1. Introduction

In general, kaolin is upgraded by physical methods such as water-washing or froth flotation. Kaolin particles are predominantly below 25 μm and are flat shaped particles. The industrial separation is commonly achieved by the dispersion of the mined ore and classification using multistage hydrocyclones. The kaolin reports to the overflow which is then reprocessed in other smaller cyclones. Due to inefficiencies associated with hydrocycloning, most plants are not able to produce clean kaolinite products and after the 4th or 5th hydrocyclone stage, the underflow cannot be separated further. The underflow is disposed as waste or sold cheaply to the cement industry and brick-manufacturing or used as back fill in the quarry [1–5].

Zonouz mine, which is located in eastern Azerbaijan Province, has the only kaolin-washing plant in Iran. The plant has a considerable amount of tailings containing about 15% Al₂O₃. The tailings mineralogical constituents are quartz,
kaolin and iron oxide. The tailing has fine particles (100% finer than 100 μm and about 30% finer than 20 μm); the fine particles can be easily dispersed by wind and settle down by rain and snow. Without treatment or recycling, the tailing would cause environmental pollution. It is important to re-evaluate the tailings because of economic and environmental causes. The evaluation will be economically feasible since it will not require additional mining cost. Kaolinite can be retrieved from the tailings by using flotation. However, flotation of kaolinite from the tailing is difficult because kaolinite and quartz, the two main minerals in the tailings, have the same flotation behavior.

Point of zero charge of quartz is at pH = 1.8 and zeta-potential of kaolinite is negative in a wide range of pH values, then both minerals can be floated by amine collectors in acidic and alkaline medium [6–8].

Many studies have been carried out on kaolinite flotation (pure samples) by cationic collectors such as ether diamine, hydroxyl-alkyl-diethanolamine, Cetylpyridinium chloride, cetyltrimethylammonium bromide, and dodecylamine. The results of these studies showed that kaolinite flotation by cationic collectors is better in acidic an environment than in a alkaline environment [7–13]. Yuehua et al. [11] tried to increase kaolinite recovery in alkaline medium by using a macromolecule as a flocculant. Without polyacrylamide, the kaolinite recovery decreased from 70 to 15%, with increasing the pH from 2 to 10. But, with polyacrylamide as a flocculant, kaolinite recovery increased under both acidic and alkaline environments [11].

Comparison of flotation of kaolinite and quartz show that two collectors (dodecylamine and EDA Flotigam) and two quaternary ammonium salts (Cetylpyridinium chloride and cetyltrimethylammonium bromide) are among the most effective collectors for floating both kaolinite and quartz. But, the time required for kaolinite flotation is 5–10 times that for the quartz flotation, depending on the type of the collector [10].

The purpose of the present study is to investigate the recovery of kaolinite from tailings of kaolin washing plants using flotation and flotation-flocculation.

2. Experimental

2.1. Material

Samples used in this study were taken from the tailing dam of Zonouz kaolin washing plant in East Azerbaijan Province, Iran. The particle size distribution of the representative sample was carried out by laser diffraction (Fig. 1). It is observed that the percent passing 100 μm and 50 μm is respectively 100% and 50% and more than 30% of the particles were smaller than 20 μm (slime particles).

According to the mineralogical analyses by X-ray diffraction, it was found that the sample contains quartz, kaolinite and calcite as the main minerals, and muscovite, biotite, montmorillonite and iron-rich epidote as the minor minerals. Chemical composition of the sample is given in Table 1.

2.2. Flotation experiments

Flotation experiments were carried out in a 1000 cm³ conventional laboratory cell (Denver model), at 25% solids ratio and agitation rate was 850 rpm. The suspension was added to the flotation cell and conditioned for 5 min. The pH was adjusted to a desired value by adding NaOH or H₂SO₄. Cetylpyridinium

Table 1 – Chemical composition of the sample.

