

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

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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. 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:

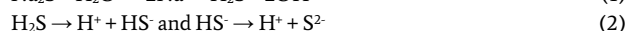
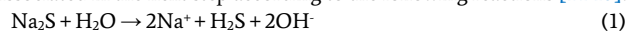
- Mixed sulfide and oxide lead-zinc ores,
- Oxide lead-zinc ores,
- Oxide zinc ore with little or no lead present [1].

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 ($ZnCO_3$), hydrozincite ($2ZnCO_3 \cdot 3Zn(OH)_2$), zincite (ZnO), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) 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_2S , 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-established industrial practice for enrichment of oxidized copper and lead ores. Amines have proved to be the most influential collectors for beneficiation of hemimorphite and willemite, when utilized after a sulphidization stage [13].

Sodium sulfide is the sulphidizing agent which yields the best performance in most flotation systems [13]. Sodium sulfide (Na_2S) which acts as a sulphidizer, can react with water and H_2S can be dissociated in the next step according to the following reactions [14-16]:



The amount of produced H^+ is still less than that of OH^- , the alkalinity of the solution is hence increased and the sodium sulfide also acts as a pH regulator [15]. The amount of sulphidizing reagent and pH of the pulp must be carefully controlled in amine flotation. When the pH value decreases, there is a drop in recovery [13 and 17]. By adding the Na_2S , the net charge on the surface of zinc silicate mineral become more negative with the zeta potential about -110 mV, compared with about -70 mV at the same pH [15]. The best flotation performance was achieved in the pH range above 10, indicating that free amine plays a significant role in these systems. In the pH range of zinc silicates flotation, the predominant species of sodium sulfide dissociation is HS^- . Most investigators consider that this species is adsorbed onto the zinc silicate surfaces. It is assumed that the Sodium sulfide renders the surfaces more negative, favoring the electrostatic attraction mechanism between amines and the mineral's surface. Another theory considers

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that Na₂S seals off the surface of zinc silicates [13].

Among the additives, sodium hexametaphosphate (NaPO₃)₆ is a dispersant widely used in clay industry [18]. It was also reported to be the most effective reagent generating an increase in the dispersion degree in flotation of calamine zinc ores [19]. Sodium hexametaphosphate (SHMP) was used as a dispersant in flotation of hemimorphite [19]. Also, stearyl amine (Octadecylamine, (CH₃(CH₂)₁₇NH₂)) was used as a cationic collector in flotation of zinc ore [15]. Tallow amine acetate (TAA) (16–18 carbon atoms in the alkyl chain) is used as the cationic collector for flotation of different minerals and was obtained from Akzo Nobel Co. with commercial name "Armac T" [20].

In the case of flotation of hemimorphite and willemite, it has been reported that the percentage of zinc recovery was maximized at pH=10 by using stearyl amine as a collector [13 and 21]. The chemical structures of sodium hexametaphosphate (SHMP), stearyl amine (Octadecylamine) and Armac T (Tallow amine acetate) are shown in Fig. 1.

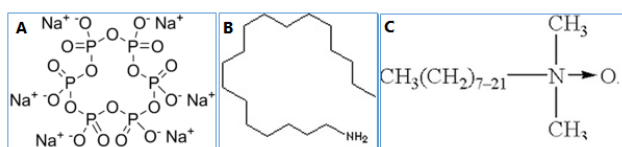


Fig. 1. Chemical structures of SHMP (A), Octadecylamine (B) and Armac T (C) [15, 20].

Bustamante & Shergold performed micro-flotation tests in a Hallimond tube with smithsonite, hemimorphite and willemite, employing dodecyl amine as the collector [22 and 23]. Hemimorphite, the predominant zinc-bearing mineral in calaminic ores, presents maximum floatability in the pH range of 11 to 12, suggesting that the collecting entity is molecular amine RNH. According to van Lierde's research, the presence of RNH₃⁺ 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 (sulphidizing 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.

2. 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 riffing 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, -350+210, -210+149, -149+105, -105+74, -74+53, and -53 μm, were obtained.

