



Title	Mineral processing of complex sulfide ores combined with extraction, flotation, and cementation for sustainable development of complex sulfide deposits [an abstract of entire text]
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Citation	北海道大学. 博士(工学) 甲第15380号
Issue Date	2023-03-23
Doc URL	http://hdl.handle.net/2115/89521
Type	theses (doctoral - abstract of entire text)
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Summary

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学 位 論 文 題 名

Title of dissertation submitted for the degree permission

Mineral processing of complex sulfide ores combined with extraction, flotation, and cementation for sustainable development of complex sulfide deposits

(複雑硫化鉱の持続可能な開発のための抽出・浮選・セメンテーションを組み合わせた選鉱手法の開発)

Complex sulfide ores, some of the most important sources of critical metals, are typically composed of several metal sulfide minerals like chalcopyrite, galena and sphalerite. Complex sulfides consisting of copper (Cu), lead (Pb), and zinc (Zn)-sulfide minerals are typically processed via flotation—a separation technique based on the differences in wettability of minerals—to produce concentrates of each mineral. Some complex sulfides (e.g., seafloor massive sulfides obtained from around Japan, one of the promising sources of critical metals in the future) contain not only galena but also anglesite, which is not typically contained in the conventional ores. The presence of anglesite is problematic for the separation of Cu, Pb and Zn-sulfide minerals by flotation due to the unwanted activation of ZnS by lead ions released from anglesite. In addition, anglesite rejected to tailings dam contaminates its surrounding environment. To address these problems, a sufficient method for depressing sphalerite floatability to separate it from Cu and Pb-minerals and preventing lead pollution around the surrounding environment of tailings dam are necessary. In this study, a promising process of mineral processing for complex sulfide ores combined with extraction, flotation, and cementation for sustainable development of complex sulfide deposits in harmony with environment was investigated. In Chapter 1, background and objectives of this study and a literature review on depression of sphalerite floatability in flotation of complex sulfide ores were described. In Chapter 2, a process of mineral processing for complex sulfide ores combined with extraction, flotation, and cementation using ethylene diamine tetra acetic acid (EDTA) was investigated. The results of extraction tests showed that EDTA extracted 99.8% of

anglesite in sphalerite-anglesite mixture and the results of cementation tests using zero-valent iron (ZVI) showed that 99.7% of extracted lead ion was recovered from the leachate after extraction with EDTA (EDTA pretreatment). The flotation results of the residue after EDTA pretreatment showed that the floatability of ZnS was depressed from 82% to 30% by applying EDTA pretreatment. The results of thermodynamics calculations for lead activation reaction and surface analysis using XPS for sphalerite with and without EDTA pretreatment indicated that lead activation of sphalerite was limited due to the decrease of lead ion concentration, resulting in depression of sphalerite floatability.

In Chapter 3, alternative extractants of anglesite to EDTA were investigated using ammonium acetate and acidic sodium chloride. The results of extraction tests showed that ammonium acetate extracted almost of all anglesite when S/L ratio was ≤ 0.5 g/10 mL. The results of cementation tests using ZVI showed that almost of all extracted lead ion was recovered from the leachate after extraction with ammonium acetate. While extraction of anglesite using acidic sodium chloride was limited due to the solubility of lead-chloride species, almost of all anglesite was extracted and recovered when the coupled extraction and cementation (CEC) method using ZVI was applied. The flotation results of the residues after extraction using ammonium acetate or the non-magnetic fraction after CEC using acidic sodium chloride and ZVI showed that the floatability of sphalerite was depressed.

In Chapter 4, effects of pyrite on the separation of chalcopyrite and sphalerite were investigated to further depress the floatability of sphalerite in the cleaner stage of Cu flotation. While the floatability of sphalerite was depressed from $>90\%$ to $<12\%$ with zinc sulfate in the absence of pyrite, the floatability of sphalerite increased to $>80\%$, indicating that pyrite inhibited the depressive effect of zinc sulfate toward sphalerite. Based on the results of contact angle measurements of sphalerite and pyrite with air bubble and flotation tests under anoxic condition, the mechanism that pyrite inhibits the depressive effect of zinc sulfate toward sphalerite in the presence of chalcopyrite via promoting the release of copper ion due to galvanic interaction between chalcopyrite and sphalerite was proposed.

In Chapter 5, effects of pyrite on the floatability of lead-activated sphalerite were investigated to clarify whether the addition of activators such as copper sulfate is necessary to separate lead-activated sphalerite from pyrite in Zn flotation. The flotation results with and without pyrite showed that pyrite depressed the floatability of lead-activated sphalerite from 81.5% to 1.4%. Based on the results of contact angle measurements between PbS and air bubble with and without electrical connection with pyrite and dissolution tests of PbS with and without pyrite combined with surface analysis,

the mechanism that pyrite depressed the floatability of lead-activated sphalerite due to dissolution of PbS layer on sphalerite via galvanic interaction between pyrite and PbS was proposed.

And finally, Chapter 6 summarized important findings of this dissertation and proposed a possible application.