<table>
<thead>
<tr>
<th>Composition</th>
<th>%</th>
<th>Composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>74.67</td>
<td>CaO</td>
<td>1.74</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.35</td>
<td>SrO</td>
<td>&gt;0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.25</td>
<td>P₂O₅</td>
<td>&gt;0.01</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.11</td>
<td>MgO</td>
<td>&gt;0.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.33</td>
<td>loss on ignition</td>
<td>7.54</td>
</tr>
</tbody>
</table>
chloride (CPCI) or dodecylamine (DDA) solution was then added as the collector and the suspension was conditioned for 3 min. Aluminum chloride was added as the depressant of quartz and the suspension was conditioned for 3 min. Finally, pin oil (150 g/ton) was added as the frother then after 3 min air was delivered to the cell for a total of 8 min and the concentrate which was floated and remained in the suspension was collected, filtered and dried in a well-ventilated oven at 120 °C. In the flotation-flocculation experiments, before adding the collector, polyacrylamide (PAM) was added as the flocculant for kaolinite particles and the suspension was conditioned for additional 3 min. All reagents used in this study were of analytical grade and supplied by Merck company.

The experiments were conducted in 8 series. In each series, the effect of only one parameter was examined and, the other parameters were kept constant.

3. Results and discussion

3.1. Effect of pH with CPCI as collector (series 1)

The first series of the experimental investigation was conducted to evaluate the effect of pH on the flotation results when CPCI was used as a collector. The results are illustrated in Fig. 2. It can be seen, with increasing pH from 3 to 9, the Al₂O₃ recovery decreased and SiO₂ recovery increased. Al₂O₃ and SiO₂ assay were respectively assumed as the kaolinite and quartz indicator recovery.

Fig. 3 shows the structure of kaolinite crystal. At low pH (pH < 4) the layer to layer interaction between the alumina face surface (001), and the silica face surface (001) is significant, as well as the interaction between the alumina face surface and the edge surface (010). In this case, the cluster structures, and even more complex network structures, are formed by kaolinite particle aggregation. A simple drawing in Fig. 4 illustrates the adsorption of cationic collector by the kaolinite cluster at low pH (pH < 4), forming a hydrophobic structure.

In alkaline medium, the interaction between a cationic collector and the plane (001), which contains oxygen, was stronger than that of the plane (001), which contains Al. The plane (001) adsorbed hydrophobic collector; but, the plane (001) did not adsorb collector due to having Al, and remained hydrophilic. As a result, collectors of the plane (001) were accumulated and formed structures whose outer surface was hydrophilic (Fig. 5). Therefore, as indicated in Fig. 2, kaolinite recovery decreased with increasing pH. A pH of 3 was chosen as the optimum condition and for further works.

3.2. Effect of concentration of CPCI collector (series 2)

The maximum recovery obtained for Al₂O₃ in the first series was around 45% which was significantly low. For increasing the recovery of Al₂O₃, the effect of concentration of CPCI on

![Fig. 2 – Flotation recovery of Al₂O₃ and SiO₂ as a function of pH with CPCI as collector (CPCI = 400 g/t, without depressant and de-slimming).](image)

![Fig. 3 – Structure of kaolinite [9].](image)

![Fig. 4 – Kaolinite cluster adsorption of cationic collector at low pH, dark surfaces represent the silica face surfaces of kaolinite particles, and gray surfaces represent the alumina face surfaces of kaolinite particles [13].](image)

![Fig. 5 – Schematic description of the kaolinite–amines interactions [9].](image)
the flotation results was investigated. Also, the slime particles below 38 μm were removed and aluminum chloride was used as the depressant.

The results in Fig. 6 indicate that the Al₂O₃ recovery increased with the increase concentration of CPCi up until a value of 600 g/t. The Al₂O₃ recovery at a 600 g/t of CPCi exceeded 85%. By more increasing in the concentration of CPCI to 700 g/t, Al₂O₃ recovery was decreased to 81%, probably because the critical micelle concentration phenomenon or bubble armouring were occurring. Although, more research and evidence are needed to prove it. Also, it is observed that the SiO₂ recovery was constant at about 20%. It can be attributed to depress of quartz particles by aluminum chloride. The maximum separation efficiency (81%) was achieved at 600 g/t of CPCI.

3.3. Effect of aluminum chloride concentration in flotation by CPCI collector (series 3)

The results of series 2 showed that the Al₂O₃ recovery and separation efficiency were increased by using aluminum chloride as a quartz depressant. In this series the effect and the role of aluminum chloride was investigated. Fig. 7 indicates that with increasing the concentration of aluminum chloride from 300 to 600 g/t, significant changes were not observed in Al₂O₃ and SiO₂ recoveries. However, the best result was related to aluminum chloride value of 500 g/t which produced a concentrate with recovery of 86.28% Al₂O₃ and 20.19% SiO₂ and assay of 38.42% Al₂O₃ and 52.96% SiO₂ with separation efficiency of 83.51%.