Flotation experiments were performed in a 2 Lit Denver cell running at 1100 rpm using 500 g ore sample (25% pulp density). The weighted sample with 1.5 lit 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', sulphidizer 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 filtration 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 Fig. 5. The recovery was calculated according to the following equation, where R_c 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_t represents the zinc loss in the tail.

$$R_c = \frac{C \cdot c}{F \cdot f} \times 100\% \quad (3)$$

$$R_t = 100 - R_c \quad (4)$$

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 concentration 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.

Chemical	Concentration	Supplier	Role	Dosage range
Octadecylamine	-	Merck	Collector	1-1.8 (kg/t)
Armac T	99	Akzo Nobel	Collector	0.2-0.6 (kg/t)
Sodium sulphide	75	Merck	Sulphidizing reagent	8-20 (kg/t)
Sodium Hexametaphosphate	96	Samchun	Depressant	1.2-2 (kg/t)
Pin oil	99	Penn Chemical	frother	120 (g/t)
HCl	---	Merck	pH adjuster	Required
NaOH	---	Merck	pH adjuster	Required

Flotation tests were carried out in two steps as follows:

- Step 1, Flotation tests were performed to optimize the size distribution of pulp feed in three ranges of -150, -106 and -75 μm (d₈₀) in the absence and presence of Armac T as a co-collector.
- Step 2, Flotation tests were carried out to optimize the other influential variables such as the concentration of sodium hexametaphosphate (as depressant), octadecylamine and Armac

T (as collectors) in combined form, sodium sulfide (as sulfidizing agent) and also pH which are discussed in details in the next section. Furthermore, the effect of prior feed de-sliming on the process efficiency was also evaluated.

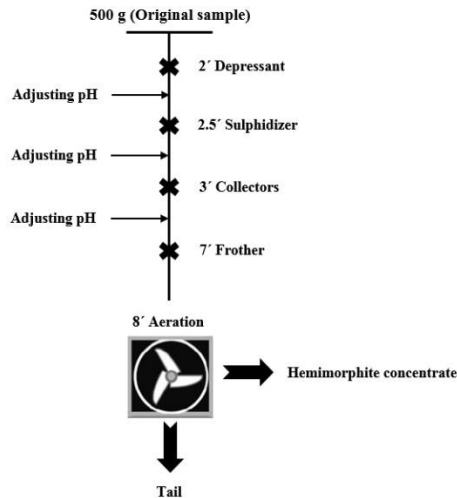


Fig. 5. The schematic flotation process and step of every reagent added in pulp.

For better understanding of the presence of major and minor minerals and the distribution of elements such as Zn, Si, Ca and Pb in the original sample and final concentrate, the SEM-EDS analysis (PHILIPS, XL30) was carried out. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analyses (EDS) were conducted on the polished and grain samples. The polished sections and grain samples were gold coated to obtain electron conductive surfaces. The examination of the internal structure of the samples, the distribution of mineral phases, and the choice of areas for EDS-analyses were carried out in a scanning electron microscope using the Back Scattered Electrons (BSE) technique. Fourier Transform Infrared Spectroscopy, also known as FTIR analysis or FTIR Spectroscopy, is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials. This instrument was used in this study (Thermo Nicolet NEXUS 670 FTIR) and it is capable of collecting data over a wave number range of 350-7800 cm^{-1} and can be configured to run in a single-beam, ratio or interferogram modes. These spectra were measured at 0.09 cm^{-1} resolution. FTIR analysis was used to interpret the synergistic effect of collectors and to identify the organic or inorganic species and bonds created on the hemimorphite particles.

3. Results and Discussions

3.1. 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 (SiO_2), Hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$), Calcite (CaCO_3) and Dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) 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 (Fig. 2).

The results of XRF analysis (Siemens 303 SRS and Philips magix pro) showed that SiO_2 , ZnO, Fe_2O_3 , CaO, PbO, Al_2O_3 are major oxides and MgO, BaO, SO_3 , K_2O , As_2O_3 and P_2O_5 are minor oxides. The XRF results is presented in Table 1. More than 66% of original sample have been formed from two species of SiO_2 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 ore, 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.

