Effects of Metal Ions on Flotation of Sulfide Minerals

Mayumi Ito¹, *Atsuhiro Tokuda², Tatsuya Segawa², Tsuyoshi Horiguchi², Carlito Baltazar Tabelin¹ and Naoki Hiroyoshi¹

¹Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Japan ²Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Japan *Corresponding author – tkdathr@gmail.com

Abstract

Flotation is a mineral processing method that using deference of Hydrophilicity/hydrophobicity. In flotation, air bubbles are induced to the slurry that contains ground ore and water. Hydrophobic minerals are attached to air bubbles and floated to the surface of the slurry, and hydrophilic minerals remains in the slurry. Hydrophilic/hydrophobic property of minerals can be controlled by chemical reagents: Collectors like xanthate adsorbs on Cu and Pb sulfide minerals and make the mineral surface hydrophobic.

If ore contains several minerals, interaction of the minerals on the floatation is observed: Sphalerite has less affinity to xanthate and low floatability. When anglesite exists with sphalerite, however, Pb²⁺ released from anglesite react with sphalerite and PbS-like compounds is formed on the surface, which has a high affinity to xanthate, resulting in the high floatability of sphalerite.

Using a model sample containing galena, sphalerite, pyrite, anglesite, pyrrhotite and barite, the effects of Zn^{2+} on the flotation of the minerals was investigated with DOW#250 as frother, potassium amyl xanthate as collector, Na₂SO₃ as depressant, H₂SO₄ and NaOH as pH adjuster. When 500 ppm of Zn²⁺ was added, floatability of sphalerite was suppressed. The suppression mechanism of sphalerite by Zn²⁺ is discussed based on the experimental results.

Keywords: Galena, Hetero-coagulation, Mineral processing, Precipitates, Sphalerite

1. Introduction

Floatation is one of the important processing methods of minerals. As a general froth floatation research, method for determining the optimal volume of air to be added to flotation cells, and its distribution has been developed by Jan Cilliers et al. [1].

In the flotation of poorly crystalline complex sulfide ores, the recovery of valuable minerals is strongly influenced by coexisting minerals and dissolved ions. One problem of this type of ore is the rapid dissolution of its mineral components. This study investigated the effects of Zn²⁺ on the flotation of model sample containing sphalerite, galena, anglesite and gangue minerals.

2. Materials and Methods

2.1 Samples and Reagents

Galena, sphalerite, anglesite and

representative gangue minerals were used in this study. These minerals were crushed to under 75 μ m by a Disc mill (RS-100, Retsch Inc., Germany) for the flotation experiments and under 38 μ m for the zeta potential measurement.

Flotation was carried out with DOW#250 as frother, potassium amyl xanthate (KAX) as collector, sodium sulfite (Na₂SO₃) as depressant, and sulfuric acid (H₂SO₄) or sodium hydroxide (NaOH) as pH adjuster. To evaluate the effects of Zn^{2+} , $ZnSO_4$ was used as the source of Zn^{2+} .

Zeta potential measurement was carried out with Na_2SO_4 as electrolyte, sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) as pH adjuster, and ZnSO₄ as the source of Zn precipitate.

2.2 Flotation

A mixture of galena (3%), sphalerite (15%), anglesite (5%) and gangue minerals (77%) was used in the of mixed sample flotation and sphalerite and galena were used in the flotation of single mineral. Flotation was carried out with an agitair-type mechanical flotation machine using a pulp volume and density of 400 mL and respectively. 5%, For the conditioning of the pulp, the following order of reagent additions: $ZnSO_4 \rightarrow$ $Na_2SO_3 \rightarrow pH adjuster \rightarrow KAX \rightarrow$ DOW#250. Each conditioning time lasted for 3 minutes and after condition, air was introduced at 1 L/min. Once nothing floated anymore, aeration was stopped and more KAX was added. This was repeated three times for a total KAX addition of 100 g/ton. Products were analyzed by XRF.

2.3 Zeta Potential Measurement

To evaluate the effects of Zn precipitates on flotation, the zeta potentials of the minerals and precipitate were measured with 10^{-2} M of Na₂SO₄ as electrolyte.

3. Results and Discussion

Fig. 1 shows the recovery of zinc, lead and barium with KAX at pH 4 in the flotation of mixed samples without Zn²⁺. With increasing addition of KAX without Zn²⁺, zinc and lead recovery increased (Fig. 1). Generally, the affinity of KAX for sphalerite at low concentration is low and activation using Cu²⁺ is required. However, in the model sample, dissolved Pb²⁺ from anglesite activated sphalerite [2][3] (Equation (1)). In the case of galena and anglesite, the former is more easily recovered by KAX than the latter, resulting in a lead recovery of 60% because only galena floated.

 $ZnS(surface) + Pb^{2+} \rightarrow PbS(surface) + Zn^{2+}$ (1)

Fig. 2 illustrates the effects of Zn^{2+} on the recovery of zinc and lead with KAX at pH 4 in the flotation of mixed samples. The results showed that increasing addition of Zn^{2+} suppressed the floatability of sphalerite at pH 4 because Zn^{2+} did not precipitate in the pulp due to its high solubility (up to 64,000 ppm) that promoted the back reaction shown in Equation 1. In the case of lead, higher concentration of Zn^{2+} also suppressed its floatability, which could be attributed to the KAX consumption of Zn^{2+} .

