Reagents in zinc recovery from Pb- flotation tailings of Dandy mineral processing plant

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Abstract

Effect of concentration parameters on recovery of zinc oxidized minerals from lead flotation tailings of Dandy mineral processing plant in north-western Iran was studied. A sulfidization-flotation method has been used on a laboratory scale to investigate the effect of various reagents such as sodium sulfide as sulfidizing agent, primary amine as collector, dispersants and flocculants with different concentrations to reach an optimum zinc recovery. Among the dispersants tested, hexametaphosphate gave a higher zinc grade 40.4% and 70% recovery. Usually de-sliming is used to increase the recovery of zinc, however, analyses have shown that fine particles in the sample mostly contain zinc, thus de-sliming is not suggested.

Keywords: Zinc Oxidized Ores - Disperssants - Concentration - Lead Flotation Tailings

Introduction

Zinc is an important base metal in galvanizing and battery manufacturing industries. Most of the metallic zinc, which is produced in the world, comes from sphalerite that can be concentrated easily by flotation. As the global sources of sphalerite are near to be finished in some decades, oxidized zinc ores are the considerable alternative source of zinc metal. Oxidized zinc ores are in carbonate and silicate forms such as smithsonite ($ZnCO_3$), hydrozincite ($2ZnCO_3.3Zn(OH)_2$), Zincite (ZnO), willemite ($ZnSiO_4$) and hemimorphite ($Zn_2SiO_3.H_2O$).

In practice, the commonly used method for the recovery of oxidized lead and zinc minerals from ores is flotation [1,2,3,4]. The tailings of the lead flotation stage may contain significant quantities of zinc as well as interfering and gangue minerals (undesirable impurities) such as silicates and carbonates [3].

Sulfidization-flotation is the most commonly used method for the recovery of zinc oxidized ores. Usually sodium sulfide is the sulfidizing agent which yields the best performance in most flotation systems [5,6,7]. Salum et al. [8] studied on the role of sodium sulfide in amine flotation of silicate zinc minerals. They found that sodium sulfide effect on Willemite is stronger than on Hemimorphite as well as the increase in Na_2S concentration in pre-sulfidization enhances the Willemite floatability up to a limiting concentration.

For oxidized ores, cationic collectors such as amines are used as collectors. The amines are neutralized for easier handling and improved solubility. Amine concentration increases with pH, reaching 50% at pH=10 and approaching 100% at pH=11 [9].

The major problem in processing the lead flotation tailings is the large amount of fines and slimes increasing reagent consumption, causing the so-called slime coating phenomenon, hindering selectivity and, in some cases, rendering the process unfeasible. To preclude this, de-sliming and using different reagents such as flocculants, coagulants, dispersants and depressants can be applicable [9].

Peres et al. [9] investigated the effect of dispersion degree on the floatability of an oxidized zinc ore. Sodium hexametaphosphate and sodium tripolyphosphate were used to decrease the effect of a large number of slimes and fines.

Finally, it was found that a combination of dispersion and de-sliming could increase selectivity.

Effect of depressing agents on the flotation of an oxidized zinc minerals which contained 17% Zn was studied by Marabini et al. [10]. Four classes of reagents such as guar, starch, celluloses and acrylic polymers were used. The Zn recovery ranged from 70% to 80% and the Zn grade ranged from 27% to 29%. Moreover the compounds that showed the best separation efficiency were tripolyphosphate and guar of methylcarboxylic sodium salt.

The current paper reports on the separation of zinc oxidized minerals from Pb-flotation tailing of Dandy mineral processing plant, using a sulphfidiszation-flotation method. In this study, the effect of sodium sulfide and amine concentration as well as various flocculating and dispersing reagents has been investigated on the recovery of zinc.

Experimental

The dry fine lead flotation tailing from Dandy was passed thorough a ¼ inch sieve, split into approximately 1 kg sub-samples, using a riffle. One of the sub-samples was split into approximately 50gr sub-samples. These sub-samples were employed for chemical analyses using X-ray diffraction

Table1 : Reagents used in the experiments.

