Flotation of zinc silicate ore: A focus on effective parameters, synergistic effect of mixed cationic collectors and its mechanism

Pouya Karimi a, b, Hadi Abdollahi a, *, Sied Ziaedin Shafaei a, Aysan Molaei c

a School of Mining Engineering, College of Engineering, University of Tehran, Tehran, Iran
b Golgohar Iron Ore and Steel Research Institute, Sirjan, Kerman, Iran
c Department of Mining and Materials Engineering, McGill University, Montreal, Québec, Canada

ABSTRACT

The present study addresses the direct flotation route for the concentration of a zinc silicate ore. Flotation of hemimorphite faces some challenges due to the similarity of hemimorphite and quartz surface properties. XRD, and XRF analyses, optical mineralogy and SEM with X-ray mapping were performed for characterization. The results showed that the quartz, hemimorphite, calcite and dolomite are the main minerals. In the flotation process, combined form of Octadecylamine and Armac T, as mixed cationic collectors were introduced. Flotation tests were employed in two steps to evaluate the individual effect of the variables such as: size distribution of feed and the presence of Armac T in the first step, alkalinity, types and concentrations of reagents (Armac T and stearyl amine (collectors), sodium sulfide (sulphidizing agent), and sodium hexametaphosphate (dispersant) in the second step. In optimal conditions, the grade and recovery of zinc in concentrate were ~33% and 83%, respectively. Finally, for removing the detrimental effect of fine particles, de-sliming of pulp feed accomplished which resulted in a remarkable increase in the recovery of hemimorphite concentrate (12.67%) and a decrease in the grade of zinc in tailing (6.11%). FTIR analysis showed the adherence of collectors on hemimorphite particles increased after de-sliming.

Keywords: Flotation, Surface properties, Zinc-silicate minerals, Hemimorphite, Synergistic effect of mixed collectors

1. Graphical Abstract

2. Research Highlights

• The effects of important parameters on flotation of zinc silicate ore were investigated.
• The parameters were size distribution, alkalinity, types and dosages of different reagents.
• Synergetic effect of mixed cationic collectors increased the recovery and grade.
  • In optimal conditions, maximum grade and recovery (~32% and ~83% respectively) were obtained.
  • De-sliming had a positive effect and increased recovery to ~95 with identical grade.
  • FTIR showed the adherence of collectors on the hemimorphite increased after de-sliming.
3. Introduction

There are a variety of mixed sulfide-oxide and oxide lead-zinc ores which cannot be classified into any specific group due to the vast differences in geology and mineral compositions. From a processing point of view, these ores can be classified into the following groups:

- Mixed sulfide and oxide lead-zinc ores,
- Oxide lead-zinc ores,
- Oxide zinc ore with little or no lead present [1].

From an economic point of view, there are a variety of zinc oxide ores which are categorized in three basic types: (a) ores with hemimorphite as the predominant zinc oxide mineral, (b) ores with smithsonite as dominant zinc oxide mineral and (c) ores with a mixture of smithsonite and willemite [1]. Oxidized ores contain zinc in various carbonate and silicates minerals, such as smithsonite ($\text{ZnCO}_3$), hydrosilicate ($\text{Zn}_2\text{SiO}_3\cdot\text{Zn}($$\text{OH})_2$)), zincite ($\text{ZnO}$), willemite ($\text{Zn}_2\text{SiO}_4$) and hemimorphite ($\text{Zn}_2\text{SiO}_4\cdot(\text{OH})_2\cdot\text{H}_2\text{O}$) and etc. [2].

In practice, the commonly used method for the recovery of oxidized lead and zinc minerals from ores is flotation [3]. The flotation of oxidized lead and zinc minerals, particularly zinc minerals, is much more difficult than the flotation of corresponding sulfide minerals [4-6]. Normally, the fatty acids are used to recover the zinc oxide minerals such as smithsonite, hemimorphite and calamine via froth flotation method [7-10]. The most common flotation technique used commercially for the treatment of zinc oxide minerals is sulphidization with Na$_3$S, followed by treatment with conventional cationic collectors, namely amine [3, 9, 11, and 12]. Sulphidization followed by flotation with xanthate as the main collector is a well-known flotation technique. However, the performance of these collectors is not the best and it is difficult to recover zinc oxide minerals (dispersant widely used in clay industry) that NaN$_3$ is adsorbed onto the zinc surface of zinc silicates amine minerals. According to van Hallimond tube with smithsonite, hemimorphite and willemite, employing dodecyl amine as the collector [22 and 23]. Hemimorphite, the predominant zinc-bearing mineral in calamine ores, presents maximum floatability in the pH range of 11 to 12, suggesting that the collecting entity is molecular amine RNH$_2$. According to van Lierde’s research, the presence of RNH$_2$ cations increases the floatability of gangue minerals [22 and 24].

