

Article



Flotation of Seafloor Massive Sulfide Ores: Combination of Surface Cleaning and Deactivation of Lead-Activated Sphalerite to Improve the Separation Efficiency of Chalcopyrite and Sphalerite

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Abstract: The purpose of this study is to propose the flotation procedure of seafloor massive sulfide (SMS) ores to separate chalcopyrite and galena as froth and sphalerite, pyrite, and other gangue minerals as tailings, which is currently facing difficulties due to the presence of water-soluble compounds. The obtained SMS ore sample contains CuFeS₂, ZnS, FeS₂, SiO₂, and BaSO₄ in addition to PbS and PbSO₄ as Pb minerals. Soluble compounds releasing Pb, Zn^{2+} , Pb^{2+} , and $Fe^{2+/3+}$ are also contained. When anglesite co-exists, lead activation of sphalerite occurred, and thus sphalerite was recovered together with chalcopyrite as froth. To remove soluble compounds (e.g., anglesite) that have detrimental effects on the separation efficiency of chalcopyrite and sphalerite, surface cleaning pretreatment using ethylene diamine tetra acetic acid (EDTA) was applied before flotation. Although most of anglesite were removed and the recovery of chalcopyrite was improved from 19% to 81% at 20 g/t potassium amyl xanthate (KAX) after EDTA washing, the floatability of sphalerite was not suppressed. When zinc sulfate was used as a depressant for sphalerite after EDTA washing, the separation efficiency of chalcopyrite and sphalerite was improved due to deactivation of leadactivated sphalerite by zinc sulfate. The proposed flotation procedure of SMS ores-a combination of surface cleaning with EDTA to remove anglesite and the depression of lead-activated sphalerite by using zinc sulfate—could achieve the highest separation efficiency of chalcopyrite and sphalerite; that is, at 200 g/t KAX, the recoveries of chalcopyrite and sphalerite were 86% and 17%, respectively.

Keywords: seafloor massive sulfide; flotation; lead-activated sphalerite; anglesite; EDTA

1. Introduction

Seafloor massive sulfide (SMS) deposits, also referred to as submarine hydrothermal polymetallic sulfide deposits, have gained increasing attention as new metal resources because they consist of various forms of polymetallic sulfide including Cu, Pb, Zn, Au, Ag, etc. SMS deposits were found in a variety of volcanic and tectonic settings on the modern ocean floor in worldwide [1,2]. A number of scholars have studied SMS deposits, examples of which include formation mechanisms [3–5], exploration [6–8], mining methods [9–12],



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and environmental impacts [13–15]; however, only a few studies on mineral processing of SMS ores have been carried out [16,17].

In Japan, the program for the development of SMS deposits around Japan has been conducted by the Ministry of Economic, Trade and Industry (METI) and Japan Oil, Gas and Metals National Corporation (JOGMEC). Not only seafloor mining, but also mineral processing and extractive metallurgy of SMS ores have been studied. Masuda (2011) [18] reported that SMS resembles the Kuroko on land in terms of deposit origin, which implies that similar processing and refining technologies applied to Kuroko can also be utilized for SMS ores. However, the previous studies on mineral processing of SMS ores conducted by JOGMEC indicated that mineral processing behaviors of the SMS ores are quite different compared to those of Kuroko [17]. METI and JOGMEC (2018) [16] reported distinct features of SMS ores obtained from around Japan: (1) lead minerals in the SMS ores are mostly present as anglesite ($PbSO_4$) with a minor amount of galena (PbS), and (2) metal ions are highly dissolved from the SMS ores (e.g., [Zn²⁺], 1700–3000 ppm). Moreover, some researchers reported various metal ions like Cu²⁺, Pb²⁺, and Zn²⁺ are released from the SMS ores obtained from the Trans-Atlantic Geotraverse active mound on the Mid-Atlantic Ridge [10] and the Izena Hole in the middle Okinawa Trough, Japan [11]. These distinct features of SMS ores around Japan—the presence of anglesite and the release of metal ions—would make mineral processing of SMS ores composed of Cu-Pb-Zn sulfide minerals complicated.

