Flocculation Behavior of Borax Clayey Tailings in Mono- and Dual-Flocculant Systems: Effect of Tailings Slurry Characteristics and polyDADMAC Type

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Abstract: The effect of tailings slurry characteristics such as solid ratio and solid particle size both, in mono- and dual-flocculant systems, were studied as well as the effect of POLYDADMAC type in dual-flocculant system. Oppositely charged flocculants, a polyacrylamide (PAM)-typed anionic and two poly diallyl-dimethyl-ammonium chloride (polyDADMAC)-typed cationic polymers, were employed for the flocculation. Tailings slurry samples were taken on different dates from the discharge point of Kırka Borax Concentrator. Flocculation performance was characterized by the initial settling rate as well as the residual turbidity of supernatant and the extent of sediment compaction. All tests were performed at the natural pH of the tailings slurry (~pH 9.4) at which borax buffered the suspension. The results showed that an increase in solid load of the tailings slurry results in a dramatic decrease in settling rate of flocculated tailings regardless of flocculant system employed. This can be attributed to the possible change in rheological property of the slurry due to the increasing clay content of the slurry with solid ratio. While the solid ratio has an influence on the settling rate of the flocculated tailings, the amount of slimes determines the optimum dosage of cationic flocculant to obtain clear supernatant in dual-flocculant system. When anionic and cationic flocculants were used in combination, the best synergy was achieved with low weight cationic flocculant. Increasing molecular weight of the cationic flocculant from low to medium resulted in two-fold increase in the required dosage to obtain the same flocculation performance. In dual-flocculant system, optimum results were obtained by anionic and cationic flocculant combination at around 0.4 kg/ton and 0.8 kg/ton solid dosages, respectively, indicating 11.7 cm/min of settling rate and 85.7% of transmittance value.

Keywords: Borax, clayey tailings, flocculation, polyDADMAC, polyacrylamide.

1. INTRODUCTION

Mineral processing operations generally produce very large amounts of colloidal dispersions as tailings that need to be disposed. The commonly used method for impounding of tailings is to use a pond or a dam. Because of its low solid loadings and poor consolidation, the impoundment of these voluminous tailings represents a significant problem to the mining industry worldwide. From environmental and social point of view, the need of large areas for impoundment and challenges in rehabilitation of poorly consolidated storage ponds/dams are some of the drawbacks of non-dewatered tailings disposal. Moreover, due to the increasing demand of water by the industry as well as an increasing water scarcity due to the climate change, sustainable mining operations must rely on the efficient and sustainable usage of water resources by recovering and recycling of process water that is discharged into tailings.

In some mining operations, tailings that include clay minerals deteriorate the condition of tailings disposal. Minerals, such as smectite can cause very difficult dewatering and handling problems because of its unique properties such as swelling and space filling "card house structures" which results in high yield stress. Therefore, effective dewatering of colloidal stable clayey tailings has been an environmental and technical challenge to the mining industry.

Flocculation is used as a way of thickening dilute tailings consisting of colloidal particles, including aggregation of particles by the addition of a polymeric flocculant either natural or synthetic having a wide range of molecular weights and ionic characters. Depending on the flocculant type and suspension characteristics, the flocculation process may occur by one or a combination of such mechanisms, namely: polymer bridging, charge compensation, polymer-particle surface complex formation or depletion flocculation [1, 2]. Among flocculants, polyacrylamide based synthetic types are commonly used in dewatering of clayey tailings. Conventionally, a single flocculant is used for this treatment, but there have been many recent studies on dual-flocculant system searching for enhancing the flocculation of suspended particles in tailings or waste waters [3-5].

In this study both polyacrylamide (PAM)-typed anionic and polyDADMAC-typed cationic polymers were utilized for clayey tailings conditioning to enhance flocculation and dewatering of Kırka borax concentrator tailings. While there are some studies on flocculation of Kırka borax clayey tailings in mono-flocculant system [6-12], dual-flocculant system with oppositely charged

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flocculants is not studied in detail yet. But in author's previous study, it was shown that mono-flocculant system with anionic polyacrylamide is inefficient to get clear water and dual-flocculant system could be a means of enhancing flocculation performance. However, it is documented that floculation behavior of borax tailings is varied by clay rock characteristics in the ore deposit [6, 7, 11, 13]. It mainly consists of smectite type swelling clay and dolomite minerals in varying proportions, having a range of colors from very pale to white [14]. However, the purpose of this study was to investigate the effect of tailings slurry characteristics such as solid ratio and particle size on flocculation behavior of borax clayey tailings both in mono- and dual-flocculant systems and compare the flocculation performance of two polyDADMAC flocculants in dual-flocculant system.