The objective of the present study was to maximize both recovery and grade of zinc in the flotation concentrate which contains hemimorphite as a zinc silicate mineral. In order to achieve this goal, the strategies of optimization (one factor at a time (OFAT) in every stage), synergistic effect of mixed collectors and feed de-sliming pretreatment were used. In this regard, the effects of influential variables such as pulp feed size distribution, alkalinity and the types and concentrations of different reagents (Armac T and stearyl amine (as main collectors), sodium sulfide (sulfidizing agent), and sodium hexametaphosphate (dispersant)) in the froth flotation were comprehensively investigated and consequently optimized. The results can reflect some insights into the mechanisms of function of these additives in froth flotation of zinc silicate ore. Also, different characterization studies such as XRD, XRF, SEM, and FTIR were used to confirm some phenomenon in the process.

4. Materials and Methods

Representative sample was supplied with a systematic sampling procedure from the Zn-Pb index located in west of Isfahan province, Iran and about 350 kg of ore were used for flotation experiments. After four comminution stages (two jaw crushers, one cone crusher and a roller crusher), primary sample size was ~2830 μm. In the next step, two kilogram samples were prepared by riffling and cone and quartering methods. The chemical analysis of zinc and lead were carried out by using Atomic Adsorption Spectroscopy Technique (Perkin Elmer 2100, 5100 and Varian AA-20).

Semi-Quantitative X-Ray Diffraction (SQXRD) technique was used to determine the major and minor (trace) minerals in the sample. X-ray powder diffraction patterns were obtained using a Siemens D-500 diffractometer with Ni-filtered Cu–Kα radiation, and a goniometer speed of 1° 2θ/min. The diffraction profiles with a 0.01 precision of d-spacing measurements were conducted from 4° to 70° (2θ). The representative sample was also analyzed using X-Ray Fluorescence (XRF) technique to determine major and minor oxides.

Mineralogical studies were carried out by using a polarizing microscope and Scanning Electron Microscope (SEM) on the polished and thin sections of original samples; the different size fractions consisted of -2000+1410, -1410+1000, -1000+840, -840+590, -590+350, -350+210, -210+149, -149+105, -105+74, -74+53, and -53 μm in order to determine the degree of liberation for zinc-bearing mineral, type of gangue minerals and the amount of their interlocking. Due to the very similar optical properties of quartz and hemimorphite, SEM and chemical scanning analysis (EDS) were carried out and the constitutive minerals and their liberation degrees in different size fractions were precisely determined. An amount of about 2kg of the original sample was subjected to the wet sieve analysis to investigate the changes in metals’ grade and the distribution of different size fractions. Sieving was carried out and consequently twelve size fractions consisting of -2830+2000, -2000+1410, -1410+1000, -1000+840, -840+590, -590+350, -
Flotation experiments were performed in a 2-L Denver cell running at 1100 rpm using 500 g ore sample (25% pulp density). The weighted sample with 1.5 L of water was transferred into the flotation glass cell. The pulp pH was adjusted with HCl and NaOH aqueous solution and then was mixed for 2 min. After adding the desired amount of reagents in specific time (depressant in time 2’, sulfidizer in time 2.5’, collectors in time 3’), the suspension was agitated for 4 mins, and the frother was added one minute before aeration. In every stage, pH was monitored and adjusted to desired level especially before adding frother. Aeration was started in time 8’. The aeration and collecting process was conducted for 5 mins. The products and tails were weighed separately after filtering and were subjected to drying and then the recovery values were calculated after measuring zinc grades. The schematic flotation process used in this study is shown in Figure 5. The recovery equation was calculated according to the following equation, where \( R_{f} \) represents the zinc recovery in the froth as concentrate; \( F \) and \( C \) are the weights of feed and froth product (concentrate) and \( f \) and \( c \) are the grades of zinc in feed and concentrate, respectively. Also, \( R_{c} \) represents the zinc loss in the tail.

\[
R_{f} = \frac{C}{F} \times 100 \%
\]


\[
R_{c} = 100 - R_{f}
\]

For these tests, sodium hexametaphosphate (as depressant), octadecylamine and Armac T (as collectors in sole and combined forms), sodium sulfide (as sulfidizing agent) were used for the flotation of hemimorphite which all were of analytical grade. In all experiments, two drops of pine oil (120 g/t) was added as frother. List of reagents used in flotation tests and their dosage ranges are summarized in Table 2. The chemical analysis of zinc in different samples (concentrates and tails) was carried out by using AAS (Perkin Elmer 2100, 5100 and Varian AA-20) technique.