Cu-Pb-Zn sulfide minerals are generally processed via two flotation stages whereby Cu- and Pb-sulfide minerals are first recovered, followed by floating Zn-sulfide minerals [19]. When anglesite is contained in Cu-Pb-Zn sulfide minerals, it is readily dissolved and releases Pb²⁺ that activates sphalerite via the formation of PbS-like compounds on sphalerite surface, as explained in Equation (1). Activation of sphalerite by Pb²⁺ is known to increase the sphalerite floatability because the PbS-like compound has a higher affinity with xanthate than sphalerite [20–23].

$$ZnS(s) + Pb^{2+} = PbS(s) + Zn^{2+}$$
 (1)

Thus, activation of sphalerite by Pb²⁺ is an unwelcomed side reaction because it dramatically limits the separation of Cu-Pb-Zn sulfide minerals. To improve their separation efficiency in the presence of anglesite, depression of lead-activated sphalerite is necessary. In practice, zinc sulfate and sulfoxy reagents (e.g., sulfite, metabisulfite, and bisulfate) are used as depressants for sphalerite [24] and, moreover, the former can also be used for the depression of lead-activated sphalerite [25,26]. The aim of this study is to propose a flotation procedure of SMS ores that is facing difficulty of separating chalcopyrite and sphalerite due to the presence of water-soluble compounds like anglesite. To improve the separation efficiency of chalcopyrite and sphalerite, depression effects of sodium sulfite and zinc sulfate on sphalerite floatability in the floatation of SMS ores were examined. In addition, a chemical pretreatment using ethylene diamine tetra acetic acid (EDTA) to remove anglesite and other soluble species (e.g., oxidation products) having potentials to affect flotation process was investigated. Finally, a flotation procedure of SMS ores to separate chalcopyrite and sphalerite in the presence of soluble compounds like anglesite using a combination of surface cleaning with EDTA and depression of lead-activated sphalerite by zinc sulfate was proposed.

2. Materials and Methods

2.1. Samples

A submarine hydrothermal polymetallic sulfide ore sample (named as sample A) obtained from around Japan and provided by JOGMEC, and seven types of minerals were used in this study: chalcopyrite (CuFeS₂, Copper Queen Mine, Cochise County, AZ, USA), sphalerite (ZnS, Kamioka Mine, Hida, Japan), galena (PbS, Beni Tadjit, Figuig, Morocco), anglesite (PbSO₄, Puit 9 Touissit, Oujda,, Morocco), pyrite (FeS₂, Huanzala Mine, Huanuco, Peru), quartz (SiO₂, 99% purity, Wako Pure Chemical Industries Co., Ltd., Tokyo, Japan), and barite (BaSO₄, Jungcheon Changdo Mine, Kimhwa County, South Korea). The mixtures of chalcopyrite, sphalerite, pyrite, quartz, and barite with galena or anglesite were used as model samples for flotation experiments. Sample A and the above-mentioned mineral samples were characterized using X-ray fluorescence spectroscopy (XRF, EDXL300, Rigaku Corporation, Tokyo, Japan) and X-ray powder diffraction (XRD, MultiFlex, Rigaku Corporation, Tokyo, Japan), and the chemical and mineralogical compositions of these samples are summarized in Table 1 and shown in Figure 1, respectively. The XRD pattern of the submarine hydrothermal polymetallic sulfide ore sample (sample A) shows that it contains chalcopyrite, sphalerite, galena, anglesite, barite, pyrite, and quartz (Figure 1a).

Comm10			Ma	ss Fraction	(%)		
Sample	Cu	Zn	Pb	Fe	S	Si	Ba
Sample A	7.4	13.6	7.1	24.5	35.7	3.5	1.5
Chalcopyrite	24.5	0.7	-	34.1	26.0	8.8	-
Sphalerite	-	66.5	0.1	3.5	24.8	2.7	-
Galena	-	-	84.8	-	8.3	1.5	-
Anglesite	1.3	0.7	88.0	0.2	7.6	0.7	-
Pyrite	-	-	-	42.3	52.5	1.0	-
Barite	-	-	-	-	17.9	0.3	67.8

Table 1. Chemical composition of sample A based on X-ray fluorescence spectroscopy (XRF).