Ions of aluminum chloride (Al³⁺) play two positive roles during the flotation. From one side, they act as the depressant of quartz. In fact, these ions sit on the surface of quartz, which has negative charges and competes with the collector ions and prevent quartz flotation. However, the excessive increased level of Al³⁺ increases the kaolin zeta potential. On the other side, these ions increase the ionic strength of the pulp. In a high ionic strength environment, although the negative charge on the basal of planes [001] and [001] is constant, the zeta potential caused by the surface charge on both basal planes and edges is significantly screened and thus aggregation of kaolinite particles can occur (Fig. 8). The screened surface charge at high ionic strength also weakens the self-aggregation between the negatively charged [001] planes and the positively charged edge planes in acidic pulp. Thus the pH dependence of kaolinite flotation becomes less pronounced.

3.4. Effect of pH on the flotation with DDA collector (series 4)

Previous studies showed, dodecylamine (DDA) is an effective collector for floating both kaolinite and quartz [10]. In this series, flotation of kaolinite by DDA in the presence of aluminum chloride as quartz depressant was evaluated. Fig. 9 shows that during kaolinite flotation with DDA collector, with increasing pH, both recoveries of Al₂O₃ and SiO₂ were increased. The maximum recovery of Al₂O₃ and SiO₂ was obtained at pH = 9. It seems, there are differences between the DDA and CPCI results. As it can be seen in Fig. 2, by using CPCI, with increasing pH, Al₂O₃ recovery was decreased. Effect of pH on selectivity separation is clearly shown in Fig. 9, so that at pH = 3, the difference in Al₂O₃ and SiO₂ recovery was around 28% and good selectivity was achieved; with increasing pH, this difference was reduced and recoveries of Al₂O₃ and SiO₂ were almost equal at pH = 9. The best results were achieved at pH = 3 where a concentrate with recovery of 66.25% Al₂O₃ and 37.74% SiO₂, respectively, and assays of 20.84% Al₂O₃ and 69.93% SiO₂ with separation efficiency of 35.61% was obtained.

3.5. Effect of concentration of DDA collector (series 5)

The results of series 4 showed satisfactory separation of kaolinite and quartz by the DDA collector in the presence of
aluminum chloride can be approached in acidic pHs, but high dosage of the collector is required. In this series the effect of DDA concentration was studied.

Fig. 10 indicates that the maximum recovery of Al₂O₃ at a concentration of 300 g/t was equal to 80%; but, increasing DDA concentration decreased assay of Al₂O₃. Also, SiO₂ recovery increased from 20% to 38% by increasing in DDA concentration. The best flotation conditions in term of assay and recovery of Al₂O₃ and separation efficiency was resulted in the collector concentration of 300 g/t. In this condition, a concentrate with a assay of 36% Al₂O₃ and 52% SiO₂ and recovery of 80% Al₂O₃ and 21% SiO₂ with separation efficiency of 75.48% was obtained.

3.6. Effect of pH on the flotation with DDA collector and PAM flocculant (series 6)

The results from series 1–5 showed that kaolinite flotation by DDA and CPC1 collectors is better in an acidic environment than in an alkaline environment. This is consistent with the observations reported by several researchers [7,9–12]. Flotation under acidic condition causes problems such as equipment erosion at industrial scale. However, the results of study by Yuehua et al. [11] showed the recovery of kaolinite in alkaline environments can be improved in the presence of polyacrylamide (a macromolecule) as a flocculant [11], although the effect of the macromolecule on quartz flotation and separation of kaolinite from quartz was not studied.

In this series, the effect of pH on the flotation with the DDA collector in the presence of polyacrylamide (PAM) was studied. Fig. 11 indicates that with increasing pH from 3 to 7, the recovery of Al₂O₃ slightly was increased from 78 to 79%; but, with increasing pH from 7 to 9 decreased the Al₂O₃ recovery. SiO₂ recovery also increased with increasing the pH; the lowest SiO₂ recovery (20%) was related to pH = 3.