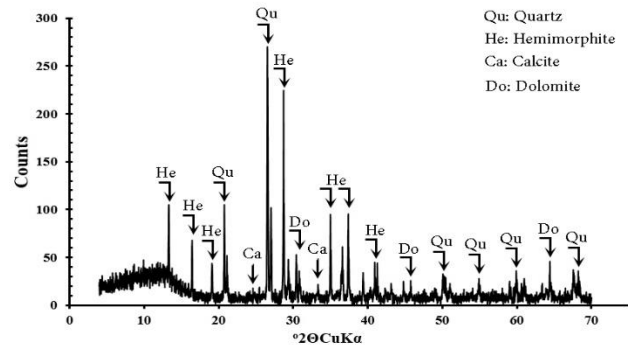


Fig. 2. X-ray diffractogram of representative sample.

Table 1. The XRF analysis of representative sample.

Major		Component	SiO_2	ZnO	Fe_2O_3	CaO	PbO	Al_2O_3
		%	38.72	27.41	6.57	6.50	2.84	2.26
Minor		Component	BaO	MgO	SO_3	K_2O	As_2O_3	P_2O_5
		%	1.51	1.34	0.91	0.58	0.58	0.27
Total		Component	L.O.I		Total			
		%	9.82		99.31			

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 $d_{80} = -100 \mu\text{m}$ and 100% of liberation degree was observed in size fraction with $d_{80} = -30 \mu\text{m}$. 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 Figs 3A and 3B.

Based on the Sieve analysis results, d_{80} of sample was determined 1608 μm . The grade and distribution of Zn and Pb in different size fractions are presented separately in Figs 4 (A and B).

As shown in Figs 4 (A and B), maximum grade and distribution of zinc were observed in size fractions of $-590+350 \mu\text{m}$ and $-53 \mu\text{m}$, respectively. But maximum values for both factors (grade and size distribution) for Pb were observed in size fraction of $-53 \mu\text{m}$. 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.

3.2. 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 (NaPO_3)₆ as a dispersant, octadecylamine ($\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$) as the main collector, Armac T as a

co-collector, sodium sulfide (Na_2S , $9\text{H}_2\text{O}$) 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.

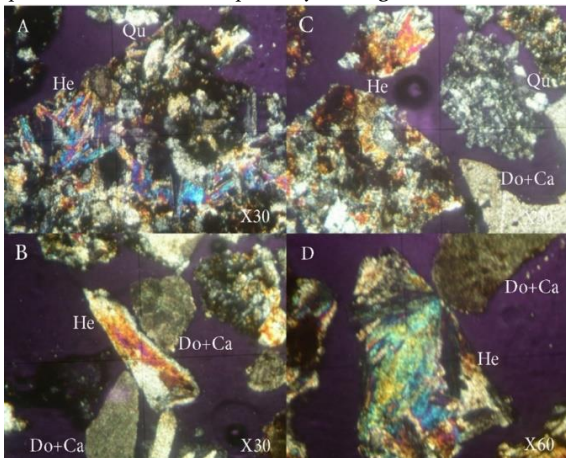


Fig. 3A. Hemimorphite in bladed shape interlocked with quartz, -1410+1000 μm (A), liberated hemimorphite and carbonate minerals, -590+350 μm (B), hemimorphite, quartz and carbonate minerals, -590+350 μm (C), liberated hemimorphite and carbonate minerals, -53 μm (D).