The samples were ground by using a vibratory disc mill (RS 100, Retsch Inc., Haan, Germany) and were screened to obtain a size fraction of $-75 \,\mu$ m. For the flotation experiments, potassium amyl xanthate (KAX, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) as a collector, Methyl Isobutyl Carbinol (MIBC, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) as a frother, and sodium sulfite (Na₂SO₃, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and zinc sulfate (ZnSO₄, Wako Pure Chemical Industries Ltd., Osaka, Japan) and sulfuric acid (H₂SO₄, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and sulfuric acid (H₂SO₄, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and sulfuric acid (H₂SO₄, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as pH adjusters. For surface cleaning to remove the oxidation products present on mineral surface and/or contained in sample A, ethylene diamine tetra acetic acid (EDTA, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used [27,28].

2.2. Experimental Methods

2.2.1. Flotation

Prior to flotation tests, samples were deslimed by the following procedure: (1) a 20 g sample was added into 300 mL distilled water and then ultrasonication using high-speed switching oscillation between 24 kHz and 31 kHz (W-113 MK-II, Honda Electronics Co., Ltd., Toyohashi, Japan) was carried out for 1 min, (2) the suspension was allowed to be settled down for 5 min, and then the supernatant was removed. These treatments were done in triplicate, and the settled portion was used for flotation experiments.

An agitator-type flotation machine (FT-1000, Heiko-Seisakusyo, Tokyo, Japan) equipped with a 400-mL flotation cell was used and flotation experiments were conducted under the following conditions: pH, 6.5; temperature, 25 °C; pulp density, 5%; impeller speed, 1000 rpm; air flow rate, 1 L/min. After flotation, froth and tailing products were dried in an oven at 105 °C for 24 h and analyzed by XRF to determine the recovery of Cu, Zn, Pb, Fe, Si, and Ba. Flotation experiments were carried out based on the flowchart, as illustrated in Figure 2.



Figure 1. The X-ray powder diffraction (XRD) patterns of (**a**) sample A, (**b**) chalcopyrite, (**c**) sphalerite, (**d**) galena, (**e**) anglesite, (**f**) pyrite, and (**g**) barite. Note differences in the scale of the y-axes.



Figure 2. Flotation procedure with sequential addition of collector (KAX).

2.2.2. Surface Cleaning of Sample A

Surface cleaning with EDTA: (1) a 20 g sample was added into 300 mL solution containing EDTA (25 g/L) and then ultrasonicated for 1 min, (2) the supernatant of the suspension was removed after settling for 5 min. These treatments were done in triplicate and flotation experiments were conducted immediately after this surface cleaning.

2.2.3. Leachability Test of Sample A with DI Water

To check the amounts of soluble species in sample A, a leachability test was carried out. To achieve this, 0.4 g of sample A and 40 mL distilled water (i.e., pulp density: 1%) were added into a 50-mL centrifuge tube and shaken by a roller shaker (MIX ROTOR VMR-5R, AS ONE Co., Ltd., Osaka, Japan) at 100 rpm for 10 min. Afterward, the leachate was collected by filtration using 0.2 μ m syringe-driven membrane filters and immediately analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, ICPE 9820, Shimadzu Corporation, Kyoto, Japan) (margin of error = ±2%) to measure the concentration of Cu²⁺, Pb²⁺, Zn²⁺, and Fe^{2+/3+} released from sample A.

3. Results and Discussion

3.1. Effect of Sodium Sulfite on the Separation of Chalcopyrite and Sphalerite in the Flotation of Sample A

Figure 3 shows the flotation results of sample A with various dosages of sodium sulfite (0, 5, or 20 kg/t) to evaluate its suppressive effect on the floatability of pyrite as well as sphalerite. The floatability of pyrite was apparently suppressed as Na₂SO₃ dosage increased; that is, about 45% of pyrite was recovered at 100 g/t KAX in the absence of Na₂SO₃ (Figure 3a), but it decreased to ~30% with 5 kg/t Na₂SO₃ and ~22% with 20 kg/t Na₂SO₃ (Figure 3b,c). However, sphalerite was recovered as froth together with chalcopyrite, irrespective of the amount of depressant added. In the case of Pb minerals (i.e., anglesite and galena), their recovery was low at around 30–40%, suggesting that anglesite is most likely the main Pb mineral in sample A. As mentioned earlier, the presence of anglesite can dramatically change the flotation behavior of sphalerite because of Pb²⁺ released from anglesite that activates sphalerite.



