident only in the anionic PAMs. The stabilisation effect is closely associated with polymer and suspension characteristics. McLaughlin and Bartholomew (2007) using a 50 g L^{-1} suspension showed stabilisation concentrations of >1 mg L^{-1} PAM. They concluded that texture and mineralogy was slightly correlated with reductions in turbidity. Lentz et al. (1996) reported that an increase in turbidity of high concentration PAM solutions may induce steric stabilisation or repulsion.

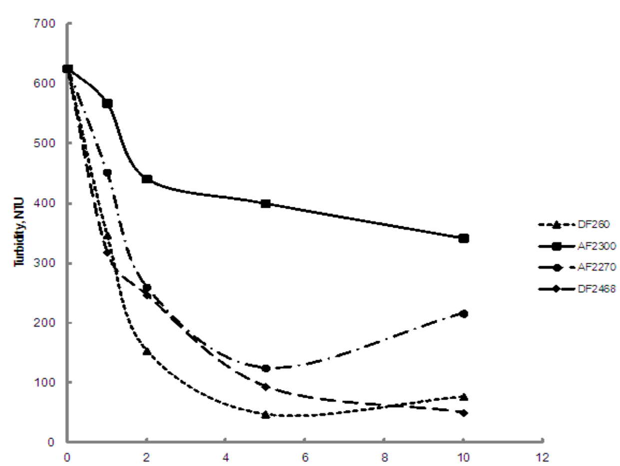

Figure 3. Effects of PAM type and concentration on supernatant turbidity of aggregate tail water

Hogg (2000) suggested that particle destabilisation by polymer absorption occurs preferentially on coarser particles. The textural variation in the aggregate tail water possibly influenced in the stabilisation of the anionic polymers, even at the low concentrations used. Minimum turbidity values were not attained for the cationic and non-ionic PAM, alluding to the fact that current polymer concentrations were suboptimal. DF 2468 (cationic) resulted in greater supernatant clarity at high polymer concentrations.

However, DF 260 performed similarly at low polymer concentrations. Nasser and James (2006) explained that the high negative zeta potential of particles treated with the anionic polymer is linked to lower supernatant clarities than those treated with cationic polymers; although optimal conditions are attained with smaller doses of the former. At 10 mg L^{-1} the non-ionic PAM was ineffective in practically reducing the suspension turbidity. Greater than 50 % of the initial turbidity remained at this concentration. Dihang et al. (2008) reported similar findings for a non-ionic PAM in promoting turbidity reduction of high turbidity laterite suspensions. However, the same authors reported significant improvements when the non-ionic polymer was combined with a coagulant. Environmentally, cationic PAM poses the greatest toxicological risk (Mason et al., 2005). The use of non-ionic and anionic polymers should be encouraged, since the final discharge of non-recycled process water is natural surface water bodies.

The lower charged, lower molecular weight anionic PAM showed non-significant differences in turbidity with the cationic PAM, but resulted in significantly lower turbidity values than the higher charged, higher molecular weight anionic PAM (Table 3). Mc Laughlin and Bartholomew (2007) reported similar findings. Sabah and Cengiz (2004) postulated that strong electrostatic repulsive forces are in effect between medium anionic polymer and negatively charges colloids, which prevents the flocculation of colloidal clays. Across all polymers turbidity decreased significantly ($P < 0.05$) with concentration until 5 mg L^{-1} (see Table 4). Higher concentrations of PAM induced a stabilisation effect.

4. Conclusion

Characterisation of the aggregate tail water from Vega Minerals showed a solid rich suspension comprising > 50 % clay. The size distribution of particles affected the flocculation performance, especially as measured by turbidity. Sedimentation tests in the presence of charged polymers at various concentrations were preformed. All polymers showed increasing settling rates with increasing PAM concentration, the non-ionic polymer being least effective. An optimal settling rate was not determined for the concentration ranges used for the aggregate tail water. However, the high charged anionic polymer had the fastest settling rate. Supernatant clarity as measured by turbidity showed an inverse relationship to settling rate for the various polymers with concentration. The cationic polymer resulted in the lowest turbidity although a minimal value was not attained. Along the concentration range, the two anionic polymers (DF 260 and AF 2270) showed stabilisation effects at Pam doses > 4 mg L^{-1}. In this case, the lower charged anionic polymer was more effective in reducing turbidity at natural pH. For aggregate tail water flocculation, the low charged anionic PAM is recommended.

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