Table 2. List of reagents used in flotation tests and their dosages range.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration</th>
<th>Supplier</th>
<th>Role</th>
<th>Dosage range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecylamine</td>
<td>-</td>
<td>Merck</td>
<td>Collector</td>
<td>1.8-18 (kg/t)</td>
</tr>
<tr>
<td>Armac T</td>
<td>99</td>
<td>Akzo Nobel</td>
<td>Collector</td>
<td>0.2-0.6 (kg/t)</td>
</tr>
<tr>
<td>Sodium sulphide</td>
<td>75</td>
<td>Merck</td>
<td>Sulphidizing agent</td>
<td>8-20 (kg/t)</td>
</tr>
<tr>
<td>Sodium hexametaphosphate</td>
<td>96</td>
<td>Samchun</td>
<td>Depressant</td>
<td>1.2-2 (kg/t)</td>
</tr>
<tr>
<td>Pin oil</td>
<td>99</td>
<td>Penn Chemical</td>
<td>frother</td>
<td>120 (g/t)</td>
</tr>
<tr>
<td>HCl</td>
<td>---</td>
<td>Merck</td>
<td>pH adjuster</td>
<td>Required</td>
</tr>
<tr>
<td>NaOH</td>
<td>---</td>
<td>Merck</td>
<td>pH adjuster</td>
<td>Required</td>
</tr>
</tbody>
</table>

Figure 5. The schematic flotation process and step of every reagent added in pulp.

5. Results and Discussions

5.1 Ore Characterization

The results of chemical analysis showed that grades of zinc and lead in the representative sample were 18.20 % and 2.03 %, respectively. Based on the XRD results, Quartz (SiO₂), Hemimorphite (ZnSiO₄(OH)·H₂O), Calcite (CaCO₃) and Dolomite (CaMg(CO₃)₂) were distinguished as the major phases of the representative sample. For precise assessment, this qualitative analysis was performed in double. These minerals are reported in abundant order in the graph (Figure 2).

The results of XRF analysis (Siemens 303 SRS and Philips magix pro) showed that SiO₂, ZnO, Fe₂O₃, CaO, PbO, Al₂O₃ are major oxides and MgO, BaO, SO₃, K₂O, As₂O₃ and P₂O₅ are minor oxides. The XRF results are presented in Table 1. More than 66% of original sample have been formed from two species of SiO₂ and ZnO.

Preliminary mineralogical studies of a rock sample revealed that quartz and hemimorphite are the main minerals with iron hydroxides and manganese as the minor components. According to the results, this Zn-Pb ore was categorized as silicate-carbonate one, because plenty of the main minerals including quartz and hemimorphite (as silicate
minerals) and also calcite and dolomite (as carbonate minerals) were observed in the sample.

The results of SEM and EDS analyses showed that quartz is the main mineral which is interlocked with hemimorphite and start to liberate in size fraction finer than 100 µm. This represented that 80% of liberation degree was observed in size fraction with d80= -100 µm and 100% of liberation degree was observed in size fraction with d80= -30 µm. It was also found that 90 % of carbonate minerals are available in liberated form in the samples. Iron hydroxides (Limonite and Goethite) were formed in the space between grains of hemimorphite and quartz and due to the low thickness of iron hydroxides, it is difficult to separate them from the target minerals in the beneficiation process. SEM analysis also showed that carbonate minerals such as calcite and dolomite were formed either between grains of quartz and hemimorphite or filled-out fractures. Furthermore, hemimorphite as the only zinc-bearing mineral in the sample was distinguished in two forms:

1. In the forms of fiber or bladed shape texture which was grown in the empty space.
2. In the forms of zoning or regional texture due to the gradual growth of hemimorphite around a nucleus composed mainly of carbonate.