Figure 3. Flotation results of sample A with sodium sulfite (a) 0 kg/t, (b) 5 kg/t, and (c) 20 kg/t.

To clarify the effects of Pb minerals on the floatability of sphalerite, flotation tests were conducted using model samples, prepared based on the actual mineralogical composition of sample A obtained by norm calculation (Table 2).

Table 2. Norm calculation results of sample A.

Mass Fraction (%)					
CuFeS ₂	ZnS	PbS	FeS ₂	SiO ₂	BaSO ₄
21.7	20.6	8.4	39.2	7.5	2.6

Specifically, two types of model samples (PbS-type and PbSO₄-type) were prepared considering PbS or PbSO₄ as the only Pb mineral. Flotation experiments using the PbS-type or the $PbSO_4$ -type model sample were carried out with 5 kg/t Na₂SO₃. As shown in Figure 4, chalcopyrite and galena were floated first followed by sphalerite in the flotation of the PbS-type model sample, whereas sphalerite was floated together with chalcopyrite in the flotation of the PbSO₄-type model sample. In general, Cu-Pb-Zn sulfide ores are processed via two flotation stages whereby Cu- and Pb-sulfide minerals are first recovered, followed by Zn-sulfide minerals. The flotation result of the PbS-type model sample (Figure 4a) is in good agreement with the report of Woodcock et al. (2007) [19]. On the other hand, Zn was floated together with Cu in the flotation of the PbSO₄-type model sample (Figure 4b), indicating that the floatability of sphalerite increased in the presence of anglesite, and this increased floatability of sphalerite was also observed in the real sample (sample A, Figure 3). In the case of the PbSO₄-type model sample (Figure 4b), the recovery of Pb was lower than 20% because anglesite has low affinity with xanthate [29,30]. Trahar et al. (1997) [23] and Wills and Napier–Munn (2005) [31] reported that the floatability of sphalerite can be increased by metal ions (e.g., Cu²⁺ and Pb²⁺) due to the formation of CuS/PbS-like compounds which have higher affinity with xanthate than ZnS. In the case of the PbSO₄-type model sample, sphalerite may be activated by Pb²⁺ released from anglesite because of its higher solubility than that of PbS (Ksp of anglesite and galena are $10^{-7.79}$ and $10^{-26.77}$, respectively) [32]. These results indicate that the conventional flotation procedure of Cu-Pb-Zn ores is not applicable for SMS ores and needs to be modified to minimize the effect of anglesite on the floatability of sphalerite.



Figure 4. Flotation results of (a) PbS-type model sample and (b) PbSO₄-type model sample.

3.2. Leachability Test of Sample A with DI Water

Leachability test of sample A with DI water was conducted to confirm how much dissolved metal ions are released from sample A. As shown in Table 3, the concentrations of Pb^{2+} and Zn^{2+} were 38 ppm and 20 ppm, respectively, while the concentrations of Cu^{2+} and $Fe^{2+/3+}$ were below the detection limit of ICP-AES (final pH: 5.12). Fuchida et al. (2018) [11] reported that Pb²⁺ and Zn²⁺ were released in the saline water from sulfide samples collected by seafloor drilling from the Izena Hole in the middle Okinawa Trough, Japan. Other authors also reported the release of metal ions like Cu^{2+} , Pb^{2+} and Zn^{2+} from the samples obtained from SMS deposits such as the Trans-Atlantic Geotraverse (TAG) active mound on the Mid-Atlantic Ridge [10] and Hakurei Site in the Okinawa Trough, Japan [16]. These suggest that metal ions are released from SMS ores, which supports our deduction that Pb^{2+} and Zn^{2+} are released from sample A. According to Aikawa et al. (2020) [33], Rashchi et al. (2002) [22], and Trahar et al. (1997) [23], lead activation of sphalerite can occur above 5 ppm of Pb^{2+} , resulting in dramatic increase in the floatability of sphalerite. This indicates that activation of sphalerite by Pb²⁺ would occur during flotation of sample A, making not only CuFeS₂ but also ZnS float, so their separation becomes difficult in the presence of soluble Pb minerals like anglesite.