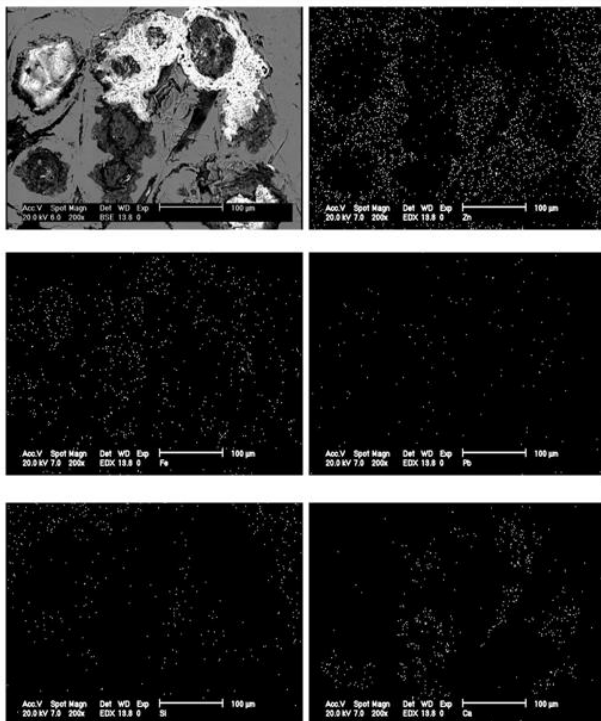


Fig. 3B. SEM micrograph and the corresponding EDS mapping of Zn, Fe, Pb, Si and Ca.

3.2.1. The Effect of Feed Size Distribution

With respect to the importance of feed size distribution (d_{80} 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

($d_{80} = -149 \mu\text{m}$, $d_{80} = -105 \mu\text{m}$ and $d_{80} = -74 \mu\text{m}$). 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.

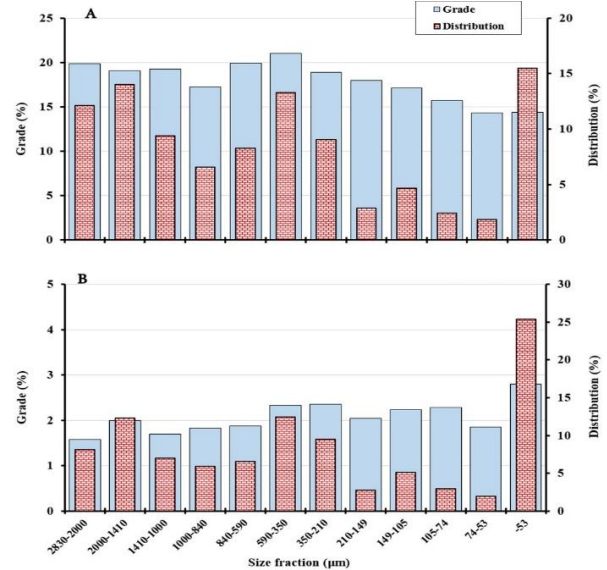


Fig. 4. Grade and distribution in the different size fractions, Zinc (A), Lead (B).

As it can be seen in the Fig. 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 $d_{80} = -74 \mu\text{m}$ 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.

3.2.2. The Effect of Armac T Presence

In this stage, three flotation tests were carried out on the samples in three different size fractions ($d_{80} = -149 \mu\text{m}$, $d_{80} = -105 \mu\text{m}$ and $d_{80} = -74 \mu\text{m}$) 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 Fig. 6B.

As it can be concluded from Fig. 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.

3.3. 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 $-74 \mu\text{m}$ 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 $-74 \mu\text{m}$ and in the presence of 0.4 g/kg Armac T as co-collector.

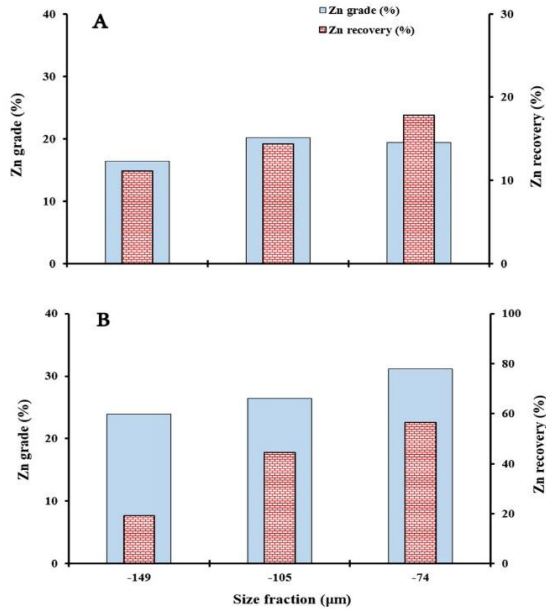


Fig. 6. Grades and recoveries of zinc in flotation concentrates; without Armac T (A), with Armac T as co-collector (B).

