Characterization and dewatering of borax clayey tailings by mono- and dual-floculants systems

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ABSTRACT

This study includes dewatering of Kirka Borax Concentrator tailings by flocculation with mono- and dual-floculants systems. Four polyacrylamide (PAM)-typed anionic and a poly dialyl-dimethyl-ammonium chloride (PolyDADMAC)-typed cationic polymers were used as floculants in mono- and dual-floculants systems to flocculate tailings. Tailings slurry sample used in the experiments were taken from the discharge point of Kirka Borax Concentrator. Prior to the flocculation tests, physical, chemical and mineralogical analysis were carried out to characterize the tailings slurry. Results reveal that while tailings solid consists mainly of dolomite and montmorillonite with some unrecoverable boron mineral fines and very minor amount of calcite and quartz, tailings water is typical with the content of quite high dissolved carbonate and borax with a pH of 9.4. Flocculation tests were performed in one liter graduated cylinder at inherent pH of the tailings slurry sample. Settling rate and turbidity of overflow was measured as important factors for evaluating the flocculation performance of different floculants. The tailings slurry as received showed a very low settling behavior due to the clay content and high percentage of fine particles. Flocculation of tailings with anionic floculants accelerated the settling rate of particles without providing a clear supernatant. But, dual-floculants system, in which anionic and cationic type polymeric floculants were used, was able to provide a clear supernatant at relatively higher settling rates.

1. Introduction

Tailings, a kind of mining waste, are the fine grained residue of the mineral processing plant in which the desired raw materials are separated from the gang minerals and appear as slurries due to mixing with water during processing. The disposal of these tailings has been a major issue in many mines and generally a public relations challenge for the mining industry. The traditional method of disposing of the tailings is to use a tailings pond and a dam. However, from the environmental point of view, thickening tailings disposal system has been accepted as a more effective method (Newman et al., 2001); the removal of water not only can create a better storage system but can also assist in water recovery which is major issue as many mines where the water is scarce.

Borate deposit in Kirka is known as the largest Na-Borate deposit in the World. The deposit contains primarily borax, with only secondary colemanite and ulexite and minor amounts of hydroboracite, inderite, inyoite, kurnakovite, meyerhofferite, tincalconite, and tunellite (Garrett, 1998). Borate layers in the deposit, containing minor amounts of celestite, calcite, and dolomite, are interlayered with clay horizons containing some volcanic tuff (frequently altered to zeolites), quartz, biotite, and feldspar. The clay rock is mainly consists of smectite type swelling clay and dolomite minerals in varying proportions, having a range of colors from very pale green to white (Helvaci, 2015).

The run-of-mine ore, having an average grade of 25% B₂O₃ and containing high amounts of insoluble impurities, is processed in the Kirka Concentrator to
produce a borax concentrate of 32–34% $\text{B}_2\text{O}_3$. The beneficiation process is comprised of washing the crushed and scrubbed ore at ambient temperature to remove gangue minerals which generate borax saturated tailings slurry containing 8-10% clay-sized particles. The tailings solid is mixture of clay minerals, dolomite and of fewer amounts of other finely divided gang minerals as well as considerable amount of borax (Garrett, 1998). This tailings slurry is directly sent to the tailing ponds by gravity for natural settling without any treatment. Although, process water is further collected and re-used in the beneficiation process, a large amount of water and large areas of land are tied up by impounding these clayey tailings for a long period of time. This situation causes serious technical and environmental problems in terms of the need for additional ponds and the challenges for the closure and rehabilitation of the tailings ponds. Therefore, an effective tailings disposal method is necessary for the borax clayey tailings regarding to both environmental and technical point of view. In this regard, surface disposition of tailings in paste form has been accepted as a new disposal method for minimizing the engineering and environmental challenges associated with the tailings disposal (Karapınar, 2009). Paste is simply dewatered/thickened tailings with little or no water bleed that has non-segregating nature (Robinsky, 1999; Newman et al., 2001; Verbung, 2001). Thickened tailings disposal involves taking the process tailings, thickening it (and simultaneously dewatering) with a high-rate or paste thickener, then pumping it to the disposal site. Unlike conventional thickener, those thickeners produce a thickened underflow in the form of paste rather than slurry and could be disposed of by surface stacking instead of impounding. Regardless of the type of the thickener employed, flocculation process is a compulsory pretreatment step in dewatering of the fine and colloidal suspensions and it involves destabilization of fine/colloidal particle dispersions by addition of a flocculants either natural or synthetic having a wide range of molecular weights and ionic characters. Depending on the flocculant types and suspension characteristics, the flocculation process may occur by one or a combination of mechanism, namely: polymer bridging, charge compensation or neutralization, polymer-particle surface complex formation and depletion flocculation (Gregory 1985, 1987).