2. MATERIALS AND METHODS

Flocculation experiments were carried out by using two separate tailings slurry samples taken on different dates from the discharge point of Kırka Borax Concentrator to evaluate the effect of tailings slurry characteristics on the flocculation. Apart from the previous study, two polyDADMAC flocculants were tested in dual-flocculant system to find out the best flocculant combination in terms of supernatant clarity. Particle size analysis was carried out by wet sieving technique. Electrokinetic measurements were conducted by using a Zetasizer Nano-Z meter at natural pH of the suspension.

Experimental procedures for flocculation test and preparation of flocculant solution are the same as those used in previous study [15] and not given here. Settling rate, turbidity of supernatant and underflow compaction were measured to evaluate the effectiveness of the flocculation process. Following a 5 min of settling period, a 20 ml sample of the supernatant was withdrawn from the suspension depth of 3 cm with the help of a glass pipette, and its turbidity, as the percentage of transmittance, was measured using a UV spectrophotometer at the wavelength of 675 nm. The initial settling rate of the flocculated slurry in the 1000 cm^3 cylinder was determined by recording the time taken for the "mud line" (solid-liquid interface) to pass between the 900 and 735 cm^3 marks (5 cm of distance in free settling zone). The underflow compaction performance was characterized by the volume of mud at the 10th minute of sedimentation. All tests were done under ambient conditions at 22.0 ±0.1 °C.

A PAM-typed commercial anionic flocculant (Hengfloc 64014) and two PolyDADMAC-typed cationic flocculants (Hydrofloc CPX 400 and CPX 500) were used in flocculation experiments (Table **1**). PolyDADMAC was selected due to its high charge density while PAM was due to high molecular weight.

3. RESULTS AND DISCUSSION

3.1. Tailings Characteristics

Mineralogical composition of tailings and chemical composition of both solid and liquid phases of tailings are given in author's previous paper [15]. The main minerals present in the tailings were dolomite and montmorillonite. Some unrecoverable borax fines and very minor amounts of calcite and quartz were also present there. In addition to the findings reported before, d-spacing broad peaks of the clay mineral increased up to 17.26 °A after ethylene glycolation procedure, revealing that this clay mineral has the swelling property (Figure **1**).

Both samples are similar from mineralogical point of view, but slightly varied in chemical composition [16]. Solid ratios of first and second slurry sample are %10.5 and %6.3, respectively. Both samples are different in terms of particle size. Second sample includes much finer particles than first sample (Figure **2**).

The chemistry of liquid phase of both tailings samples is similar (Table **2**) and they contain a variety of dissolved ions due to the dissolution of carbonate

Table 1: Characteristics of Flocculants Used*

Commercial name	Type	Charge density	Molecular weight
Hengfloc 64014	Anionic (PAM)	Medium/High	Medium
Hydrofloc CPX 400	Cationic (PolyDADMAC)	Unknown	low
Hydrofloc CPX 500	Cationic (PolyDADMAC)	Unknown	medium

*obtained from the supplier.
**no information provided.

and boron minerals and the release of ions from clay mineral into the solution, leading to the formation of alkaline water with a high ion content and a density of 1015 g/L. Dissolved borax buffers the suspension at pH 9.3-9.4, at which borax has minimum solubility [17].