For overall estimation, representative sample have about 35% quartz, and 40% hemimorphite. The amounts of calcite and iron hydroxides were determined roughly 10% and 6%; respectively. Some of the mineralogical studies and SEM micrograph with the corresponding EDS mapping of Zn, Pb, Fe, Si and Ca are presented in Figures 3A and 3B.

Based on the Sieve analysis results, d80 of sample was determined 1608 µm. The grade and distribution of Zn and Pb in different size fractions are presented separately in Figures 4 (A and B).

As shown in Figures 4 (A and B), maximum grade and distribution of zinc were observed in size fractions of -590+350 µm and -53 µm, respectively. But maximum values for both factors (grade and size distribution) for Pb were observed in size fraction of -53 µm. It seems that Zn and Pb bearing minerals are brittle and hence inclined to concentrate in finest fraction after crushing stages. It is worth to be noted that due the importance of zinc in the sample during the flotation experiments, only the zinc element was measured and its recovery for every stage was calculated.

5.2 Preliminary Flotation Tests (First Step)

According to the literature review, several essential variables affect the flotation of hemimorphite such as type and concentration of different chemical reagents, feed size distribution and pH of the environment. Chemical reagents used in the flotation of hemimorphite include sodium hexametaphosphate (NaPO3)6 as a dispersant, octadecylamine (CH3(CH2)17NH2) as the main collector, Armac T as a co-collector, sodium sulfide (Na2S, 9H2O) as a sulphidizer and pine oil as frother. With respect to the multitude of variables in the flotation process, optimization of effective variables were carried out in two steps.

In the first step, feed size distribution and the effect of presence of Armac T (co-collector) as two variables were comprehensively studied.
on the flotation efficiency for hemimorphite in optimal conditions based on the literature review and some previous experiments. On the next step, and according to the results of six preliminary experiments in the first step, other influential variables such as concentration of sodium hexametaphosphate, octadecylamine, sodium sulfide, and Armac T and also pH of environment were precisely investigated.

5.2.1 The Effect of Feed Size Distribution
With respect to the importance of feed size distribution (d<sub>50</sub> of feed) and according to the liberation degree achieved from mineralogical studies (75-80 % of hemimorphite liberated in size fraction of -105 μm and 85-90 % liberated in size fraction of -53 μm), three flotation tests were carried out on the original samples in three different size fractions (d<sub>50</sub> = -149 μm, d<sub>50</sub> = -105 μm and d<sub>50</sub> = -74 μm). Other variables were adjusted according to the optimal values obtained from literature survey. Based on the results from other researchers, 1.67 g/kg, 1.43 g/kg and 14.28 g/kg were considered as optimum concentrations for sodium hexametaphosphate, octadecylamine and sodium sulfide, respectively. Also, pH of the environment was set on 10 (the optimal value according to the work of other researchers). According to the results obtained from the initial flotation experiments and according to the lack of adequate grade and recovery for zinc in the flotation concentrates in the absence of Armac T, it seemed that changing the flotation methodology or reagents (type and concentration) would be inevitable.

As it can be seen in the Figure 6A, maximum zinc grade in floated part as concentrate was obtained in the second experiment and was equal to 20.16 %, while maximum zinc recovery was achieved in third test equal to 17.84 %. It seems that more crushing and finer size distribution of the feed would result in appropriate recovery. Therefore, sample with d<sub>50</sub> = -74 μm was selected as an optimal size of the feed sample in later flotation experiments. Also, after investigating the results of the tests, Armac T was added in the flotation as a co-collector in another strategy which are comprehensively studied in the next step. The concentration of Armac T in the flotation tests was 0.4 g/kg.

5.2.2 The Effect of Armac T Presence
In this stage, three flotation tests were carried out on the samples in three different size fractions (d<sub>50</sub> = -149 μm, d<sub>50</sub> = -105 μm and d<sub>50</sub> = -74 μm) with 0.4 g/kg concentration of Armac T as a co-collector. All other conditions were the same as the tests mentioned in the previous section. Grade and recovery values of zinc in flotation concentrates are summarized in Figure 6B.

As it can be concluded from Figure 6B, grade and recovery values of zinc in concentrate for all size fractions were improved remarkably when Armac T was added to the flotation process as a co-collector. Based on the results, maximum grade and recovery values of zinc in the floated part (as concentrate) were obtained in the last experiment with size fraction of -74 μm as 31.20 % and 56.54 %, respectively. It is completely clear that the combination of octadecylamine and Armac T as mixed cationic collectors can have a synergistic effect on the flotation of hemimorphite and results in appropriate grade and recovery of zinc in all size fractions. Therefore, a mixture of these two cationic collectors was used for the optimization of different effective parameters which are interpreted in details in the next step.