There are few studies on understanding the flocculation behavior of borax clay tailings, carried out both on the actual plant tailings (Sabah and Yeşilkaya, 2000) and on the synthetic dispersions prepared in laboratory by using clayey materials obtained from the deposit (Gür et al., 1994, 1996; Hoşten and Çirak 2013; Çirak and Hoşten, 2012, 2015). These include comparative studies between Polyacrylamide (PAM) and Polyethylene Oxide (PEO) typed flocculants, i.e. conventional and non-conventional (3-D branched structure) PAM-typed anionic flocculants, PAM- and PEO-typed non-ionic flocculants. It was reported that the nonionic PEO performed better than the PAM-typed flocculants in reducing the supernatant turbidity (Gür et al., 1994; 1996; Hoşten and Çirak 2013; Çirak and Hoşten, 2012; 2015). Sabah and Yeşilkaya (2000) reported that the PAM-typed anionic flocculants performed much better than PAM typed non-ionic flocculant in terms of the settling rate, but still at quite a high flocculant consumption of 1176 g/ton solids and the use of coagulants together with an anionic flocculant did not improve the flocculation efficiency.

Apart from above studies, Taşpınar and Çalışan (nd) studied the flocculation and filtration behavior of four different colored clay minerals supplied from Kirka borax deposit by using four different types of surfactants (non-ionic, anionic, cationic, amphoteric) and a non-ionic PAM-typed flocculant. They reported that surfactants used together with flocculant result in a decrease in flocculation efficiency in terms of turbidity and its effect is varied with the composition of the clay material in terms of its montmorillonite and dolomite content. Çebi et al. (1994) studied the dewatering of the concentrator and Borax Refinery Plant tailings by centrifuge decanter. They reported that flocculant addition is needed for the mechanical dewatering even when the centrifuge decanter is used to enhance solid-liquid separation.

In this study, laboratory flocculation experiments were carried out with the aim of the defining the effective flocculant(s) for the dewatering of Kirka Borax Concentrator tailings either in mono- flocculant system with PAM-typed anionic flocculant and dual-flocculants system with PAM- typed anionic and poly diallyl-dimethyl-ammonium chloride (polyDADMAC)-typed cationic flocculants.

2. Materials and Methods

Tailings slurry sample (60 L) used in the experiments were taken from the discharge point of Etibor Kirka Borax Concentrator. Tailings characterization studies were carried out both in terms of tailings solids and water. For analysis, 1 L
A representative sample was filtered and both solid and liquid phases were analyzed. The mineral composition of the tailings was determined by X-Ray diffraction analysis. The chemical composition of the tailing solid was analyzed by X-ray fluorescence (XRF) spectrometer. The boron content of the tailings solids was only determined by volumetric analysis. Tailings water was analyzed for cations by ICP-MS. Titration method was used for the determination of carbonate content of the tailings water. Particle size analysis was carried out by wet sieving technique. Solid content of tailings slurry was determined.