Table 3. Results of leaching tests of sample A with DI water.

Concentration (ppm)				Einel all
Cu	Zn	Pb	Fe	– rinai pri
-	20	38	-	5.12

Note: "-" denotes below the detection limit.

3.3. Effect of Surface Cleaning Pretreatment Using EDTA on the Separation of Chalcopyrite and Sphalerite in the Flotation of Sample A

The SMS ores have undergone the natural oxidation process under atmosphere and/or seafloor, resulting in the formation of oxidized phases [10,34]. According to Fuchida et al. (2019) [35] who compared metal leaching of both non-oxidized (non-exposed to atmosphere before and during exploitation) and oxidized (exposed to atmosphere after lifting and recovery) seafloor hydrothermal sulfides, the oxidized sulfides readily released large amounts of various metal(loid)s (e.g., Mn, Fe, Zn, Cu, As, Sb, and Pb) compared to non-oxidized ones. These suggest that oxidation products (e.g., oxide, hydroxide, sulfate, and carbonate) may be deposited on the surface of minerals and/or contained in sample A. These oxidation products present on mineral surface would contribute to the decrease in the floatability of sulfide minerals, especially chalcopyrite [36–39]. In addition, sample A contains the oxidation product, anglesite (lead sulfate), which makes the separation of

chalcopyrite and sphalerite difficult due to the improved floatability of the latter by lead activation. To minimize the effects of oxidation products, surface cleaning pretreatment using EDTA was applied prior to floation tests with the aim of improving the floatability of chalcopyrite, as well as depressing the floatability of sphalerite. EDTA was used for surface cleaning because of its ability to form stable complexes with metal ions dissolved from anglesite (lead sulfate)—a problematic mineral for Cu-Zn separation—as well as other oxidation products, while it does not react with metal sulfides [37,40–42].

Figure 5 shows the flotation results of sample A with and without surface cleaning pretreatment using EDTA. The dosage of sodium sulfite as a depressant in this flotation experiment was fixed at 20 kg/t. After EDTA washing, chalcopyrite was floated first followed by sphalerite (Figure 5b). Moreover, the recovery of Pb minerals was high (i.e., $\sim 80\%$ at 100 g/t KAX) compared to that without EDTA washing (Figure 5a). This increase in the floatability of Pb minerals is due most likely to the dissolution of most of anglesite after EDTA washing. Comparing the XRD patterns of sample A before and after EDTA washing (Figure 6), the latter showed that the peak intensity of anglesite apparently decreased while that of galena was not changed. This implies that the ratio of galena/anglesite increased, so the recovery of Pb minerals became high. Not only Pb minerals, but also the recovery of chalcopyrite at 20 g/t KAX increased from 19% to 81% after EDTA washing (Figure 5a,b). This may have been achieved by the removal of oxidation products present on the surface of chalcopyrite by EDTA. After EDTA washing, leachate contains a large amount of dissolved Pb (3200 ppm) with minor amounts of other metals (e.g., [Cu²⁺], 9 ppm; [Zn²⁺], 137 ppm; [Fe^{2+/3+}], 6 ppm) (Table 4), confirming that oxidation products and anglesite were dissolved after EDTA washing (Figure 6).

Due to the increase in the floatability of chalcopyrite, the separation efficiency of chalcopyrite and sphalerite was improved; however, the depressive effect of EDTA washing on the floatability of sphalerite was limited. In the floatation of sample A with EDTA washing, Zn was recovered as froth together with Pb, suggesting that sphalerite may be activated by Pb²⁺ forming PbS-like compounds on the surface of sphalerite. To further improve the separation efficiency of chalcopyrite and sphalerite, the depression of lead-activated sphalerite by zinc sulfate, a common depressant for sphalerite, was investigated in the next subsection.

Concentration (ppm)				
Cu	Zn	Pb	Fe	
9	137	3200	6	

Table 4. The concentrations of dissolved metals in the supernatant after surface cleaning with EDTA.



Figure 5. Flotation results of sample A (**a**) without surface cleaning and (**b**) with ethylene diamine tetra acetic acid (EDTA) washing.



