A study on collectorless flotation of lead and zinc sulphide present in the Derekoy ore in the presence of sodium sulphide was performed. The parameters of the process and influence of sodium sulphide, zinc sulphide, conditioning time, pH and cleaning of concentrate were investigated. The results were compared with collector added flotation using several types of collectors.

Key words: flotation, galena, zinc sulphide, conditioning time, pH

INTRODUCTION

Sulphide minerals are readily amenable to flotation, but in most cases after a proper surface treatment. Thiol type collectors are most widely used to render selected constituents of a sulphide ore hydrophobic. However, at the Tsumeb concentrator in South Africa, galena and sphalerite are floated selectively from chalcopyrite without using any collector in the first 8 cells of each rougher bank (Boyce et al., 1970). Lepetic (1974) has also shown that chalcopyrite can be floated successfully by using frother alone after a dry autogenous grinding. These reports on collectorless flotation have rekindled an old controversy as to whether or not the sulphide minerals are naturally hydrophobic (Stewart and Finkelstein, 1973; Finkelstein et al., 1975; Fuerstenau, 1975; Heyes and Trahar, 1977; Gardner and Woods, 1979).

Over the years, experimental evidences have suggested that hydrophobicity of sulphide minerals varies from none to that of sulfur. Gaudin (1932), Ravitz and Porter (1933), Fuerstenau (1975), Yoon (1981), Luttrell and Yoon (1984), Hayes and Ralston (1988), Matabishi et al. (2000) showed that collectorless flotation of sulphide minerals
are possible under proper conditions. The proper conditions have been discussed by authors with different explanations. Yoon (1981) suggested the collectorless flotation was possible with the addition of sodium sulphide (Na$_2$S) to the pulp. The sulphide ions were thought to displace the hydrophilic surface oxidation products such as SO$_4^{2-}$, S$_2$O$_3^{-2}$, etc., due to difference in the fresh, unoxidised sulphide surface.

Luttrell and Yoon (1984) suggested that under the light of the thermodynamic instability of elemental sulphur in alkaline solution, polysulphide (i.e. S$_x^{2-}$; 2<x<8) rather than elemental sulphur (Sº) causes the collectorless flotation. They also suggested that the increased floatability at low pH is due to a greater stability of elemental sulphur which has greater hydrophobicity compared to polysulphide.

Miller (1988) also stated that sulphide minerals are thermodynamically unstable and sufficient oxygen remains in the system to cause oxidation, presumably leading to the formation of elemental sulphur. This hypothesis originally proposed by Wark (1938). Plaksin (1949) stated that adsorbed oxygen decreases surface hydration, thereby, rendering hydrophobicity to mineral. On the other hand, formation of metal deficient surface was proposed by Buckley et al. (1985) as the key species for self-induced floatability.

Luttrell and Yoon (1982, 1983) stated the importance of pulp potential (Eh) which is a critical factor in the collectorless flotation. Typically, when sodium sulphide was added to the pulp, the potential immediately dropped and no flotation was possible. Only after approximately 15 minutes of conditioning time, when potential become positive, the flotation was possible. Several researchers suggested that sulphide minerals can be floated under mild to modest oxidising condition.

It was shown that the collectorless floatability of each sulphide studied was directly linked to its ease of oxidation as well as to the stability of the hydrophobic surface state which was produced. The hydrophobic surface species might be elemental sulphur or polysulphide or a sulphur-rich metal-deficient surface.

**EXPERIMENTAL**

Lead and zinc sulphide ore from Şebinkarahisar - Giresun in Turkey was tried to float without collector. The mineralogical analysis of the specimens showed that main ore minerals were sphalerite, galena, pyrite, chalcopyrite, fahlerz (tennantite and tetrahedrite), cerussite-anglesite, quartz (~ 40-45 %), limonite and other siliceous minerals. Sphalerite, having more massive appearance, had sometimes chalcopyrite inclusions in it. The size of the inclusions was sometimes as low as 5 microns. Chalcopyrite was also found as free grains in galena and sphalerite together with fahlerz. Liberation size of minerals was around 150 microns. The sample contained 3.34 % Pb, 11.68 % Zn, 0.20 % Cu, 11.3 % S and 0.36 % Al.

The ore was ground to –1 mm and stored in a double nylon bags with a weight of 300 gram to prevent possible surface oxidation. Flotation experiments were carried out with Denver Sub-A flotation machine having 1.1 dcm$^3$ cell after the grinding of ore to
100 % passing 150 µm (80 % -69 µm). Rotational speed of the impeller was 1500 rpm and aeration rate was 2.75 dcm³/min throughout the experiments. The frother (MIBC) dosage was kept constant in all tests as 90 g/Mg.

Figure 1 shows the general flowsheet for collectorless flotation. In this research, effect of sodium sulphide, zinc sulphide, conditioning time, pH and cleaning of concentrates were investigated. Optimum result was compared with that of a conventional flotation using different types of collector.