The flocculation tests were performed in one liter graduated cylinder with 900 ml slurry in mono-floculant and 800 ml slurry in dual-floculants system. The tests were done at inherent pH of the sample which was about 9.4. Stock solutions of anionic and cationic floculants were prepared in the concentration of 0.2 (w/v) and 2 % (v/v), respectively. The stock solutions were used within 7 days of preparation. A fresh daily working diluted anionic and cationic flocculant solutions were used and added by pouring into slurry as 100 ml solution of each. In mono-floculant tests, immediately after the addition of the floculant, the cylinder was shaken and stirred by five upside down for good mixing. The flocculated slurry was then left for settling for 24 hours. In dual-floculants tests, a desired amount of anionic floculant solution was first added to the slurry. After the shaking, cationic floculant was added and the slurry was shaken by additional five upside down, and finally left for settling. At appropriate time intervals, mud height was measured. Four PAM-typed commercial anionic floculants (Hengloc 64014, Hydrofloc 9180 LV, Magnofloc 336, Magnofloc 1011) and one PolyDADMAC-typed cationic floculant (Hydrofloc CPX 400) were used in flocculation experiments (Table 1).

Settling rate and turbidity of overflow were measured as important factors for evaluating the flocculation performance of different floculants. 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 glass pipette and its turbidity as percent 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). All tests were done under ambient conditions at 22.0 ±0.1 °C.

3. Results and Discussion

3.1. Characterization of Tailings

Mineralogical analysis showed that tailings solid mainly consists of dolomite, montmorillonite and boron minerals and minor amount of calcite and quartz (Figure 1). Chemical composition of tailings solid as well as the tailings water was given in table 2 and table 3.

Tailings water contains high amount of dissolved Na and boron (Table 2) due to the solubility of borax in water even at ambient temperature. Measured pH of

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>19.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.4</td>
</tr>
<tr>
<td>CaO</td>
<td>17.2</td>
</tr>
<tr>
<td>MgO</td>
<td>14.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.9</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.9</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>12.6</td>
</tr>
<tr>
<td>LoI</td>
<td>28.97</td>
</tr>
</tbody>
</table>

### Table 1- Characteristics of floculants used*

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Type</th>
<th>Charge density</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hengloc 64014</td>
<td>Anionic (PAM)</td>
<td>medium/high</td>
<td>medium</td>
</tr>
<tr>
<td>Hydrofloc 9180 LV</td>
<td>Anionic (PAM)</td>
<td>medium/high</td>
<td>high</td>
</tr>
<tr>
<td>Magnofloc 1011</td>
<td>Anionic (PAM)</td>
<td>low</td>
<td>high/very high</td>
</tr>
<tr>
<td>Magnofloc 336</td>
<td>Anionic (PAM)</td>
<td>medium</td>
<td>high/very high</td>
</tr>
<tr>
<td>Hydrofloc CPX 400</td>
<td>Cationic (PDADMAC)</td>
<td>**</td>
<td>low</td>
</tr>
</tbody>
</table>

*obtained from the supplier  **no information provided
the tailings is about 9.4. It is known that the dissolved borax buffers the suspensions at about pH 9.3 at which borax has minimum solubility (Hançer et al., 1993). Therefore, the tailings slurry discharged from the borax concentrator contains both dissolved and solid boron, as saturated with the borax. In addition to borax dissolution, high amount of dissolved carbonate and bicarbonate of tailings water revealed that the carbonate minerals such as dolomite and calcite are dissolved in buffered borax solution. Therefore, carbonate and bicarbonate ions in tailings water will contribute to the buffering capacity of the tailings water (Stumm and Morgan, 1996). However, when compared with carbonate content of the tailings water, concentration of dissolved Ca and Mg ions is rather low. This is probably the result of largely due to the precipitation of Ca and Mg boron and/or carbonate compounds rather than due to the removal of cations by clay particles via adsorption/ion exchange. Indeed, XRD pattern of the tailings solid indicates the sign of the existence of amorphous compound confirming the precipitation of Ca and Mg compounds in the slurry. Similarly, Sari (2008) showed that cations released from the dissolution of dolomite and calcite in boric acid solutions may cause the loss of boron by post precipitation borates compounds. In fact, the ratio of boron to sodium of tailings water (0.4) is smaller than its theoretical ratio of borax solid (0.95), indicating the dissolved boron loss from the tailings water.