3.3.1. 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 Fig. 7A. According to the results presented in Fig. 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.

3.3.2. 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 Fig. 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% .

3.3.3. 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 Fig. 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.

3.3.4. 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 Fig. 7D.

Based on the results shown in Fig. 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 8.65% 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.

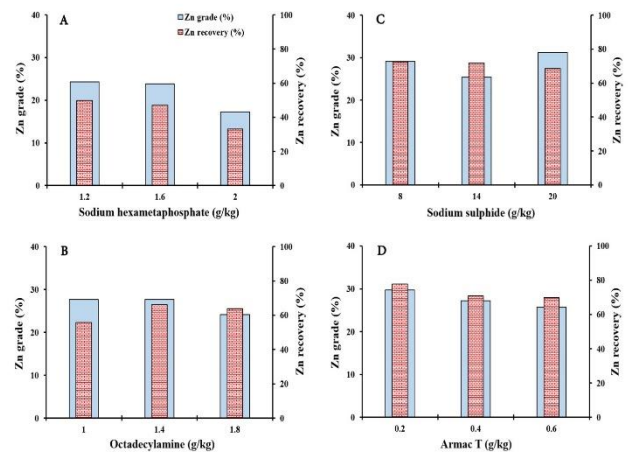


Fig. 7. Grades and recoveries of zinc in flotation concentrates with different dosages of reagents; SHMP (A), ODA (B), SS (C) and Armac T (D).

3.3.5. 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 Fig. 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.

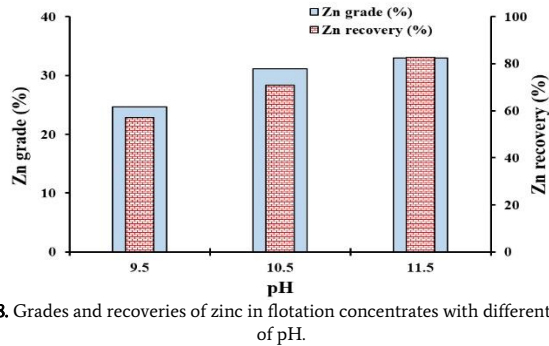


Fig. 8. Grades and recoveries of zinc in flotation concentrates with different levels of pH.

3.3.6. 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 -25 μm 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 Fig. 9.

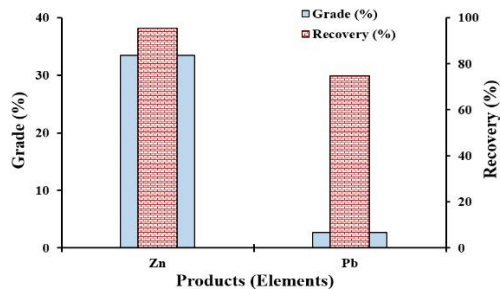


Fig. 9. Grades and recoveries of Zn and Pb in final flotation concentrate, after de-sliming of feed.

As shown in Fig. 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 (SiO_2) in the concentrate and tail were also analyzed for flotation tests with and without de-sliming process (Table 3).

As can be concluded from Table 3, de-sliming of feed has a significant positive effect on the selectivity behaviour of mixed collectors. In other words, by means of de-sliming of feed prior to flotation test, the percentage of silica in the concentrate decreases about 17 % compared to the test without de-sliming. Furthermore, the higher amount of silica in the tail (in the flotation test with de-sliming) 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-sliming process.

Process	Product	SiO_2 grade (%)	SiO_2 distribution (%)
Without slime	Concentrate.	18.56	37.10
	Tail	50.87	62.90
With slime	Concentrate.	35.16	64.90
	Tail	20.28	35.10

3.3.7. 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-sliming 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 Fig. 10.

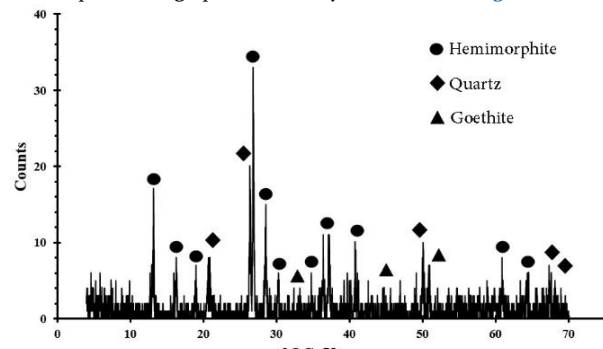


Fig. 10. XRD analysis of concentrate obtained from final flotation test.