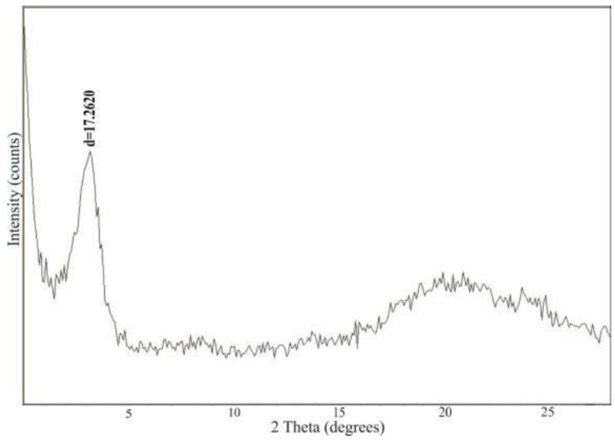


Figure 1: Identification of the clay fraction of the tailings solid: ethylene glycol-solvated preperation.

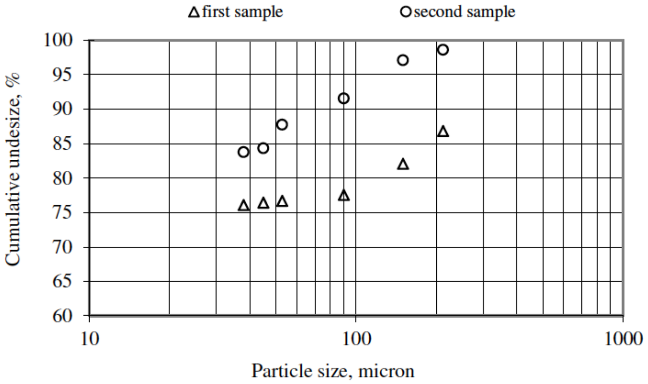


Figure 2: Particle size distribution of tailings.

When the tailings dry solid was dispersed in distilled water for electro kinetic measurement, it was observed that even the diluted suspension has a buffering capacity. This was due to the presence of borax in clay matrix [6] and the existence of either primary or secondary boron compounds in addition to the gang minerals in the tailings. During the measurements, there were limitations because of both the high conductivity of the solutions and the high amount of pH modifiers that were needed to adjust the suspension pH due to the buffering effect of borax. It has been reported that even suspensions including clay samples taken from the Kırka deposit exhibited buffering effect at 9.3 [17]. In addition, destabilization of the suspension was observed because of "the card house structure" formation among clay minerals at acidic pH values of the measurement.

The measured zeta potential value of the tailings solids in this study was about -30.5 mV at the natural pH of 9.4, which is in agreement with the literature results [9, 10, 13, 17].

3.2. Flocculation Tests

Measured pH of the tailings slurry was around 9.4 at which dissolved borax buffered the suspension. Due to the challenges to modify the buffered pH of the tailings slurry, flocculation test were performed at the natural pH of the tailings slurry

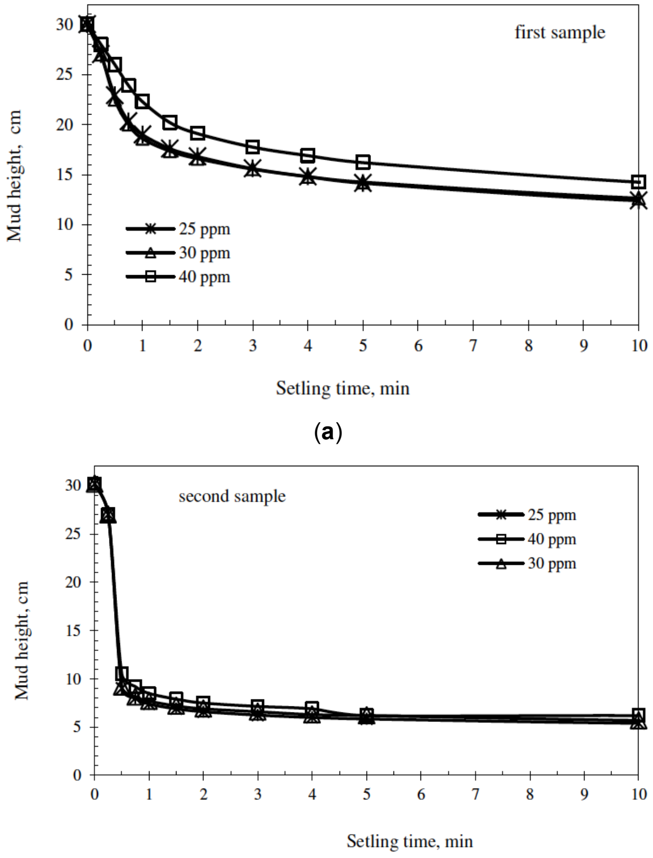
3.2.1. The Effect of Tailings Slurry Characteristics on Flocculation in Mono-Flocculant System