Chemicals	Grade	Supplier	Usage
Primary Amine	Undiluted	Hochest	Collector
Sodium Sulfide	50%	Tianjin Gangia	Sulphdizing agent
Pine Oil	Undiluted	Cyanamid	Frother
Sodium Silicate	97%	Carlo Ebara	Dispersant
Sodium Hexametaphosphate	96%	Merck	Dispersant
Sodium Tripolyphosphate	97%	Merck	Dispersant
Sulfuric Acid	98%	Merck	pH adjuster
Sodium Hydroxide	97%	Merck	pH adjuster

(XRD) employing a Philips instrument model XPERT PRO with 3000W, X-ray fluorescence (XRF) utilizing a Philips model PW2400 with 3000W and atomic absorption spectrophotometer (AAS), Varian AAS model Spectra A50. The sodium sulfide used in sulfidization experiments was a product of Tianjin Gangia Chemicals Company. To exclude air and minimize oxidation, it was stored in a dessicator. Other reagents used in the study are shown in Table (1).

The flotation experiments were done in a Denver D-12 machine and the impeller speed was 1200 rpm.

Size distribution analysis was performed using a 50g sub-sample. According to the size distribution analysis; 50% of the residue was under $30 \mu m$. In addition, wet sieve analysis was performed and each fraction was analyzed for zinc by AAS.

A 300g sub-sample was fed to flotation cell (2.6 L). The pulp density was 30% and sodium sulfide was added to the pulp at pH 7.8 and conditioned for 5 minutes. After conditioning, pH reached to 11 which was considerably suitable for adding other reagents especially collectors [9]. After adding the collector, the dispersant or flocculant was added and the slurry was conditioned for 10 minutes, pH extent reached to 11.5. Finally pine oil was added to the slurry as frother.

Sodium suphide, sodium hexametaphosphate, sodium tripolyphosphate and floc N-100 solutions were, 3%w, 0.1 M, 5%w and 1%w respectively. After the flotation stage the tails and concentrates were filtered, dried, weighed and analyzed for Zn by AAS.

Results and discussion

According to XRD analysis (Figure 1), the residue contained mainly smithsonite ($ZnCO_3$), quartz (SiO_2) and muscovite

($KAl_2Si_3AlO_{10}(OH)_4$). The result of XRF analysis on the main sample is shown in Table 2. The sample contains 20.2% ZnO and 34.6% SiO_2. According to the size by size analysis shown in Table (3), Zn content in fine particles is higher than that in coarse ones and the most Zn content (23.6%) is within the -275+325 fraction. It is mentioned before that fine particles and slimes increase reagent consumption and cause problems such as slime coating. However, in this case, since zinc recovery is the target and table 3 shows that most of the zinc is in the fines, therefore, de-sliming leads to Zn loss and is not suggested.
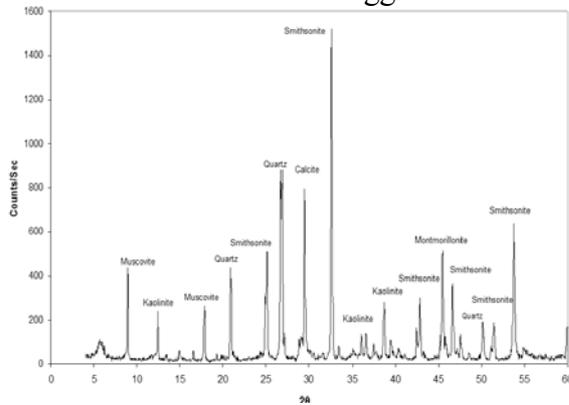
Figure 1: XRD analysis of tailings.

Table 2.XRF analysis of tailings

Chemical Composition	%
SiO2	34.6
Al2O3	8.9
ZnO	20.2
PbO	2.59
SO3	1.73
MgO	1.05
K2O	1.6
TiO2	0.52
MnO	0.057

Table 3 : AAS analysis of classified tailings for Zn content.

Mesh	Zn%
+50	9.67
-50+100	9.23
-100+200	19.07
-200+275	20.81
-275+325	23.61
-325+400	22.67
-400	22.35

Effect of Amine dosage

In these set of experiments, amine dosage was increased from 178 g/t to 3560 g/t. Sodium sulfide as sulfidizing agent with a concentration of 3400 g/t and pine oil as frother with a concentration of 60g/t were also added. The results are shown in Figure 2. Increasing amine dosage to 356 g/t amine resulted in an increase in the Zn grade, however, dosages more than 356 g/t amine led to a decrease in the Zn grade and leveled out at ca. 1067 g/t.

