

Sustainable Flotation Strategies Using Organic and Amino Acids for the Selective Separation of Sulfide Minerals

ドア アシラフ エルアデル

<https://hdl.handle.net/2324/7443433>

出版情報 : Kyushu University, 2025, 博士 (工学), 課程博士
バージョン :
権利関係 :



氏 名 : Doaa Ashraf Eladl (ドア アシラフ エルアデル)

論 文 名 : Sustainable Flotation Strategies Using Organic and Amino Acids for the Selective Separation of Sulfide Minerals
(有機酸およびアミノ酸を用いた硫化鉱物の選択的分離に向けた持続可能な浮選プロセスの研究)

区 分 : 甲

論 文 内 容 の 要 旨

In recent years, the increasing demand for base metals such as zinc (Zn), lead (Pb), and copper (Cu), combined with the depletion of high-grade ores, has highlighted the need for the efficient utilization of sulfide minerals. Selective separation between sphalerite (ZnS) and galena (PbS) is generally achievable when ZnS remains unactivated under controlled flotation conditions. However, the separation becomes significantly more difficult once ZnS is activated by Pb^{2+} , which enhances its floatability and reduces the contrast in surface properties between the two minerals. In addition, conventional inorganic depressants commonly used to address this problem generate secondary pollution. Therefore, there is a growing need for environmentally sustainable alternatives capable of selectively depressing Pb-activated ZnS, while preserving PbS floatability. To address this challenge, this study systematically evaluates fifteen organic acids (OAs) and biological amino acids (BAAs) as eco-friendly depressants and elucidates the fundamental mechanisms governing selective separation, aiming to establish rational and sustainable flotation strategies.

Chapter 1 provides an overview of ZnS and PbS flotation and reviews the key challenges associated with Pb^{2+} -activation of ZnS. Recent developments in environmentally friendly depressants are evaluated, focusing on their molecular structures and flotation performance. The objectives of this study are defined as: (1) to investigate the efficacy of OAs and AAs as environmentally friendly alternatives for the selective separation of Pb-activated ZnS and PbS; and (2) to elucidate the underlying separation mechanisms using flotation tests and surface analysis.

Chapter 2 describes the experimental methodologies adopted throughout the study.

Chapter 3 focuses on screening and evaluating three OAs (oxalic acid (Ox); citric acid; tannic acid) and twelve BAAs which are classified as hydrophobic amino acids (glycine; valine; isoleucine; phenylalanine; tyrosine), hydrophilic positively-charged amino acids (arginine (Arg); lysine; histidine), alcohol-containing amino acids (serine; threonine), and sulfur-containing amino acids (methionine; cysteine). Preliminary single-mineral flotation tests were conducted under fixed conditions (pH 9; 30 g/t potassium amyl xanthate (PAX) as collector; 0.6 mM depressant) to identify the most promising depressants based on the flotation recovery (%) of ZnS and PbS. The separation performance strongly depended on chemical structures and functional groups. Hydrophilic positively-charged amino acids (such as Arg) and Ox showed the highest selectivity, reducing Pb-activated ZnS recovery from 56% to 18%, while maintaining PbS recovery at ~60%.

Chapter 4 then advances from screening in **Chapter 3** to detailed mechanistic analysis by using micro-flotation tests and surface characterization, focusing on Ox as a representative depressant under varying

conditions (pH 6, 8, 9, 10, 11; Ox 0, 0.3, 0.6 mM; PAX 30, 120 g/t). Single-mineral flotation tests first showed that Ox reduced ZnS recovery from 35% to 20%, while maintaining PbS recovery at 59% (pH 9; 0.6 mM Ox; 120 g/t PAX). Mixed-mineral flotation further confirmed this selective depression of ZnS, decreasing its recovery from 73% to 17%, while maintaining PbS recovery at 83%. Spectroscopy analyses, including Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS), revealed that on Pb-activated ZnS, surface-adsorbed Pb^{2+} acts as activation sites that strongly coordinate with PAX to form hydrophobic $\text{Pb}(\text{AX})_2$, enhancing ZnS floatability. When Ox is added, it reacts with these surface Pb^{2+} ions to first form insoluble PbOx species, which detach from the mineral surface. PAX subsequently binds to these PbOx particles to form PbOx-AX complexes, thus blocking further collector adsorption on the exposed hydrophilic ZnS surface. As a result, ZnS loses hydrophobicity and remains depressed during flotation. Atomic Force Microscopy (AFM) confirmed the detachment of PbOx-AX particles and the re-exposure of the intrinsically hydrophilic ZnS surface. In contrast, Pb in PbS is structurally incorporated into the crystal lattice and cannot be removed by Ox, allowing direct formation of hydrophobic $\text{Pb}(\text{AX})_2$ to continue and thereby maintaining PbS floatability.

Chapter 5 investigates Arg as the second candidate depressant selected from the **Chapter 3** screening. Micro-flotation tests were conducted under varying conditions (same as **Chapter 4**). Single-mineral flotation showed that Arg decreased ZnS recovery from 66% to 26%, while largely preserving PbS recovery at 74%. Mixed-mineral tests further demonstrated effective selectivity reducing ZnS recovery from 73% to 21% while maintaining PbS recovery at 79% (0.6 mM Arg, pH 9, and 120 g/t PAX),

XPS and FTIR revealed that Arg interacts specifically with surface-adsorbed Pb^{2+} on Pb-activated ZnS to form hydrophilic $\text{Pb}(\text{Arg})_2$ complexes, hindering subsequent adsorption of PAX. As a result, ZnS remains hydrophilic and depressed during flotation. Zeta potential measurements confirmed this electrostatic interaction, showing a positive shift after Arg treatment, and contact angle results indicated enhanced hydrophilicity (from 58° to 50°). AFM imaging further verified consistent surface coverage of $\text{Pb}(\text{Arg})_2$ complexes. Although $\text{Pb}(\text{Arg})_2$ complexes also form on PbS, their depression effect is significantly weaker. This is because structurally incorporated Pb in PbS strongly reacts with PAX to form hydrophobic $\text{Pb}(\text{AX})_2$ species, whose adsorption strength outweighs the hydrophilizing effect of $\text{Pb}(\text{Arg})_2$ complexes. Consequently, PbS floatability is maintained despite Arg adsorption.

Chapter 6 concludes the mechanistic insights obtained in Chapters 4 and 5 and highlights the key differences in how Ox and Arg achieve selective depression of Pb-activated ZnS. Ox suppresses ZnS through an activation-site elimination mechanism, in which surface-adsorbed Pb^{2+} is converted into insoluble PbOx and removed from the mineral surface, preventing hydrophobic $\text{Pb}(\text{AX})_2$ formation. Arg, in contrast, functions via an activation-site masking mechanism, where Pb^{2+} is retained on the surface but converted into a strongly hydrated $\text{Pb}(\text{Arg})_2$ layer that blocks PAX adsorption while maintaining ZnS hydrophilicity. In both cases, PbS floatability remains unaffected due to its lattice-incorporated Pb, which directly reacts with PAX to form strongly hydrophobic $\text{Pb}(\text{AX})_2$ species. The mechanistic framework developed here provides practical guidance for designing green flotation reagents and support future industrial implementation for complex Pb–Zn sulfide ore processing.