Flocculation behavior of each tailings slurry sample by anionic flocculant is given in Figure **3**. The results show that better flocculation-settling behavior is obtained with low solid ratio of the slurry. An increase in solid ratio of the slurry results a dramatic decrease in settling rate of the solid even with much coarser particle size distribution. This result reveals that solid ratio of the slurry is more influential than the particle size of the tailings solid in mono-flocculant system with anionic flocculant. This might be due to the changing rheological property of clayey tailings with the increase of solid load in the slurry.

In fact, the flocculation behavior of both tailings samples to produce a clear supernatant was very poor. Indeed, the turbidity of the supernatant was too high to be measured. Moreover, the supernatant was so turbid that a second solid/liquid interface occurred after a period of time (Figure **4**). This suggested that a significant amount of the fine fraction of the tailings lagged behind the settling mass still remaining

Table 2: The Chemistry of Liquid Phase of the Tailings

	Component, ppm						
	B_{Total}	Na	Ca	Mg	K	CO_3^{2-}	HCO_3^-
First Sample	2234	5760	2.5	5.78	176	4650	4453
Second Sample	2252	5470	3.0	20.3	149	4635	4438



(a)

(b)

Figure 3: Flocculation-settling behavior of tailings slurry sample with commercial anionic PAM Hengfloc 61014 (**a**) first sample having solid ratio of 10.5 % (**b**) second sample having solid ratio of 6.3%.

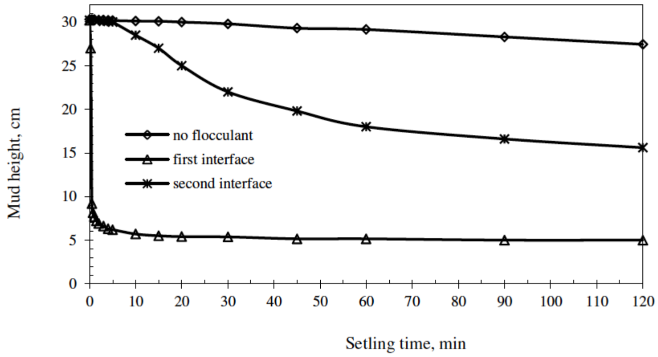
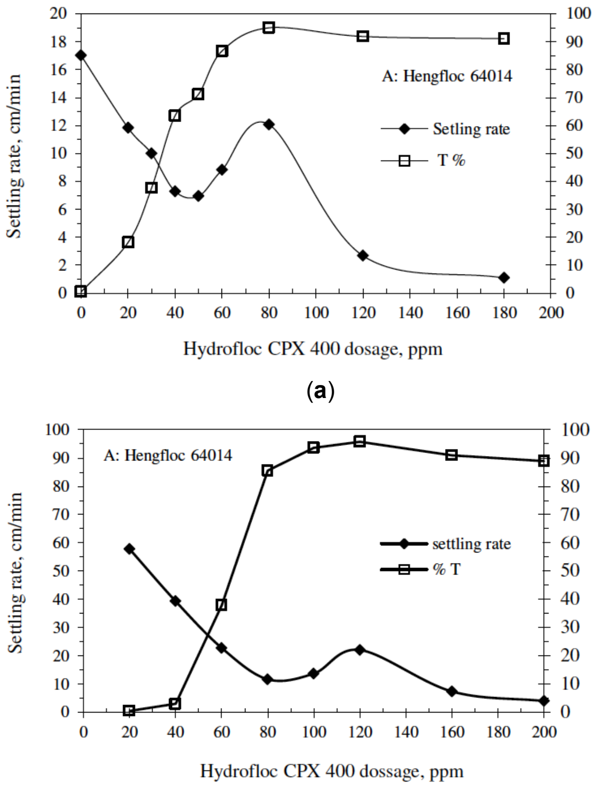


Figure 4: Settling behavior of non-flocculated tailings slurry and of flocculated tailings slurry with 30 ppm of commercial PAM Hengfloc 61014.

suspended. It was observed that even at lower settling rates and/or additional anionic flocculant, the clarity remained drastically low. However, the settling behavior of particles constituting to the supernatant turbidity with anionic flocculant was better than the tailings slurry itself (Figure **4**). The possible reasons for the relatively low flocculation behavior of borax clayey tailings by anionic PAM were discussed in author's previous paper, thus not given here.