5.3 Supplementary Flotation Tests (Second Step)
The preliminary flotation tests in the first step were carried out to determine the optimal size fraction of pulp feed and also to determine the influence of the presence and absence of Armac T as co-collector on the flotation efficiency of hemimorphite. The results of these experiments showed that a size fraction of -74 μm was an optimal range among all size fractions among different flotation tests and also the grade and recovery of zinc in the concentrate were considerably improved in the presence of Armac T as co-collector. In the supplementary flotation tests as a second stage of investigation, other influential factors such as concentration of sodium hexametaphosphate, octadecylamine, sodium sulfide, and Armac T and also alkalinity of solution were precisely studied and optimized. All tests were performed with feed size fraction of -74 μm and in the presence of 0.4 g/kg Armac T as co-collector.

5.3.1 The Effect of Concentration of Sodium Hexametaphosphate (SHMP)
At this stage, the effect of concentration of sodium hexametaphosphate on the grade and recovery of zinc in the concentrate were thoroughly studied. In order to optimize this factor, the concentrations of 1.2, 1.6 and 2 g/kg were considered as different levels of this variable. The values for the other variables affecting the flotation process were based on the optimal conditions determined in the previous experiments. The grade and recovery values of zinc in flotation concentrates are presented in Figure 7A. According to the results presented in Figure 7A, it was obvious that by increasing the concentration of SHMP from 1.2 g/kg to 2 g/kg, zinc recovery decreases from 49.8 % to 33.07 %. In addition, maximum grade of zinc in floated part as concentrate was obtained in the first experiment as 24.25 % with 1.2 g/kg SHMP. Therefore, 1.2 g/kg of SHMP was considered to be the optimal consideration of this substance in the subsequent flotation experiments.

5.3.2 The Effect of Concentration of Octadecylamine (ODA)
The effect of concentration of octadecylamine on the grade and recovery of zinc in the concentrate were precisely investigated. For the optimization of this factor, the concentrations of 1, 1.4 and 1.8 g/kg as different levels of octadecylamine were considered. The values for the other factors affecting the flotation process were based on optimal conditions determined in the previous experiments. The grade and recovery values of zinc in flotation concentrates are presented in Figure 7B. It was found that by increasing the concentration of ODA from 1 g/kg to 1.4 g/kg, zinc recovery is increased from 55.81 % to 66.09 % and after that it decreases to 63.84 % in the third experiment with the substance concentration of 1.8 g/kg. Furthermore, maximum grade of zinc in concentrate was obtained in the first two experiments as about 27.65 %. Therefore, 1.4 g/kg of ODA was considered as the optimal concentration of this substance in the subsequent flotation experiments. For second test with 1.4 g/kg ODA, the grade of zinc in tail was less than 10 %.

5.3.3 The Effect of Concentration of Sodium Sulfide (SS)
The effect of concentration of sodium sulfide on the grade and recovery of zinc in the concentrate was also investigated. In order to optimize this factor, the concentrations of 8, 14 and 20 g/kg as different
levels of this substance were considered. In this stage, concentrations of sodium hexametaphosphate and octadecylamine were 1.2 and 1.4 g/kg, respectively. The values of the other influential variables were based on the optimal conditions determined in previous experiments. The grade and recovery values of zinc in the concentrates are shown in Figure 7C.

The results of the experiments showed that with an increase in the concentration of sodium sulfide, zinc recovery in concentrate decreases, but the loss in recovery has been relatively low (about 4%). The maximum grade of zinc in the concentrate and minimum in the tail were obtained with 20 g/kg of sodium sulfide (31.2 % in conc. and 9.64 % in tail). According to the experiment results and the priority of maximum zinc recovery on one hand and an approach toward less consumption of chemicals (from economic point of view) on the other hand, concentration of 8 g/kg sodium sulfide was considered as the optimal concentration in the subsequent experiments. In this concentration of SS, the grade and recovery of zinc in concentrate reached approx. 30 % and 73 %, respectively.