Generally, it was observed that with the PAM flocculant, Al₂O₃ recovery was at an acceptable level within a wide pH range, while SiO₂ recovery was low. PAM contains O and COO groups which are expected to bond with the surface of hydroxyl groups. As shown in Fig. 3, in kaolinite minerals, the plane (001) has OH group, therefore PAM establishes hydrogen bond with these planes; thus, kaolinite particles can be accumulated by this flocculant. On the other hand, as mentioned earlier, cationic collectors are well absorbed by the planes (001); therefore, cationic flotation can be improved by using PAM. Fig. 12 shows a schematic diagram of kaolinite flotation and flocculation by using PAM. The best results were related
to pH = 7 where a concentrate with recovery of 78.75% Al$_2$O$_3$ and 25.51% SiO$_2$ and assay of 32.49% Al$_2$O$_3$ and 57.87% SiO$_2$ with separation efficiency 68.18% was obtained.

3.7. Effect of PAM on the flotation with DDA as collector (series 7)

Presence of slime increases consumption of chemical reagents and decrease collector’s selectivity. In order to increase the recovery in the previous series of 1 to 6, the slime particles below 38 μm or 20 μm were removed from the initial feed by screening or settling, where this portion constituted a significant amount of the total initial feed.

In this part without de-slimming, the effect of PAM on the flotation with the DDA as a collector was studied. Fig. 13 shows that increasing PAM concentration decreased Al$_2$O$_3$ recovery and increased SiO$_2$ recovery. The best result was obtained at a concentration of 15 g/ton where Al$_2$O$_3$ recovery and assay in the concentrate were respectively 80.41% and 34.64% and SiO$_2$ recovery and assay in the concentrate were respectively 25.58% and 56.66% with separation efficiency of 72.84%. Comparison of the results of this series with previous series showed that significantly small concentration of PAM is required to improve the flotation.

3.8. Effect of aluminum chloride concentration in flotation by DDA collector and PAM flocculant (series 8)

The purpose of this series, was to find the best condition for separation of kaolinite at pH = 7 without any de-slimming.

Fig. 14 indicates that an increase in the concentration of depressant from 300 to 500 g/ton increased the Al$_2$O$_3$ recovery and decreased the SiO$_2$ recovery; however, the condition did not change considerably with further increase in the concentration from 500 to 600 g/ton and even Al$_2$O$_3$ recovery deceased from 83% to 82%. Therefore, the best condition for assay and recovery in the concentrate was obtained at a concentration of 500 g/ton. At this dosage, recovery and assay of Al$_2$O$_3$ in the concentrate were respectively 83.02% and 37.19% and SiO$_2$ recovery and assay in the concentrate were respectively 22.28% and 54.38% with the separation efficiency of 78.48%.

4. Conclusion

Results showed that for both CPCI and DDA collectors, the best condition was obtained at acidic pHs. Similar results were achieved by other researchers [7,11]. Comparing the results of the two collectors showed that CPCI collector has better selectivity. The results reported by Köster et al. also confirmed better selectivity of CPCI for kaolinite compared with quartz and feldspar at acidic pHs [7]. Depressant of aluminum chloride had considerable effect on the flotation performance, which is an effective depressant for the quartz and enhanced flotation of kaolinite. The result also agree well with reported studies [7,9]. Köster et al. showed aluminum chloride is a good depressant for quartz and feldspar in presence of kaolinite [7]. Ma et al. demonstrated that flotation of kaolinite enhanced by adding NaCl solutions because the ionic strength of solution was increased [9]. Flotation under acidic condition of pH = 3 causes problems such as equipment erosion at industrial scale. For this reason, PAM flocculant was used. Results with PAM showed that this flocculant increased the efficiency of kaolinite flotation at neutral and alkaline pHs. In the last series of the experiments, a significant result was achieved and by using only 15 g/ton PAM at neutral pH condition, a concentrate with Al$_2$O$_3$ recovery and assay of respectively 83.02% and 37.19% and SiO$_2$ recovery and assay of respectively 22.28% and 54.38% was obtained. While, the assay for Al$_2$O$_3$ and SiO$_2$ of the current concentrate in Zouzou plant are respectively 26% and 62%. This means that using the flocculation and flotation processes at neutral pH, almost 35% of the tail weight can be turned into a concentrate with acceptable assays. On the other hand, Al$_2$O$_3$ and SiO$_2$ assays of the remaining tail were respectively 15% and 74%, where the tail has significantly high SiO$_2$ assay that appropriate applications can be predicted for it as silica concentrate.

Conflicts of interest

The authors declare no conflicts of interest.
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REFERENCES