3.2.2. The Effect of Tailings Slurry Characteristics on Flocculation in Dual-Flocculant System

Results of the dual-flocculant system are given in Figure **5**. For both tailings slurry samples, it can be observed that there is a decreasing trend in settling rate with an increase in polyDADMAC dosage. But, as in mono-flocculant system, settling rate in dual-flocculant system is much higher for tailings slurry with low solid ratio. The results showed that it is possible to obtain a clear supernatant by dual-flocculant system with both slurry samples. But the required dosage of polyDADMAC increased with tailings having much finer particles even at lower solid ratio. This fact points out that optimum dosage of cationic flocculant is more related with the number of fine particles rather than the total solid.



(a)

(b)

Figure 5: Flocculation behavior of tailings slurry in dual-flocculant system (a) first sample having solid ratio of 10.5 % (b) second sample having solid ratio of 6.3% (A:30 ppm).

3.2.3. Comparison of Two Commercial polyDADMAC Flocculants in Dual-Flocculant System

It was concluded that the desired supernatant clarity is not obtained by using anionic flocculant only and oppositely charged dual-flocculant system is necessary to enhance the performance of mono-flocculant that is an alternative for borax clayey tailings. Previous study demonstrates that commercial polyacrylamide based anionic Henfloc 64014 was one of the efficient flocculants both in mono- and dual-flocculant systems. Apart from the previous study, two commercial polyDADMAC typed cationic flocculants, different in molecular weight, were tested in dual-flocculant system with Hengfloc 64014. Tailings slurry sample with lower solid ratio was used in these flocculation experiments.

The flocculation behavior of the tailings in dual-flocculant system is given in Figure **6-8**. As shown in Figure **6**, at all dosages tested, both commercial polyDADMAC flocculants improved the supernatant clarity. When the flocculation performance of two cationic flocculants in dual-flocculant system was compared, higher supernatant clarity was obtained with a lower dosage of hydrofloc CPX 400 than CPX 500.

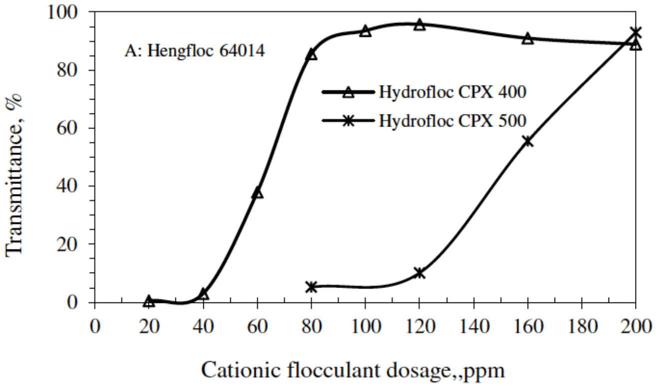


Figure 6: Effect of cationic flocculant on supernatant clarity in dual-flocculant system (A: 30 ppm).

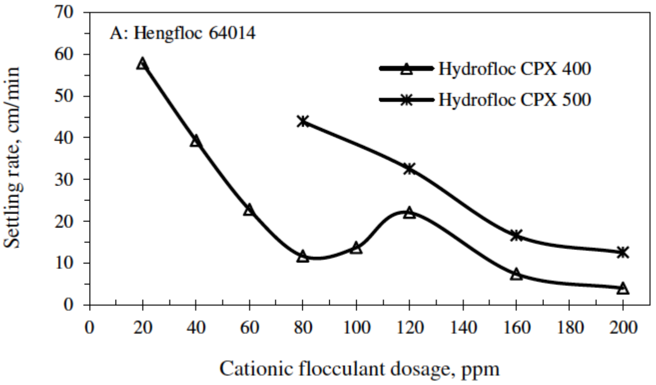


Figure 7: Effect of cationic flocculant on settling rate of borax clayey tailings in dual-flocculant system (A:30 ppm).