### 5.3.4 The Effect of Concentration of Armac T

In this stage of investigation, the effect of Armac T concentration as the co-collector on the grade and recovery of zinc in the concentrate was studied. In order to optimize this factor, the concentrations of 0.2, 0.4 and 0.6 g/kg were considered as different levels of this variable. In this step, concentrations of sodium hexametaphosphate, octadecylamine and sodium sulfide were kept constant as 1.2, 1.4 and 8 g/kg, respectively. Moreover, the values for the other influential factors were based on the optimal conditions determined in the previous tests. The grade and recovery values of zinc in the concentrates are presented in Figure 7D.

Based on the results shown in Figure 7D, an increase in the concentration of Armac T, zinc recovery decreases with a sharp gradient especially from 0.2 to 0.4 g/kg. In fact, while the concentration of Armac T increases from 0.2 to 0.4 g/kg, zinc recovery in concentrate was drastically reduced from 77.82 % to 69.9 %. Furthermore, the maximum grade of zinc in concentrate and minimum in the tail products were obtained in the first test with 0.2 g/kg of Armac T as co-collector (29.7 % in conc. and 86.5 % in tail). Therefore, 0.2 g/kg of Armac T was considered as the optimal value for concentration of this reagent in the subsequent flotation experiments.

### 5.3.5 The Effect of the pH

In order to optimize the last influential factor, pH of the environment, its effects on the grade and recovery of zinc in the concentrate were investigated. In order to find optimal value of this factor, three levels of pH: 9.5, 10.5 and 11.5 were considered in flotation experiments. In this stage, concentrations of sodium hexametaphosphate, octadecylamine, sodium sulfide and Armac T were kept constant as 1.2, 1.4, 8 and 0.2 g/kg, respectively. The grade and recovery values of zinc in the concentrates are demonstrated in Figure 8.

It is evident that with an increase in pH of solution from 9.5 to 11.5, zinc recovery in concentrate increases drastically and reaches ~83 % (in pH=11.5). This represents a very great impact of this variable on the flotation of hemimorphite mineral ore. It is concluded that the maximum grade of zinc in concentrate and minimum in tail were obtained for the test with pH=11.5 (32.95 % in conc. and 7.76 % in tail). Therefore, the pH of 11.5 was considered as the optimal value of pulp alkalinity.

### 5.3.6 The Effect of De-sliming

According to the results found in the literature review and the significant adverse effect of fine particles and slime on the grade and recovery of zinc as main responses in the flotation system of zinc-silicate sample (Hemimorphite), after the optimization of the other variables in the previous steps of the process, the effect of de-sliming of feed on the flotation efficiency was also examined at this stage. For this test and based on the optimal results obtained from previous experiments, size of the original sample was reduced to 200 mesh (~74 µm) by using wet ball milling process in the closed circuit and then the fraction below 500 mesh (~25 µm) was separated with wet sieving method. The flotation test was carried out under optimal conditions which were identified previously. The values of grade and zinc distribution of -25µm size were analyzed to be 29.8 % and 27.3 respectively. The results of this test including grade and recovery values of Zn and Pb as a by-product in concentrate are shown in Figure 9.

As shown in Figure 9, de-sliming of feed resulted in an improvement in zinc grade in concentrate of about 0.45 % and a reduction of zinc grade in tail of about 6.11 %. Therefore, zinc recovery in concentrate was increased of about 12.67 %. The zinc grade reached 33.4 % in the flotation concentrate. Although, the purpose of this study was chiefly related to the flotation of zinc-silicate ore (Hemimorphite), but during the final tests the grade and recovery values of Pb in concentrate and tail were also investigated with and without de-sliming process of the feed. When compared to each other, the results showed that there is no significant difference between the grade and recovery values for Pb in the concentrates obtained from flotation tests with or without de-sliming process (Data for flotation test without de-sliming of feed are not shown). The grade and recovery of Pb in final concentrate were 2.71 % and 74.77 %, respectively. In order to evaluate the performance of the mixed collectors for selective flotation of hemimorphite in the presence of silicate minerals such as quartz (due to the similarity of the properties of silica and hemimorphite), the amount of silica (SiO2) in the concentrate and tail were also analyzed for flotation tests with and
without de-sludging process (Table 3).

As can be concluded from Table 3, de-sludging of feed has a significant positive effect on the selectivity behaviour of mixed collectors. In other words, by means of de-sludging of feed prior to flotation test, the percentage of silica in the concentrate decreases about 17 % compared to the test without de-sludging. Furthermore, the higher amount of silica in the tail (in the flotation test with de-sludging) indicated that flotation of hemimorphite was performed selectively and it is obvious that SiO$_2$ content of concentrate for test without slime was much lower than the test with slime.