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-slimed flotation test. The images of two concentrates are shown in Fig. 11.

The distribution of Zn, Si, Pb and Ca in flotation concentrate without slime are shown in Figs 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-sliming 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 $Pb_3(AsO_4)_3Cl$ and a minor amount of galena. Mimetite contains arsenic and chlorine in its composition which was detected by x-ray mapping (data not shown).

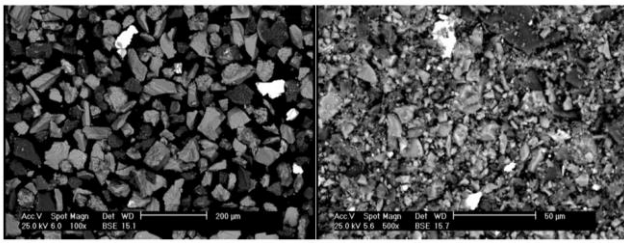


Fig. 11. SEM images of flotation concentrates, with slime (right side) and without slime (left side).

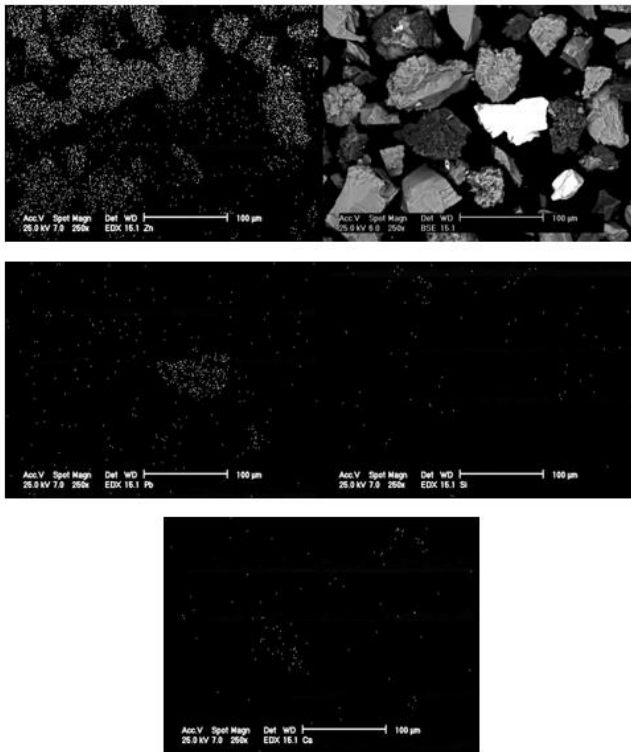


Fig. 12. SEM image and distribution of Zn, Si, Pb, and Ca in the flotation concentrate without slime.

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 Figs 13A and B.

As is clear from the Figs 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-sliming 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.

4. 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 Fig. 14 according to their results. As it is clear in Fig. 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-sliming and 95 % with de-sliming. 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.

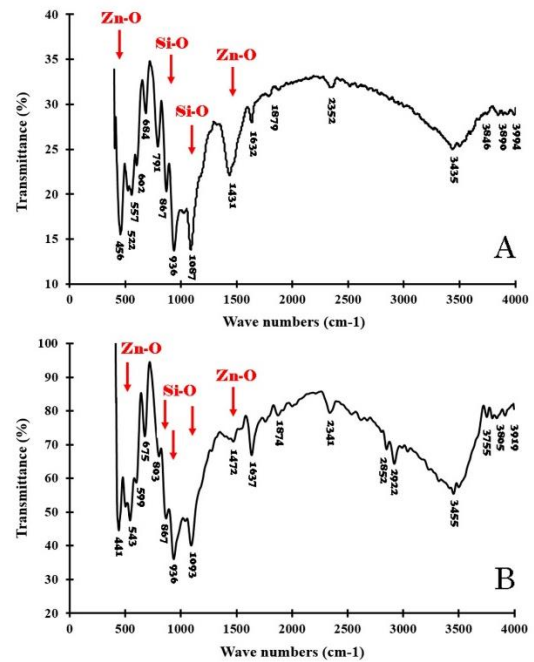


Fig. 13. The FTIR graph in the flotation concentrate, A) with slime, B) without slime.