Although bridging is the main mechanism in the flocculation system with anionic or non-ionic polymers, the mode of action of cationic polymers has been reported as a controversial issue whether charge neutralization alone or charge neutralization and bridging result in flocculation. Gregory (1973) [18] introduced the concept of “electrostatic patch” model, which explains the reason for the improvement in the coagulation process with cationic polymers. In this model, the net residual charge of the polymer patch on one particle surface can attach to the bare part of oppositely charged particles. For oppositely charged polymer and particles, Yu *et al.* (2006) [19] showed that these two mechanisms can be involved in the particle flocculation depending on the polymer characteristics i.e. charge density and molecular weight. The flocculation induced by cationic polymer with low molecular weight and high charge density can be explained by the charge neutralization whilst the high molecular weight and low charge density cationic polymers can be explained by bridging.

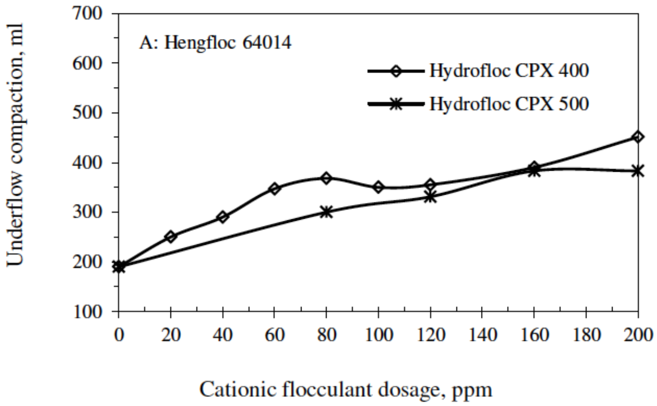


Figure 8: Effect of cationic flocculant on underflow compaction in dual-flocculant system(A: 30 ppm).

With the commercial polycation Hydrofloc CPX 500, high concentrations of polymer were necessary for obtaining the same supernatant clarity. Taking into consideration of the measured transmittance of recycled water (81.7% T), the required dosage of cationic flocculant to obtain the desired turbidity level was about 80 ppm and 200 ppm for Hydrofloc CPX 400 and CPX 500, respectively. At these dosages, the initial settling rates and transmittance values for both flocculants were almost the same i.e. initial settling rate was 11.7 cm/min with 91-93% transmittance of supernatant. In mono-flocculant system with cationic polymer, the optimum dosage is inversely proportional to the charge density rather than molecular weight [20, 21]. The flocculation behavior in dual-flocculant system (highly charged polycation prior to a high molecular weight polyanion) particularly depends on the concentration of polycation (according to the anionic character of the suspension) and the molar ratio of anionic and cationic charges [4]. Therefore, it can be postulated that high optimum dosage of Hydrofloc CPX 500 could be attributed to its charge density rather than its molecular weight. Moreover, in terms of supernatant turbidity, efficient flocculation by Hydroflc CPX400 occurs at a narrow dosage range of 40 to 100 ppm when compared with the polymer Hydrofloc CPX 500.

For the underflow compaction in dual-flocculant system (Figure **8**), Hydroloc CPX 400 produced slightly more voluminous sediment at the dosages tested on the contrary of the fact that the floc structure by the low molecular weight cationic polymer is more compact than that the one with high molecular weight due to the charge neutralization dominating the flocculation [19]. But up to 120 ppm cationic polymer dosage, there was no considerable improvement in the supernatant turbidity with Hydrofloc CPX 500 leading to fewer amounts of flocculated solids (Figure **6**). But the slurry was completely flocculated with Hydrofloc CPX 400 leading to a large amount of solid in the sediment. Therefore, this phenomenon could be explained by the amount of solid flocculated. In fact, when two conditions at which the same flocculation performance was obtained in terms of settling rate and supernatant clarity, it was shown that the sediment volume with Hydrofloc CPX 400 was slightly smaller than that with CPX 500 i.e. 368 ml and 383 ml, respectively (Figure **9**).