Fig. 3 shows the effects of Zn^{2+} on the recovery of zinc and lead with KAX at pH 8 in the flotation of mixed samples. In comparison to Fig. 2 where Zn recovery was almost 100%, Fig. 3 shows that the recovery of Zn decreased to about 60% at pH 8

(without Zn^{2+} ; KAX: 100 g/ton). There are two possible explanations for this difference: (1)activation was suppressed due to the precipitation of Pb²⁺ dissolved from PbSO₄, and (2) the Zn^{2+} released from Equation 1 precipitated on sphalerite because of its very low solubility at higher pH ppm) that made (up to 3 it hydrophilic. For galena, pH had negligible effects on its floatability.

When Zn^{2+} was added, suppression of sphalerite floatability increased with increasing Zn^{2+} addition but had little effect on the floatability of galena (Fig. 3).

Table 1 summarized the results of single-mineral flotation experiments. The addition of Zn^{2+} suppressed the floatability of both sphalerite and galena, but the effect was more dramatic in the former than the latter. This could be explained by more extensive adsorption of Zn precipitates on sphalerite than on galena.



Figure 1 - Recovery of zinc, lead, and barium with KAX at pH 4 in the flotation of mixed samples without Zn2+



Figure 2 - Effects of Zn2+ on the recovery of zinc (a) and lead (b) with KAX at pH 4 in the flotation of mixed samples



Figure 3 - Effects of Zn2+ on the recovery of zinc (a) and lead (b) with KAX at pH 8 in the flotation of mixed samples



Figure 4 - Zeta potential of PbS, ZnS, and Zn precipitates

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Table 1 - Amounts of sphalerite and galena in froth of the single-mineral flotation experiments (pH 8, Zn2+ = 1000 ppm; KAX = 100 g/ton)

Mineral name	Amount in froth (%)	
	Without Zn2+	With 1000 ppm of Zn ²
Sphalerite	89	26
Galena	86	68

Zeta potentials of sphalerite, galena, and Zn precipitate at pH 8 were about -35 mV, -15 mV, -13 mV, respectively (Fig. 4). Generally, repulsion of surfaces with equal surface charges is to be expected, which means that the weak suppressive effect of Zn precipitate on the floatability of galena could be explained by this phenomenon. However, when there is a big difference in the magnitude of surface charges even if both are negative, hetero-coagulation could occur under certain conditions as explained by the Poisson-Boltzmann equation for two parallel plates shown below [4][5][6]:

 $\frac{d^2\varphi}{dx^2} = \frac{8\pi nze}{\varepsilon} \sinh\left(\frac{ze\varphi}{kT}\right)$ (2)

where, φ is the potential in the diffuse double layer between plates (mV), n is the concentration of ions (ion/cm³), z is valence of ions, e is the elemental charge constant, ε is permittivity (F/m) of the medium, k is the Boltzmann's constant, Т is temperature (K) and x is the distance from surface with the lower magnitude of φ to the surface with higher magnitude of φ (cm).

When $\frac{ze\varphi}{kT} \ll 1$, Equation 2 could be simplified into Equations 3 and 4.

$$\frac{d^2\varphi}{dx^2} = \kappa^2 \varphi \quad (3)$$
$$\kappa^2 = \frac{8\pi n e^2 z^2}{\epsilon kT} \quad (4)$$

When $\varphi = \varphi_{s1}$ at x = 0, $\varphi = \varphi_{s2}$ at x = 2h (where 2h is distance between surface 1 and 2), φ at a given x (where

x is distance from surface 1) in Equation 3, it could be expressed as Equation 5.

$$\varphi = \varphi_{s1} \cosh \kappa x + \left(\frac{\varphi_{s2} - \varphi_{s1} \cosh 2\kappa h}{\sinh 2\kappa h}\right) \sinh \kappa h \quad (5)$$

In water at 25°C, κ could be simplified as $\kappa = zC^{\frac{1}{2}} * 10^{6}$ (cm⁻¹), where *C* is concentration of ion in mmol/l. For the calculation in Fig 5, *C* is 10⁻³ mmol/l and z = 1 (Na⁺).



Figure 5 - Calculated values of ϕ between plate surfaces 1 (-15 mV) and 2 (-35 mV)

As illustrated in the figure, when both surfaces have negative charge and the charge difference is large, repulsion is expected to occur ($\kappa h = 2$). However, once a critical distance between the two plates is reached $(\kappa h = 1),$ attractive forces becomes stronger as a result of the changes in the angle of electrical field (Fig. 5). To reach this critical distance and overcome the repulsive forces needed for attraction and addition energy, for example energy of agitation during floatation, could be provided by other forces, which are not included in Equation 5 (e.g., osmotic pressure, Van der Waals force).

5. Conclusion

In this study, the effects of pH and Zn^{2+} on the flotation of mixed sample containing sphalerite, galena and anglesite were investigated. At pH 4 in

the presence of Zn²⁺, sphalerite floatability dramatically decreased because of the deactivation of sphalerite by Pb2+ dissolved from anglesite. At pH 8 in the presence of Zn²⁺, suppression sphalerite of floatability was far stronger than that of galena. This could be attributed to hetero-coagulation the of Zn precipitates and sphalerite. This mechanism can be applied to depress the target minerals and enhance the selectivity of flotation.

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