Table 3. The amount of SiO$_2$ in the concentrate and tail for tests with and without de-sludging process.

<table>
<thead>
<tr>
<th>Process</th>
<th>Product</th>
<th>SiO$_2$ grade (%)</th>
<th>SiO$_2$ distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without slime</td>
<td>Concentrate</td>
<td>18.56</td>
<td>57.10</td>
</tr>
<tr>
<td></td>
<td>Tail</td>
<td>30.87</td>
<td>62.90</td>
</tr>
<tr>
<td>With slime</td>
<td>Concentrate</td>
<td>35.16</td>
<td>64.90</td>
</tr>
<tr>
<td></td>
<td>Tail</td>
<td>20.28</td>
<td>35.10</td>
</tr>
</tbody>
</table>

5.3.7 Surface Analyses, XRD, SEM and EDS, and FTIR

In addition to chemical analysis of concentrate and tail with the aim of determining the amounts of Zn, Si and Pb presented in the products especially in final tests which was comprehensively described in section 3.2.6, other supplementary analyses such as XRD, SEM with X-ray mapping and FTIR were also performed on the final concentrate with and without de-sludging of feed in order to obtain more detailed information about the types of minerals, elements and surface species formed during flotation tests. XRD analysis of final concentrate showed that hemimorphite, quartz and goethite are the predominant minerals in the sample. The results postulated that flotation method could ideally separate carbonate minerals such as dolomite and calcite from hemimorphite. The graph of this analysis is shown in Figure 10.

![Figure 10](image1.png)

Figure 10. XRD analysis of concentrate obtained from final flotation test.

Due to the importance of the distribution of some elements in the particles such as Zn, Pb, Si and Ca, SEM analysis with X-ray mapping was carried out on the final concentrates. The first result of this analysis is that a significant difference of two concentrates was due to the presence of fine particles as slime in one of the concentrates. The boundary and surface of the target minerals are completely recognizable in the concentrate obtained from de-sludged flotation test. The images of two concentrates are shown in Figure 11.

![Figure 11](image2.png)

Figure 11. SEM images of flotation concentrates, with slime (right side) and without slime (left side).

The distribution of Zn, Si, Pb and Ca in flotation concentrate without slime are shown in Figures 12. High abundance of Zn and low amounts of Si and Ca in the results of x-ray mapping confirmed that optimal separation was had occurred. Additionally, lower amounts of Si and Ca were detected in the concentrate without slime compared to the concentrate with slime (SEM images are not shown). It showed that de-sludging before flotation test had a positive effect on the separation efficiency of calcite and dolomite from hemimorphite. The results also showed that Pb-bearing minerals are mostly mimetite with composition Pb$_2$(AsO$_4$)Cl$_3$ and a minor amount of galena. Mimetite contains arsenic and chlorine in its composition which was detected by x-ray mapping (data not shown).

![Figure 12](image3.png)

Figure 12. SEM image and distribution of Zn, Si, Pb, and Ca in the flotation concentrate without slime.

The first stage of flotation experiments concluded that the maximum zinc recovery could be obtained as 17.84 %, using only the collector octadecylamine. But, much higher recovery (56.54 %) was observed when the combination of octadecylamine and Armac T was used in the flotation test. Therefore, it seems that Armac T or synergistic phenomenon has a more powerful effect on the floatability of hemimorphite mineral. Additionally, FTIR analysis was performed on both concentrates which their results are shown in Figures 13A and B.

As is clear from the Figures 13A and B, the peaks in the range of 850 to 1100 cm$^{-1}$ are related to the Si-O bond for both charts (Si-O bond has peaks in the ranges of 800 to 900 and 1000 to 1100 cm$^{-1}$ as wavelength) [15]. The magnitude of this peak in the concentrate without slime is bigger than the magnitude in concentrate with slime. The Zn-O bond also has the peak in the 463 cm$^{-1}$ and a range of 1435 to 1475 cm$^{-1}$ as wavelength [15]. These peaks were distinguishable in both charts, but the magnetite of peak related to the 1435 to 1475 cm$^{-1}$ is more substantial (especially in the concentrate without slime). In total, the FTIR analysis showed that de-sludging of feed prior to flotation test had an influential effect on increasing the adherence of collectors (octadecylamine and Armac T) on the hemimorphite surface and this leads to an increase in recovery and grade of zinc in concentrate.