The adsorption mechanism of amine collectors is proposed to be electrostatic [11]. Increasing the collector concentration up to 356 g/t amine results in the first layer of amine collector forming which makes the surface hydrophobic. Decreasing the zinc grade by increasing the amine concentration higher than 356 g/t amine can be attributed to formation of second amine layer on the surface which leads the ore to be more hydrophilic [11].
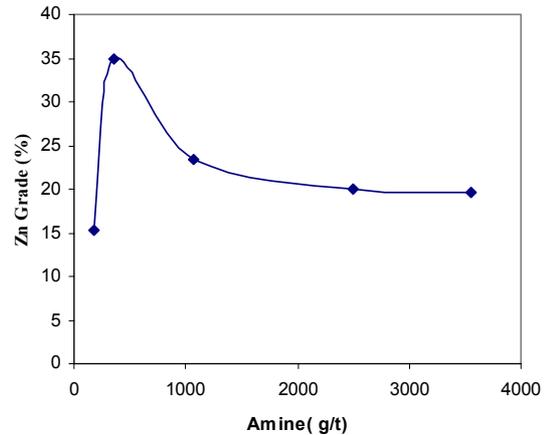
Figure 2 : Effect of amine dosage on Zn grade ([Na_2S]=3400 g/t), [pine oil]= 60 g/t).

Effect of Na_2S concentration

Effect of Na_2S concentration is shown in Figure (3). The same reagents, 356 g/t amine as collector and 60 g/t pine oil as frother were used in these experiments. According to the results, increasing in Na_2S concentration to ca. 3400 g/t (Figure 3) enhanced the Zn grade sharply to 26%, leveling out to 26.5% at 7000> [Na_2S]>3400. However, Moradi [12]

mentioned that high Na_2S concentration hinders the reaction between collector and particle surface by covering the surface causing lower grade. According to Figure 4, zinc recovery raised to 41% at 3400 g/t Na_2S which is the optimum concentration.
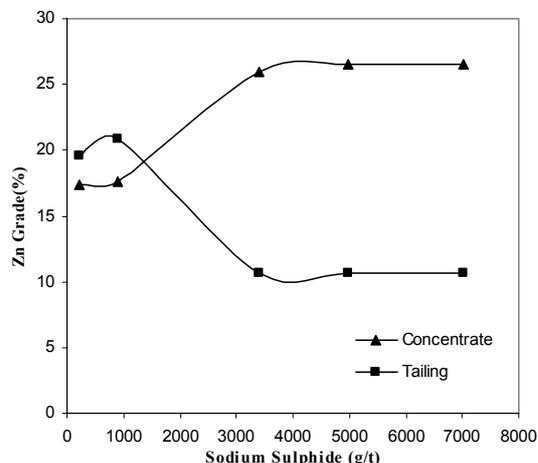
Figure 3 : Effect of sodium sulfide on Zn grade ([amine]=356 g/t, [pine oil]= 60 g/t) .
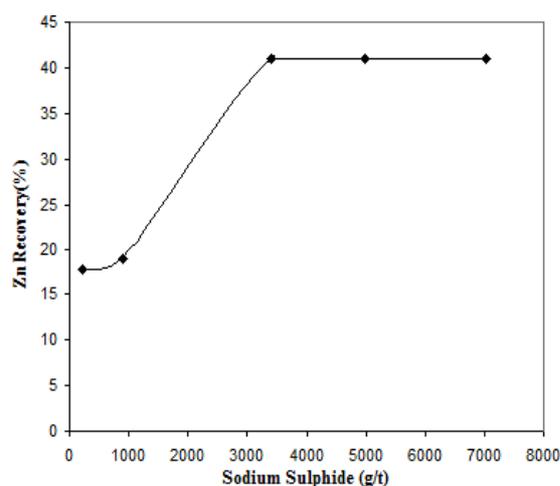
Figure 4 : Effect of sodium sulfide on Zn recovery ([amine]=356 g/t, [pine oil]= 60 g/t, pH=11) .

Figure (4) also shows that an excess of sodium sulfide does not depress the floatability of the zinc minerals. It can be concluded that the recovery increases with increase in sodium sulfide concentration up to a certain level, which depends on the flotation pH, remaining constant at this Figure at pH= 11.

An excess of sodium sulfide makes the surface more negative, therefore, the amine molecules adsorb on the surface easier and the floatability of the zinc minerals increases.