Figure 6. XRD patterns of sample A (a) without and (b) with EDTA washing.

3.4. Suppression of Lead-Activated Sphalerite by Zinc Sulfate after EDTA Washing

Figure 7a–c show the flotation results of sample A without both EDTA washing and the addition of zinc sulfate (a), with the addition of zinc sulfate (1000 ppm of Zn^{2+}) (b), and with EDTA washing followed by the addition of zinc sulfate (1000 ppm of Zn^{2+}) (c). As illustrated in Figure 7a,b, the effect of zinc sulfate in depressing the floatability of sphalerite was almost negligible; that is, sphalerite was recovered as froth together with chalcopyrite. However, when EDTA washing was adopted prior to the addition of zinc sulfate, the floatability of chalcopyrite was not affected, while it had a detrimental effect on the floatability of sphalerite (Figure 7c); for example, the recovery of sphalerite at 100 g/t KAX decreased from 88% to 8% by employing EDTA washing and the addition of zinc sulfate (Figure 7b,c). These results indicate that EDTA washing followed by Zn^{2+} addition could be an effective approach to depress the floatability of lead-activated sphalerite in the floatability of SMS ores which contain anglesite.



Figure 7. Flotation results of sample A (**a**) without both EDTA washing and the addition of zinc sulfate, (**b**) with the addition of zinc sulfate, and (**c**) with EDTA washing followed by the addition of zinc sulfate. Note that the recoveries of all minerals at 0 g/t of collector in Figure 7b,c were assumed to be zero due to the lack of froth amounts for the XRF analysis.

El-Shall et al. (2000) [25] calculated the change in free energy based on the equilibrium constant (Equations (1) and (2), where K = 1000) to evaluate the possibility of depression of lead-activated sphalerite in the presence of 1×10^{-4} mol/L of Pb²⁺ and 1×10^{-4} mol/L of Zn²⁺ at about pH 7.0. It was concluded that depression of lead-activated sphalerite by zinc sulfate is most probably due to the following reaction: $PbS_{surface} + Zn^{2+} \rightarrow ZnS$ + Pb²⁺. Basilio et al. (1996) [43] also calculated the equilibrium constant of Equation (1) to evaluate the possibility of lead activation of sphalerite based on the change in free energy (Equation (2)); however, the calculated value of K was different from the one used by El-Shall et al. (2000) [25]. As confirmed by the above two cases, the free energy strongly depends on the conditions (e.g., pH and concentrations of reactants and products), so the change in free energy in our flotation system needs to be calculated using the measured values in this study—4.08 ppm of Pb^{2+} and 1070 ppm of Zn^{2+} obtained from the suspension after addition of zinc sulfate in the flotation without EDTA washing (Figure 7b), and 1.21 ppm of Pb^{2+} and 949 ppm of Zn^{2+} obtained from that with EDTA washing (Figure 7c). For calculating the change in free energy in the flotation system of this study, the following equilibrium constants were considered: 1000 [25], 704 [44], 1059 [45], and 1127 [46]—the last three values were calculated based on Equation (3) using K_{sp} values of ZnS and PbS summarized in Table 5 [43–46].

$$\Delta G = -RT \ln K + RT \ln(Zn^{2+}/Pb^{2+})$$
⁽²⁾

$$K = \frac{K_{sp}^{ZnS}}{K_{sp}^{PbS}} \tag{3}$$

Table 5. *Ksp* values of ZnS and PbS in the literature.

K_{sp}^{ZnS}	K_{sp}^{PbS}	Reference
$1.9 imes 10^{-26}$	$2.7 imes 10^{-29}$	Helgeson (1969) [44]
$7.2 imes 10^{-26}$	$6.8 imes 10^{-29}$	Latimer (1952) [45]
$7.1 imes 10^{-26}$	$6.3 imes 10^{-29}$	Leckie & James (1974) [46]

As shown in Table 6, the calculated values of change in free energy in the flotation with the addition of zinc sulfate (Figure 7b) were negative except the value using the equilibrium constant reported by Helgeson (1969) [44]. On the other hand, those in the flotation with the addition of zinc sulfate after EDTA washing (Figure 7c) were all positive. These results support our flotation results that the depression of lead-activated sphalerite was only achieved by the combination of EDTA washing which decreased Pb²⁺ concentration due to the removal of anglesite and the addition of zinc sulfate due to the reverse reaction of Equation (1).