![General flowsheet of collectorless flotation with initial values of parameters](image)

**RESULTS AND DISCUSSIONS**

**COLLECTOR ADDED FLOTATION EXPERIMENTS**

To see the flotation characteristics of the ore, experiments were initiated with collector addition. A comparison of the results obtained with collector addition and without collector will helps to measure the success of idea of collectorless flotation of the lead and zinc minerals in the ore. The galena and sphalerite were floated selectively a sulphydryl type collectors. 100 g/Mg collector was used and conditioned for 5 minutes throughout the experiments. Sodium sulphide was not used in collector added flotation experiments. The results are given in Table 1.
Table 1. Effect of different collectors on galena and sphalerite flotation

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight, %</th>
<th>Zn, %</th>
<th>Pb, %</th>
<th>R\textsubscript{Zn}, %</th>
<th>R\textsubscript{Pb}, %</th>
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Collectorless flotation of lead and zinc sulphide from Dereköy ore deposit

COLLECTORLESS FLOTATION EXPERIMENTS

Sodium Sulphide

Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was used to clean the surface oxides of sulphide minerals as sulphidising agent. The amount of sodium sulphide added in zinc circuit was kept constant as 150 g/Mg of ore while it was changed from 0 to 300 g/Mg in lead circuit. The experimental conditions and results are shown in Figure 2.

![Graph showing the effect of sodium sulphide added in lead circuit on lead and zinc grade and recoveries in their corresponding concentrates (pH 8.1 in Pb-circuit, and pH 8.4 and 660 g/Mg CuSO$_4$ addition in Zn-circuit)](image)

Fig. 2. Effect of sodium sulphide added in Pb-circuit on Pb and Zn grade and recoveries in their corresponding concentrates (pH 8.1 in Pb-circuit, and pH 8.4 and 660 g/Mg CuSO$_4$ addition in Zn-circuit)

The Pb grade as well as the recovery and Zn grade increased with Na$_2$S addition up to 240 g/Mg Na$_2$S concentration. As it was mentioned above, Na$_2$S can be used either as sulphidising agent for oxidised minerals or a reducing agent for sulphide depression. Then, it may be concluded that the iron-oxyhydroxides, possibly coming from steel-mill grinding and pyrite, a component of the ore, and Pb and Zn-oxyhydroxides would cover mineral surfaces. So, the increasing of the Pb and Zn grade would be attributed to the removal of these interfering metal-oxyhydroxides and concomitant exposure of the sulphur-rich sub-layer (Cases et al., 1997; Grano et al., 1997). 240 g/Mg sodium sulphide gave a reasonable results by considering both Pb and Zn grades and recoveries of their corresponding concentrates. Since sodium sulphide is a strong reducing agent, it was not preferred to use more than 240 g/Mg in the lead circuit due to possibility of an adverse effect in the zinc circuit (Herrera-Urbina, 1999)
Figure 3 shows the experiment conditions and results of effect of sodium sulphide in the Zn-circuit. Results showed that Zn-recovery sharply increased up to 60 g/Mg Na$_2$S, and then gradually decreased. This would be originated from the removal of hydrophilic oxyhydroxide compounds from the sphalerite surface as pointed out above. Or, it may also be proposed that formation of a metal-deficient sulphur-rich surface (Buckley et al., 1985), adsorption of polysulphides (Luttrell and Yoon, 1984) or the presence of elemental sulphur (Gardner and Woods, 1979; Hayes and Ralston, 1988) probably contributed to hydrophobicity of the Cu-activated sphalerite surface. More than 60 g/t of sodium sulphide did not improve the zinc grade and recovery. Instead, it results in a small decrease, since Na$_2$S is a depressing agent for unoxidised sulphide minerals due to decrease in pulp potential. Therefore, this gradual decrease would be attributed to the depression of sphalerite due to reducing pulp potential values.

![Graph showing Zn-grade and recovery vs Sodium sulphide dosage](image-url)

**Zinc Sulphide**

Zinc sulphate dosage was varied from 20 g/Mg to 830 g/Mg. Zinc sulphate decreases the possible activation of sphalerite by Pb$^{2+}$ ions coming from galena, and so the loss of sphalerite in the Pb-circuit (Figure 4). However, large amounts of it made the flotation of sphalerite difficult in the zinc circuit (Figure 5), which caused the zinc losses in final tailing. In addition, its adverse effect was also observed in Pb grade and recovery of galena concentrate (Figure 4) possibly due to Zn(OH)$_2$ precipitation on...
Collectorless flotation of lead and zinc sulphide from Dereköy ore deposite

mineral surface (Laskowski et al., 1997; Trahar et al., 1997; El-Shal et al., 2000). Also, it results in the increase in Pb recovery in Zn-circuit possibly due to Cu-activation (Figure 5). Since, in the zinc-circuit copper sulphate was added to activate sphalerite and to eliminate the depressing effect of zinc sulphate. 100 g/Mg of zinc sulphate was the optimum value as seen from Figures 4 and 5.