Effect of Na_2S conditioning time

Sodium sulfide is considered to render the surface more negative, favoring the electrostatic attraction mechanism between amines and the mineral surface [5,6,7]. In fact the activating reagent Na_2S increases the zinc carbonate solubility, by fixing the Zn^{2+} ions on the mineral surface. The Zn^{2+} sites on the surface may complex with HS^- anions**.** It should be mentioned that in the pH range of zinc carbonate flotation, the predominant sodium sulfide species is HS^- [8]. Conditioning the mineral particles in sulfidizing solution for a certain time releases HS^- ions. Therefore, the necessary conditioning time studied in the Na_2S solution is another important aspect to be determined. In order to see the effect of conditioning time, 3400g/t Na_2S, 356 g/t amine and 60 g/t pine oil were used as reagents. The conditioning time was in the range of 2 to 20 minutes.
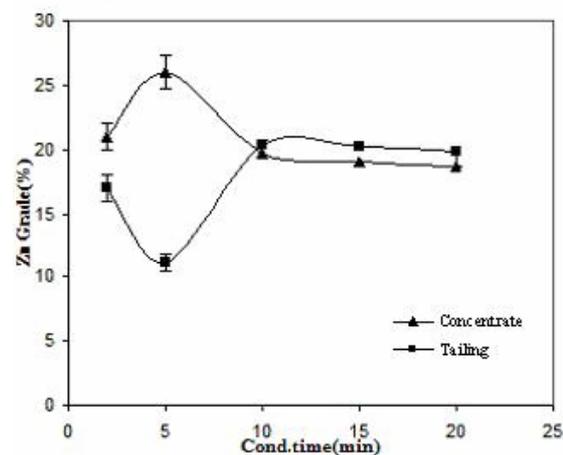
Figure 5 : Effect of Na_2S conditioning time on Zn grade ([amine]=356 g/t ,[Na_2S]=3400 g/t, [pine oil]= 60 g/t).

The Zn grade in concentrate and tailing is shown in Figure (5) as a function of conditioning time. According to this Figure, 5 minutes was considered as the optimum conditioning time. Therefore, the optimum flotation conditions used for the next stage was determined to be 356 g/t amine, pine

oil 60 g/t, 3400 g/t Na_2S and 5 minutes Na_2S conditioning time.

Effect of dispersants
Effect of sodium silicate

As it is mentioned in section 3 (Table 3), the tailing sample contains lots of fine particles. To prevent slime coating and increase selectivity, the fine particles should be dispersed and separated from the larger ones. Unfeasibility of de-sliming (section 3) led to employing reagents such as sodium silicate (Na_2SiO_3), sodium hexametaphosphate and tripolyphosphate as the dispersants.
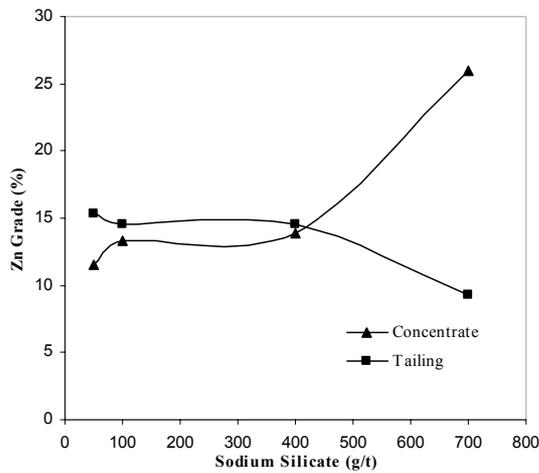
Figure 6 : Effect of sodium silicate on Zn grade ([amine=356 g/t , ,[Na_2S]=3400 g/t [pine oil]= 60 g/t) .
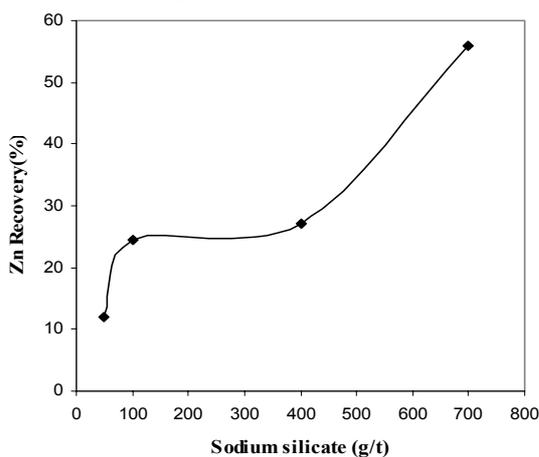
Figure 7 : Effect of sodium silicate on Zn recovery ([amine=356 g/t , ,[Na_2S]=3400 g/t [pine oil]= 60 g/t) .

Figure (6) and (7) show the Zn grade and recovery as a function of sodium silicate.

Enhancement in sodium silicate concentration up to 700g/t caused an increase in Zn grade and recovery up to 26% and 56%, respectively. This finding is attributed to the disperssing effect of the highly negatively charged silicate ions.