Table 6. The calculation results of the change in free energy at pH 6.5 in the flotation system of sample A.

К	ΔG (kJ/mol) With Zinc Sulfate and Without EDTA Washing (Figure 7b)	ΔG (kJ/mol) With Zinc Sulfate after EDTA Washing (Figure 7c)
1000	-0.46	2.26
704	0.41	3.13
1059	-0.60	2.11
1127	-0.76	1.96

Figure 8 shows the relationship between Cu recovery and Zn recovery in flotation experiments using EDTA washing and/or zinc sulfate addition. The efficiencies of pretreatments on the separation of Cu and Zn were in the following orders: with zinc sulfate after EDTA washing >with EDTA washing >with zinc sulfate. Thus, it can be concluded that EDTA washing improves the recovery of chalcopyrite, removes anglesite, and enables the

depression of lead-activated sphalerite by the addition of zinc sulfate. This proposed flotation procedure to separate chalcopyrite and sphalerite in the presence of soluble compounds like anglesite could be applied to not only SMS ores but also Cu-Pb-Zn ores in terrestrial deposits, which contain soluble compounds formed by the natural oxidations of minerals.



Figure 8. Relationship between Cu recovery and Zn recovery in flotation experiments with sodium sulfite 20 kg/t.

While El–Shall et al. (2000) [25] and Basilio et al. (1996) [43] estimated the possibility of lead activation of sphalerite using the measured ion concentration of Pb^{2+} and Zn^{2+} , Trahar et al. (1997) [23] reported that lead activation of sphalerite may occur even when solubility of Pb²⁺ is extremely low (e.g., at pH 10) where Pb precipitates like lead hydroxide are present. This means that sphalerite would be activated by not only Pb²⁺ but also Pbprecipitates (e.g., lead hydroxide and lead sulfate (anglesite)), and thus it is impossible to estimate whether lead activation of sphalerite occurs or not based on the concentration of dissolved Pb species. In other words, the required amount of Zn^{2+} to facilitate the depression of lead-activated sphalerite may increase when Pb-precipitates co-exist. As described above, sample A contains secondary products (e.g., oxidation products) and soluble Pb-bearing minerals (e.g., anglesite), both of which could be almost removed by EDTA washing. When the contents of soluble Pb-bearing minerals are high, however, EDTA washing cannot completely remove all the soluble Pb-bearing minerals, indicating that large amounts of residual Pb-bearing minerals most likely remain in the system. Therefore, detailed studies addressing the effects of co-existence of soluble Pb- bearing minerals on the suppression of sphalerite flotability by zinc sulfate will be of topical importance in the future.

4. Conclusions

This study investigated the applicability of surface cleaning with the addition of depressants for flotation separation of chalcopyrite and sphalerite from SMS ores. The findings of this study can be summarized as follows:

- The obtained SMS ore sample contains CuFeS₂, ZnS, FeS₂, SiO₂, and BaSO₄ in addition to PbS and PbSO₄ as Pb minerals. Not only these minerals but soluble compounds which release Cu²⁺, Zn²⁺, Pb²⁺, and Fe^{2+/3+} are also contained in the sample.
- 2. When anglesite co-existed, lead activation of sphalerite occurred, which made the floatability of sphalerite increase.
- 3. In the flotation of sample A with sodium sulfite as a depressant for Zn- and Feminerals, the floatability of pyrite could be suppressed, while it was not able to depress the floatability of sphalerite because Pb²⁺ released from anglesite and other soluble compounds activated sphalerite.

- 4. Surface cleaning using EDTA was effective in removing anglesite and improving the recovery of chalcopyrite by dissolving secondary products formed via natural oxidation processes. However, sphalerite was floated together with chalcopyrite, even after EDTA washing.
- 5. The proposed flotation procedure of SMS ores, a combination of surface cleaning with EDTA to improve chalcopyrite floatability and remove anglesite and the depression of lead-activated sphalerite by using zinc sulfate, could achieve high separation efficiency of chalcopyrite and sphalerite.

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