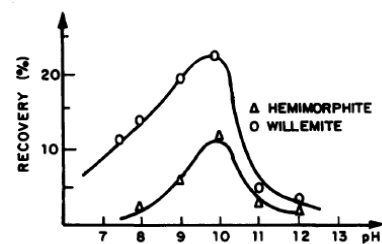


Fig. 14. The recovery of hemimorphite and willemite at different values of pH [2].

Also, it was showed that floatability of hemimorphite and willemite were not reduced due to extra amounts of added sodium sulfide in the flotation process with amine as a collector. They also stated that the effect of sodium sulfide on the flotation of hemimorphite and willemite was dependent upon the pH of solution. It was postulated that while the concentration of sodium sulfide increases, flotation recovery increases as well up to a certain level and then it would be a constant value [13]. The results of the experiments showed that with an increasing concentration of sodium sulfide (equivalent to 12 kg per ton of ore), a decrease of 4% in the zinc recovery would occur. Moreover, the experiments showed that the highest grade of flotation concentrate (equivalent to 31.2 %) was obtained at the highest concentration of sodium sulfide. It should be noted that these results were obtained at $pH=10.5$, but Salum et al. carried out their flotation tests at $pH=9$ and 10. The major problem in the cationic flotation of Zn-bearing silicate-

carbonate ore with amine is the presence of large amounts of fine particles and slime which leads to an increase in reagents consumption because a phenomenon which is called slime-coating occurs. These results lead to interruptions in flotation selectivity and in some cases, the whole process becomes unfeasible. Therefore, it seems that flotation of this type of ore would require de-sliming and (or) making adequate dispersion of the pulp by using the specific reagents would be necessary. In maximum degree of dispersion, the amount of target minerals which is transferred to tail reduces and ultimately leads in an increase in the recovery of the process [22]. According to the aforementioned description and after removing slime from flotation feed, the positive effects of de-sliming (increase selectivity, good dispersion of the pulp and reduction of the zinc minerals transfer to tail) were confirmed by a 0.45 % increase in zinc grade in concentrate and about 6 % decrease of zinc grade in tail and 12 % increase of zinc recovery in final concentrate.

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 RNH_2 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 achievable 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-sliming 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 agency in the flotation tests.

5. 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 (d_{80} , 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, $d_{80} = -74 \mu m$ 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): 1.4 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-sliming pretreatment was performed on the pulp feed and remarkable outputs were achieved. Finally and after de-sliming, 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-sliming 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.

Acknowledgments

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REFERENCES

- [1] Bulatovic, S., 2010. Handbook of flotation reagents, Elsevier Science & Technology Books.
- [2] Chen, A., Zhao, Z.W., Jia, X., Long, S., Huo, G., Chen, X., 2009. Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore. Hydrometallurgy 97(3-4), 228-232.
- [3] Önal, G., Bulut, G., Gül, A., Kangal, O., Perek, K.T., Arslan, F., 2005. Flotation of Aladag oxide lead-zinc ores. Minerals Engineering 18(2), 279-282.
- [4] Mehdilo, A., Irannajad, M., Zarei, H., 2013. Flotation of Zinc Oxide Ore Using Cationic and Cationic-Anionic Mixed Collectors. Physicochemical Problems of Mineral Processing 49(1), 145-156.
- [5] Sahinoglu, E., 2018. Cleaning of high pyritic sulfur fine coal via flotation. Advanced Powder Technology 29 (7), 1703-1712.
- [6] Ahmadi, M., Gharabaghi, M., Abdollahi, H., 2018. Effects of type and concentrations of organic depressants on pyrite floatability in microflotation system. Advanced Powder Technology, In Press.
- [7] Rey, M., and Raffinot, P., 1953. The flotation of oxidized zinc ores. Inst. Metall., London.
- [8] Kiersznicki, T., Majewski, J., Mzyk, J., 1981. 5-alkylsalicylaldoximes as collectors in flotation of sphalerite, smithsonite and dolomite in a Hallimond tube. International Journal of Mineral Processing 7(4), 311-318.
- [9] Irannajad, M., Ejtemaei, M., Gharabaghi, M., 2009. The effect of reagents on selective flotation of smithsonite-calcite-quartz. Minerals Engineering 22(9-10), 766-771.
- [10] Ejtemaei, M., Irannajad, M., Gharabaghi, M., 2011. Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors.