Chemical analysis result showed that the tailings water contains a variety of dissolved ions due to the dissolution of carbonate and boron minerals and the release from clay mineral particles in solution, leads to alkaline water as well as with high ion content.

The percent solid by weight of the tailings slurry sample was determined as 10.5 % (w/v).Particle
size analysis of tailings solid showed that 76% of the solid is below 38 μm and about 13.51% of it is above 100 μm. The percentage of slime size (< 20 μm) determined from the Gaudin-Schuhman type of plot constitutes about 71.22% of the overall material which has trouble in solid liquid separation.

3.2. Flocculation Tests

Measured pH of the tailings slurry is around 9.4 at which dissolved borax buffered the suspension. Due to the obstacles such as addition of large amount of chemicals to modify the buffered pH of the tailings slurry, flocculation test were performed at the inherent pH of the tailings slurry. Any flocculants having good performance at this pH value could be the best flocculant(s) for the flocculation of borax concentrator tailings.

Since the tailings slurry without flocculant addition settles very slowly, having a settling rate of 0.0013 cm/min (Karapınar, 2016), the effects of different anionic flocculants on tailings settling rate were investigated in the range of 25-40 ppm and the results were given in figure 2-6.

These results reveal that Hengfloc 64014 and Hydrofloc 9180 LV exhibited better flocculation
Figure 4- Settling behavior of tailings slurry flocculated by anionic flocculant Magnofloc 336.

Figure 5- Settling behavior of tailings slurry flocculated by anionic flocculant Magnofloc 1011.

Figure 6- Flocculation performance of four anionic flocculants in mono-flocculant system
performance than other two anionic flocculants in terms of settling rate. Regarding the settling rate, optimum flocculant dosages was 30 ppm for Hengfloc 64014 and Magnofloc 336. However, an increase in dosage of Hydrofloc 9180 LV leads to a descending path in settling rate. On the contrary, Magnofloc 1011 exhibit an ascending trend of settling rate with the increasing of dosage. Therefore, Hydrofloc 9180 LV and Magnofloc 1011 showed their best performance at 25 ppm and 40 ppm of flocculant dosages, respectively.

At 25 ppm flocculant dosage, flocculation performance of both Hengfloc 64014 and Hydrofloc 9180 LV and both Magnofloc 336 and Magnofloc 1011 were very close to each other, respectively. At 30 ppm flocculant dosage, flocculation performance of different flocculants decreases in following order: Hengfloc 64014>Hydrofloc 9180 LV>Magnofloc 336=Magnofloc 1011.

A summary of results presented in figure 3-6 illustrates the fact that an increase in molecular weight of the polymer with a certain anionicity causes the flocculation performance to be reduced dramatically in terms of settling rate. However, decreasing of polymer anionicity from medium to low with high/very high molecular weight leads to an increase in dosage to be obtained same degree of settling rate with polymers having medium anionicity and medium/high molecular weight.

Although, high settling rates were obtained, the effectiveness of anionic flocculants studied in providing a clear supernatant was very poor. The turbidity of supernatant was too high to be measured, suggesting that a significant amount of the fine fraction of the slurry lags behind the settling mass and remains suspended. Furthermore, the supernatant was so turbid that a second solid/liquid interface was occurred in the supernatant after a period of time.

Lower flocculation efficiency of borax clayey tailings has been attributed to both the week flocculation behavior of dolomite (Moudgil and Behl, 1993; Gür et al, 1994; Moudgil et al., 1995; Akdeniz et al., 2003; Hoşten and Çırak, 2013) and clay being Mg-rich trioctahedral clay (Çırak and Hoşten, 2015). Both mineral are Mg- rich minerals and develop Mg-enriched surfaces. Çırak and Hoşten (2015) have claimed that due to its strong hydration property of Mg-surfaces, flocculant adsorption may be hindered as well as the particle-particle interaction. Another reason for the weak flocculation behavior of borax clayey tailings has been explained by the possible lack of isolated hydroxyl group on dolomite surfaces which are vital for the particle-polymer interaction (Çırak and Hoşten, 2015).