- Discussion

Salum et al. (1992) claimed that the best performance of flotation process in order to enrich hemimorphite and willemite would be achieved at pH values above 10 [13]. This suggests an important role of the free amine in this system [7, 25 and 26]. The recovery of hemimorphite and willemite at different values of pH is shown in Figure 14 according to their results. As it is clear in Figure 14, maximum recovery of hemimorphite was obtained to be about 10 %. However, in flotation experiments of this study and after the optimization of
different variables, the recovery of hemimorphite was reached to about 80% without de-sludging and 95% with de-sludging. Additionally, with an increase in pH values to higher than 10, the recovery was greatly reduced. The research conducted in this project showed that with an increase in pH value, the recovery of hemimorphite increases as well.

Due to the similar surface properties of zinc silicate minerals such as hemimorphite and associated gauges such as quartz, the wide variety of mineralogical species and the presence of Zn-ions in solution, the selectivity decreases drastically in the flotation. In some cases, as a result of the presence of Zn-ions in the crystal structure of dolomite and some clay minerals, some portion of zinc transfers to the tail [22]. The results were confirmed in the experiments of this research.

Amines (as acetate salts) are neutralized compounds that are used in flotation thanks to their easier handling and improved solubility benefits. Long chain primary amines are fully dissociated below pH=8. Concentration of molecular amine increases with increasing pH (50% at a pH of 10 and approaching to 100% at a pH of 10) [22]. Rising trends are observed in the recovery and grade values of Zinc in the flotation concentrate with an increasing pH from 9.5 to 11.5, thus it is confirmed the higher effective concentration of Octadecylamine at pH values above 10 and hence the higher efficiency of this collector in the process.

Hemimorphite (as the dominant mineral in calamine ores) has a maximum floatability at a pH between 11 and 12. This proves the efficiency of molecular amine compound with chemical formula RNH₂ as a collector in the flotation system [22]. The results of this study have shown that with use of Octadecylamine as the sole collector in flotation tests, the maximum achievable recovery and grade of zinc in concentrate were about 18% and 20%, respectively (pH 10.5). However, the synergistic effect of using mixed collectors (two collectors Octadecylamine and Armac T in combined form) caused that the values of 80% and 33% for zinc recovery and grade in the flotation concentrate become achieveable and reported.

As a result obtained with the work of Peres et al. in 1994, the dispersion of the pulp is not enough for an acceptable flotation efficiency, but the combination of both de-sludging and pulp dispersion is required and advisable. This was also proved during of this study. According to the researchers, sodium hexametaphosphate is the best dispersive agent for flotation of hemimorphite [22]. For this reason, sodium hexametaphosphate was used as dispersive agent in the flotation tests.

6. Conclusions

Due to the influence of several variables in the flotation process of hemimorphite, optimization of the process was carried out in two steps. First, the effect of optimal feed size fraction (dₘₐₓ according to the mineralogical studies and liberation degree) as well as the influence of presence of Armac T as co-collector were examined. According to the results obtained in the first step, dₘₐₓ = 74 µm was determined to be the best size fraction for the pulp feed. On the other hand and in the same fraction, the best grade and recovery values in the concentrate was obtained in the presence of Armac T as co-collector in addition to octadecylamine as the main collector. In the second step, five influential factors including the concentrations of sodium hexametaphosphate, octadecylamine, sodium sulfide, and Armac T and also pH of environment were precisely investigated and optimized. Each variable was studied (in the OFAT methodology: one factor at a time) with three tests (for 3 different values). After optimization, optimal values of these factors were determined as follows:

- Sodium hexametaphosphate (SHMP): 1.2 g/kg
- Octadecylamine (ODA): 14 g/kg
- Sodium sulfide (SS): 8 g/kg
- Armac T: 0.2 g/kg
- pH: 11.5

Under these circumstances as the optimal conditions, grade and recovery values of zinc in the concentrate were obtained as approximately 33% and 83%, respectively. For the sake of omission of the detrimental effect of the fine particles (slime), the de-sludging
pretreatment was performed on the pulp feed and remarkable outputs were achieved. Finally and after de-slumping, grade and recovery of zinc in floated part were determined to be 33.4 % and 95.3 %, respectively. These results were examined and verified with the analyses of XRD, SEM and FTIR. As a main result of FTIR analysis, de-slumping of feed before flotation test had positive effect for increasing the adherence of collectors on the surface of target minerals and this leads to an increase in recovery and grade of zinc in the concentrate.

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