Effect of Sodium Hexametaphosphate

Same condition as for sodium silicate was performed to study the effect of sodium hexametaphosphate. Zn grade and Zn recovery as a function of hexametaphosphate concentration are shown in Figures (8) and (9).

As it can be seen, in the presence of 400-700 g/t of sodium hexametaphosphate the zinc grade in the tailing is the lowest. At this condition, the highest zinc recovery is ca.70%.
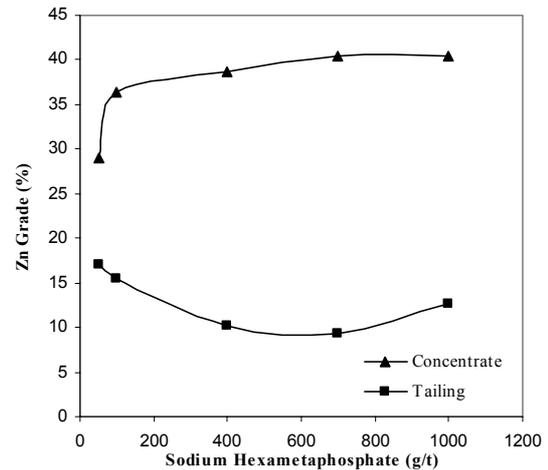
Figure 8 : Effect of sodium hexamephosphate on Zn grade ([amine]=356 g/t ,[Na_2S]=3400 g/t, [pine oil]= 60 g/t).
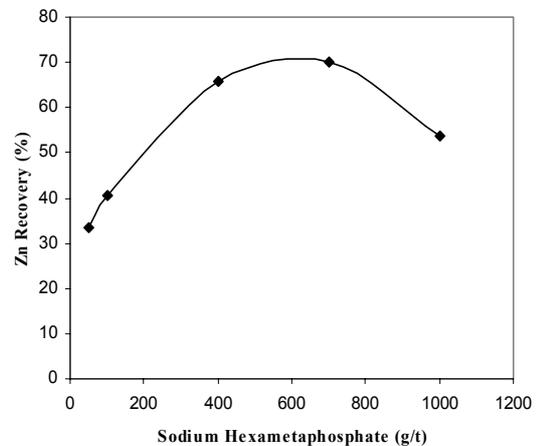
Figure 9 : Effect of sodium hexamephosphate on Zn recovery ([amine]=356 g/ t ,[Na_2S]=3400 g/t, [pine oil]= 60 g/t) .

This phenomenon could be attributed to the adsorption of hexametaphosphate at the cation sites (Zn^{2+}) conferring a high negative charge on the mineral surface, i.e., increasing the adsorption of amine collector. Hexametaphosphate is a cyclophosphate which undergoes hydrolysis at alkaline condition to produce the corresponding linear polyphosphate [13].

At a concentration higher than 700 g/t the negative sites on the surface increases so that the amine concentration is not enough, as a result the zinc recovery decreases.

3.4.3 Effect of Sodium Tripolyphosphate

Same condition as for the two previous dispersants was carried out. Results for Zn recovery and Zn grade are shown in Figures (9) and (10). The Zn grade reached to 38.9% and Zn recovery raised to 62%.

The results for the dispersants tested show that hexametaphosphate increased the zinc grade and recovery more than the others. The slight difference between the results from hexametaphosphate to tripolyphosphate simply indicates that the more negative charge on the former may affect the amine adsorption on the surface, increasing the zinc recovery more than tripolyphosphate at the same condition.
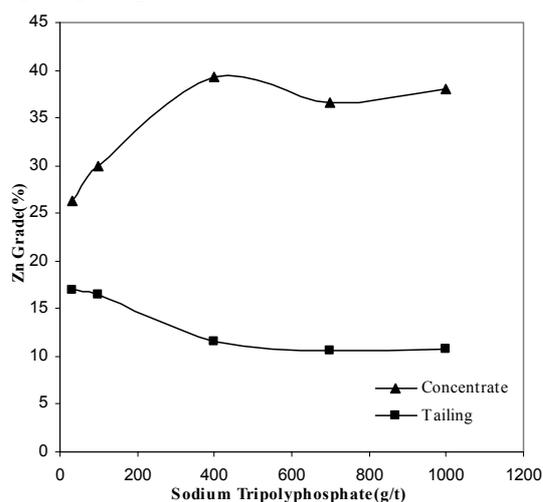
Figure 10 : Effect of sodium tripolyphosphate on Zn grade ([amine]=356 g/t ,[Na_2S]=3400 g/t, [pine oil]= 60 g/t).