Infact, for Kurka borax clayey tailings slurry in which mainly dolomite, montmorillonite and borax exist, dissolution, adsorption and cation exchange would be dominant mechanisms governing the flocculation of the suspension. Whilst the dissolution of borax even at ambient temperatures releases boron and sodium ions into the solution, dissolution of carbonate minerals in borax solution releases Ca and Mg ions into solution as well. There is also exchange cations released into solution from clay minerals. Previous studies shows that boron and magnesium adsorption onto clay surfaces deteriorate flocculation (Sabah and Yeşilkaya, 2000; Hoşten and Çırak, 2013) whereas sodium and calcium adsorption enhance the flocculation (Gür et al., 1994; Çırak and Hoşten, 2015). In addition to cations and boron anions, dissolved carbonate may govern the flocculation by affecting dissolution of carbonates, surface charge of the particles, configuration of the polymer in water and hence flocculant adsorption.

Results showed that the desired supernatant clarity was not able to be obtained by using anionic flocculant only. Therefore, oppositely charged dual-flocculants combinations were tested to enhance the performance of mono- flocculant system. The aim was to obtain more effective solid-liquid separation in terms of settling rate and overflow clarity. Hengfloc 64014 and Hydrofloc 9180 LV was chosen as an anionic flocculant in combination with PolyDADMAC- typed cationic flocculant (Hydrofloc CPX 400) for further studies in dual-flocculants tests. The amount of anionic flocculant used in dual-flocculants system was kept as 30 ppm.

The settling behavior of tailings slurry flocculated by anionic and cationic flocculants combinations are given in figure 7-8. Any amount of cationic flocculant addition resulted in an improvement of the supernatant clarity at the expense of settling rate. Flocculation performance was greatly diminished at the excess amount of cationic flocculant dosages particularly in terms of settling rate. Taking into consideration of the measured transmittance value of process water (81.7 % T), the required amount of cationic flocculant to obtain the desired turbidity level is as minimum as 60 ppm in dual-flocculants system.
4. Conclusions

Characterization of borax concentrator tailings indicates that tailings solid mainly consists of dolomite, montmorillonite and some unrecoverable boron minerals. Over 75% of tailings solid are finer than 38 μm and tailings water has a high ionic strength due to the dissolution of dolomite and borax in solution and buffered with the borax as well as carbonate.

Therefore, flocculation behavior of colloidal dolomite and clay mineral particles in alkaline water at natural pH of the slurry (about pH=9.4) define the flocculation characteristics of borax tailings slurry.

In mono-floculant tests, amongst floculants studied, Hengfloc 64014 and Hydrofloc 9180 LV showed better similar flocculation ability than the other two floculants. At 30 ppm floculant dosage,
floculation performance of different flocculants decreases to following order: Hengfloc 64014 > Hydrofloc 9180 LV > Magnofloc 336=Magnofloc 1011. In the studied range of flocculant dosages, it was not possible to obtained clear supernatant only with the use of anionic flocculants. However, any improvement in supernatant clarity was only obtained by using dual-flocculants system in which combination of anionic (PAM-typed) and cationic (polyDADMAC-typed) flocculants are used.

When compared the mono-flocculant system, a reduction in settling rate was observed but a major improvement in supernatant clarity was obtained. In dual-flocculants tests, optimum results were obtained by anionic and cationic flocculant combination at around 25-30 ppm and 60-80 ppm, respectively, indicating about 10.0 cm/min of settling rate and over 80.0 % of transmittance value.

It can be concluded that dual-flocculants combination in which PAM-typed anionic and PolyDADMAC-typed cationic polymers used is playing a favorable role in the flocculation of borax clayey tailings. But, in addition to flocculation tests for selecting correct polymer(s), a follow-up study is needed to test the obtaining of underflow paste product both at laboratory and on-site testing in order to decide thickener type and size.

References


Sarı, M. 2008. Dissolution kinetics of various minerals in boric acid solution. Thesis (M.Sc.) -- İstanbul Technical University, Institute of Science and Technology (url: http://hdl.handle.net/11527/2692)