Fig. 4. Effect of zinc sulphate on Pb and Zn grades and recoveries in Pb-concentrates (pH 8.1 in Pb-circuit)

Fig. 5. Effect of zinc sulphate on Pb and Zn grades and recoveries in Zn-concentrates (pH 8.1 in Pb-circuit and, pH 10.3 and 660 g/t CuSO₄ addition in Zn-circuit)
Conditioning Time

The conditioning period for sodium sulphide reaction on sulphide surface is an important parameter. This is not only for covering of sulphide surfaces with elemental sulphur and polysulphide ions but also important for the oxidation potential of pulp. Sodium sulphide, as it is mentioned before, is a strong reducing agent and, therefore, time is necessary for increasing the pulp potential. Also, iron coming from steel mill was a high oxygen consumer and, hence, decreased the rate of sulphide oxidation, which in turn diminished the hydrophobisation with sodium sulphide. So, conditioning time was increased to maintain oxygen and then to reduce the adverse effect of iron ions coming from the mill.

Fig. 6. Effect of conditioning time in lead circuit on both Pb and Zn grades and recoveries in their corresponding concentrates (pH 8.1 and 100g/Mg ZnSO₄ in Pb-circuit and pH 10.3 and 660 g/Mg CuSO₄ in Zn-circuit)

The conditioning time was changed from 10 to 60 minutes in the lead circuit while it was kept constant as 30 minutes in the zinc circuit. Figure 6 shows the experimental conditions and results. The results support the findings of Luttrell and Yoon (1983) that a relatively fresh surface made by sodium sulphide is needed to an oxidising environment for collectorless flotation.

pH

pH of the medium is an important factor that influences flotation. To investigate the optimum values for both circuits, pH was varied from 5 to 9 in the Pb-circuit while it was kept constant at pH 8 in Zn-circuit. After the determination of optimum pH in lead circuit, it was varied from 5 to 11 in zinc circuit. Figure 7 shows the experimental conditions and results.
Galena showed good flotation at pH 8 and similar results has been found by Matabishi et al. (2000). At very high pH values, iron hydroxides possibly coming from the steel mill and pyrite content of ore and metal-oxyhydroxides made the surface hydrophilic, thereby reducing floatability (Laskowski et al., 1997; Zhang et al., 1997). On the other hand, higher pH values (pH 10) were suitable for Cu-activated sphalerite flotation with high grade and recovery. Hukki et al. (1952) suggested that copper hydroxy species or hydroxide adsorbs rapidly on sphalerite but, because of the high solubility of Cu(OH)$_2$, the adsorbed precipitate would be converted to less soluble copper sulphide in basic solution. Ralston and Healy (1980a, b) and Laskowski et al. (1997) suggested that the hydroxide slowly releases Cu$^{2+}$ ions into solution, which in turn form a flotation active product such as (Zn,Cu)S.

Cleaning of Lead and Zinc Concentrates

Most of the sulphide concentrates can be upgraded by cleaning steps. To upgrade the rougher concentrate, an experiment with cleaning stage was performed. The flowsheet with its conditions and results are shown in Figure 8.

As shown in Figure 8, a galena concentrate assaying 43.08 % Pb with a recovery of 72.49 %, and a sphalerite concentrate assaying 59.79 % Zn with a recovery of 46.99 % were obtained by one stage cleaning. However, zinc grade in lead concentrate was
also high. More or less the same results were obtained with collector added flotation experiments. Almost about 20 % zinc grade in lead concentrate may cause penalty in lead smelter. It might be due to chalcopyrite inclusion to sphalerite mineralogically and lead activation of sphalerite during flotation.

![Fig. 8. Cleaning of lead and zinc concentrates](image)

CONCLUSIONS

Collectorless flotation of lead and zinc sulphide from ores is possible after selective rougher concentrates were obtained. The lead concentrate contained 31.70 % Pb with 85.13 % recovery and the Zn concentrate assayed 50.59 % Zn assay with 43.58 % recovery. It was able to challenge with collector added flotation results. Collector added flotation had higher recovery for both lead and zinc in their corresponding concentrates. The cleaning of concentrates obtained by collectorless flotation increased the lead and zinc grades. The final lead concentrate contained 43.08 % Pb with 72.49 % recovery and the final zinc concentrate contained 59.79 % Zn with 46.99 % recovery.

The losses of Pb and Zn in tailing can not be ignored. The tailing should be reground to recover the lead and zinc values. The loss of zinc was higher than the loss of lead in tailing. It can be explained with the size distribution of the minerals. Since the hardness of galena is less than sphalerite, it was finer during flotation, which decreased the loss of lead in tailing.
REFERENCES


Ceylan H., Hicyilmaz C., Guler T., Flotacja bez użycia kolektora rudy ołowiu i cynku z pokładu Derekoy (Turcja), Fizykochemiczne Problemy Mineralurgii, 36, (2002) 197-208 (w jęz. ang.)

Przeprowadzono badania procesu flotacji bez użycia kolektora siarczkowej rudy ołowiu i cynku, stosując siarczek sodu. Badano wpływ stężenia siarczku sodu, czasu kondycjonowania oraz pH zawiesiny flotacyjnej na parametry wzbogacania cynku i ołowiu. Określono także wpływ czyszczenia koncentratu na proces wzbogacania. Otrzymane wyniki z flotacji bez użycia kolektora porównano z wynikami, jakie uzyskano stosując szereg znanych kolektorów.