Effect of flocculant dosage

In order to study the effect of flocculant, a non-anionic flocculant, superfloc N-100,

3400 g/t Na_2S , 356 g/t amine and pine oil 60 g/t were used as reagents. The results are shown in Figures (12) and (13) for Zn grade and recovery, respectively. Increasing in floc dosage to 250 g/t raised Zn grade to 30% and Zn recovery to 54%, lowering the Zn grade slightly to 27% and Zn recovery to 35% at 700 g/t floc dosage.
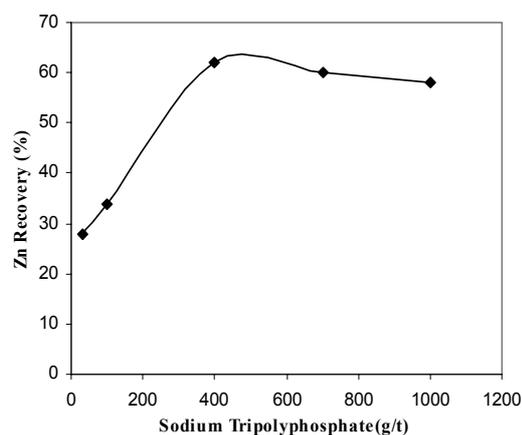
Figure 11 : Effect of sodium tripolyphosphate on Zn recovery ([amine]=356 g/t ,[Na_2S]=3400 g/t, [pine oil]= 60 g/t).
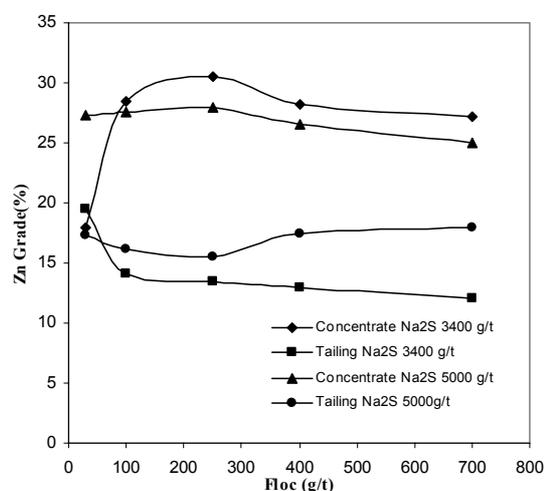
Figure 12 : Effect of superfloc N-100 on Zn grade ([amine=356 g/t , ,[Na_2S]=3400 g/t [pine oil]= 60 g/t) .

It is worth mentioning that using superfloc N-100 caused adhesion of particles which is most likely to bring silicate to the concentrate, thus reducing the grade. Moreover another set of experiments were carried out with 5000 g/t Na_2S to observe the effect of Na_2S dosage. The increase in Na_2S dosage caused a decrease

in Zn grade and recovery.
significatntly using flotation method for concentrating.
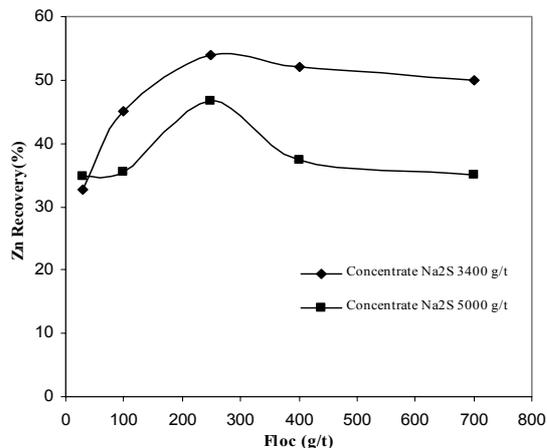
Figure 12 : Effect of superfloc N-100 on Zn recovery ([amine =356 g/t , ,[Na_2S]=3400 g/t [pine oil]= 60 g/t) .

Conclusions

1) The Zn content in fine particles is higher than in coarse ones. Therefore, desliming leads to Zn loss and is not suggested.
2) Flotation is a useful concentrating method to increase the zinc grade of the tailing.
3) The best flotation results were obtained using various dispersants. Among the dispersants tested, hexametaphosphate gave a higher zinc grade and recovery.
4) Comparing to dispersants used, it seems that super floc N-100 is not that effective in reducing problems caused by slimes.

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