- Minerals Engineering 24(13), 1402-1408.
- [11] Pereira, C.A., and Peres, A.E.C., 2005. Reagents in Calamine Zinc Ores Flotation. *Minerals Engineering* 18, 275-277.
- [12] Hosseini, S.H., and Forssberg, E., 2006. Adsorption studies of smithsonite flotation using dodecylamine and oleic acid. *Minerals and Metallurgical Processing (SME)* 23(2), 87-96.
- [13] Salum, M.J.G., de Araujo, A.C., Peres, A.E.C., 1992. The role of sodium sulfide in amine flotation of silicate zinc minerals. *Minerals Engineering* 5, 411-419.
- [14] Klassen, V.I., Mokrousov, V.A., Leja, J., Poling, G.W., 1963. *An Introduction to the Theory of Flotation*, Butterworth and Co. (publishers) Ltd., Canada.
- [15] Pomjaturad, J., Rattanakawin, C., Sriprang, N., Tongteeka, S., Chairuangs, T., 2007. Effects of additives in froth flotation of silicate zinc ore; a study by zeta potential measurement and infrared spectroscopy. *Chiang Mai Journal of Science* 34(2), 191-200.
- [16] Martins, L., Pereira, C.A., Galery, R., Peres, A.E.C., 2010. Flotation of oxidized zinc ore without desliming. *Minerals & Metallurgical Processing* 27(1), 34-41.
- [17] Hosseini, S.H., and Forssberg, E., 2007. Physicochemical studies of smithsonite flotation using mixed anionic/cationic collector. *Minerals Engineering* 20(6), 621-624.
- [18] Andreola, F., Castellini, E., Manfredini, T., Romagnoli, M., 2004. The Role of Sodium Hexametaphosphate in the Dissolution Process of Kaolinite and Kaolin. *Journal of the European Ceramic Society* 24, 2113-2124.
- [19] Hosseini, S.H., 2006. Flotation behavior of oxide zinc ore from Angouran deposit, Iran in the presence of cationic/anionic and mixed (cationic/anionic) collectors. *European Journal of Mineral Processing and Environmental Protects* 6(3).
- [20] Orhan, E.C., and Bayraktar, İ., 2006. Amine-oleate interactions in feldspar flotation. *Minerals Engineering* 19(1), 48-55.
- [21] Ejtemaei, M., Gharabaghi, M., Irannajad, M., 2014. A review of zinc oxide mineral beneficiation using flotation method. *Advances in Colloid and Interface Science* 206, 68-78.
- [22] Peres, A.E.C., Borges, A.A.M., Galery, R., 1994. The effect of the dispersion degree on the floatability of an oxidized zinc ore. *Minerals Engineering* 7, 1435-1439.
- [23] Bustamante, H., and Shergold, H.L., 1983. Surface chemistry and flotation of zinc oxide minerals: Flotation with dodecylamine. *Trans. IMM Section C*, 92, 201.
- [24] van Lierde, A., 1972. Effects of acrylate polymers on the sulphidization flotation of copper, lead and zinc oxide ores associated with a carbonate gangue. *Trans. IMM Section C*, 81, 204.
- [25] Rey, M., 1979. *Memoirs of milling and process metallurgy: 1- Flotation of oxidized ores*. *Transactions Institution of Mining & Metallurgy*.
- [26] Rey, M., Sitia, G., Raffinot, P., Formanek, V., 1954. The flotation of oxidized zinc ores. *Trans. AIME*, 199.