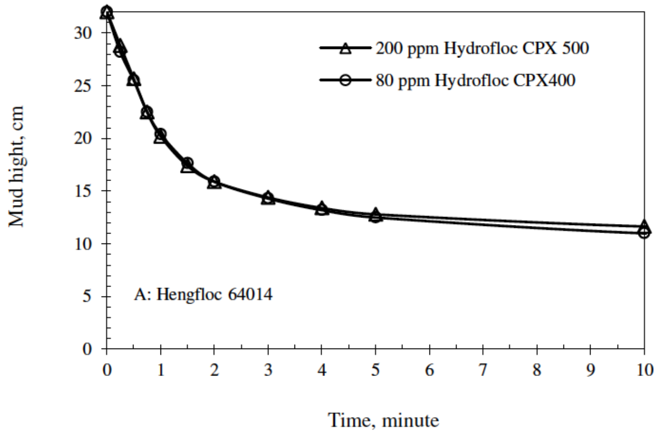


Figure 9: Underflow compaction with two cationic floculants in dual-flocculant system (A: 30 ppm).

Regarding the flocculant consumption, Hydrofloc CPX 400 appears to be the best cationic flocculant for the dual-flocculant system. So, at 80 ppm cationic flocculant dosage, the effect of anionic flocculant dosage on the flocculation performance was investigated as shown in Figure **10**. The residual turbidity was very high with "overdosing" the polyanion while the initial settling rate increased due to the formation of large flocs.

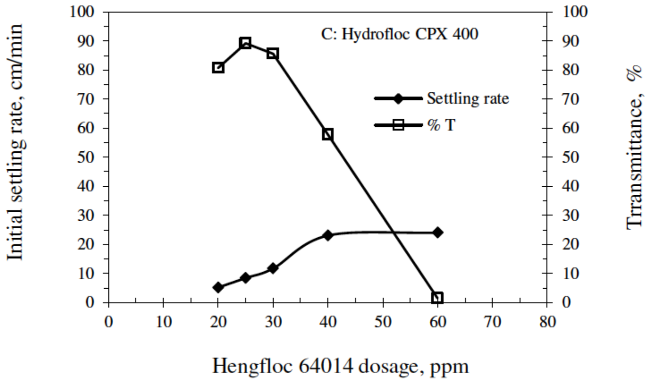


Figure 10: Effect of anionic flocculant on flocculation in dual-flocculant system (C: 80 ppm).

4. CONCLUSIONS

Flocculation and dewatering of Kırka borax tailings slurry are challenging because of its inherent characteristics in terms of solid and liquid phases of the tailings. Tailings slurry mainly consists of clay mineral (smectite) and dolomite while liquid phase of the tailings has a high ionic strength due to the dissolution of dolomite and borax and its pH is about 9.4 at which dissolved borax buffered the suspension. Moreover, due to the changing mineral composition of clay rock layer in the deposit, which also affects the mineral processing, a change in tailings slurry characteristic will inevitably affect the flocculation.

It was demonstrated that solid ratio of the slurry and particle size of the tailings solid was among parameters affecting flocculation behavior of tailings slurry both in mono- and dual-flocculant systems. While solid ratio had an effect on settling rate of flocculated tailings in each flocculant system, particle size of tailings solid determined the required dosage of cationic polymer in dual-flocculant system in order to obtain a clear supernatant. When the flocculation performance of two commercial polyDADMAC flocculants was compared, the best synergy was achieved with low weight medium/high anionic and low molecular weight cationic combination. When a medium molecular weight cationic flocculant was used instead of the low molecular weight cationic flocculant, the required optimum dosage to obtain the same flocculation performance increased (by a factor of about 2.0). In addition, overdosing of anionic flocculant at an optimum cationic flocculant dosage resulted in a dramatic reduction in the clarity of the supernatant while the settling rate increased.

In dual-flocculant system, optimum results were obtained by anionic and cationic flocculant combination at around 0.4 kg/ton-solids and 0.8 kg/ton-solids dosages, respectively, indicating 11.7 cm/min of settling rate and 85.7% of transmittance value.

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