Formation of bioscorodite for stabilization of arsenic species derived from bio-mineral processing

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論 文 名　：Formation of bioscorodite for stabilization of arsenic species derived from bio-mineral processing
（バイオミネラルプロセッシングに由来するヒ素化学種の安定化のためのバイオスコロダイト法に関する研究）

区　　分　：甲

論 文 内 容 の 要 旨

Bio-mineral processing (bioleaching and biooxidation) is considered as one of the most effective approaches to recover valuable metals (i.e. Cu, Au, Ag), especially from low-grade refractory mineral ores and concentrates. Arsenic (As) is a major impurity contaminated in metal refinery wastewaters including those deriving from bio-mineral processing, and its economically-viable and environmentally-friendly removal technique is needed. This thesis firstly demonstrated the applicability of biooxidation of highly refractory As-bearing Au-ore concentrates, and secondly investigated the factors that enable effective bioscorodite ($FeAsO_4 \cdot 2H_2O$) crystallization using the thermo-acidophilic Fe(II)-oxidizing archaeon, *Acidianus brierleyi* from dilute As(III)-bearing acidic solutions (3.3–20 mM): i.e. (i) $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratios, (ii) initial pH values, (iii) seed-feeding, (iv) SO_4^{2-} ions. Moreover, in order to evaluate microbial effect on bioscorodite crystallization, the utility of different thermo-acidophilic Fe(II)- and sulfur-oxidizing archaeal strains (*Sulfolobus metallicus* Kra23, *S. tokodaii* 7, *S. acidocaldarius* 98-3 and *Metallosphaera sedula* TH2) was also evaluated.

In **chapter 1**, background information about As properties, current As immobilization techniques and scorodite synthesis methodologies (abiotic/biotic approaches) were overviewed. Based on these backgrounds, the motivation and objectives of this thesis were presented.

In **chapter 2**, methodologies used in this work were described.

In **chapter 3**, effectiveness of different pure and mixed cultures of three moderately thermophilic bacterial strains (*Acidimicrobium ferrooxidans* ICP, *Sulfobacillus sibiricus* N1 and *Acidithiobacillus caldus* KU) were investigated for biooxidation of As-bearing highly refractory polymetallic Au-ore concentrates. Despite of the complex mineralogy and the presence of a mixture of potentially inhibitory metals and metalloids, the concentrates were readily dissolved in defined mixed cultures including both iron and sulfur oxidizers, releasing as much as 80% of soluble Fe and 61% of soluble As at 45°C. Partial As was immobilized as amorphous ferric arsenate, but not as crystalline scorodite. Applying the biooxidation pretreatment improved the recovery of both Au (from 1.1% to 86%) and Ag (from 3.2% to 87%), which was shown to be one of the most effective options compared with other abiotic pretreatment approaches (roasting, pressure oxidation, and alkali dissolution).

From **chapter 4** to **chapter 6**, bioscorodite crystallization tests were conducted using *Ac. brierleyi* at 70°C. In **chapter 4**, a range of dilute As(III) solutions (3.3–20 mM) with varying $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar

ratios (0.8–6.0) were tested. Bioscorodite was crystallized in the $[Fe(II)]_{ini}/[As(III)]_{ini}$ range of 0.8–2.0. Generally, 94–99% of As was successfully removed as crystalline bioscorodite by setting the $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio at 1.4–2.0. Molar ratio of over 2.5 resulted in the formation of amorphous ferric arsenate or jarosite. Lowering the initial pH from 1.5 to 1.2 using bioscorodite seeds lead to a steady and continuous formation of bioscorodite particles, but As removal remained relatively incomplete at pH 1.2 (91%), compared to at pH 1.5 (98%). Formation of amorphous precursors at pH 1.5 played an important role to achieve the maximum As removal from dilute As(III) solutions by inducing two-stage As and Fe precipitations.

In **chapter 5**, the effect of seed-feeding on bioscorodite crystallization from dilute 4.7 mM As(III) solution was investigated from the viewpoint of morphological and structural differences of two types of scorodite seeds; (i) bioscorodite seeds (lower-density, finer particles) and (ii) chemical scorodite seeds (higher-density, coarse particles). Feeding bioscorodite seeds enabled effective As removal from dilute As(III) solution (98% final As removal at day 21). When bioscorodite seeds were fed, hollow seed particles became increasingly filled with newly formed scorodite. On the other hand, solid chemical seeds induced their surface to be thoroughly coated with new scorodite precipitates. TCLP (Toxicity Characteristic Leaching Procedure) leachabilities of final bioscorodite products formed on bioscorodite or chemical scorodite seeds were 0.59 ± 0.08 mg/l or 1.86 ± 0.05 mg/l, respectively. The values satisfied the regulatory limit of As set by the US EPA (United States Environmental Protection Agency). Utilization of seed crystals with highly positive surface charge, such as hematite (+ 60 mV at pH 2) and bioscorodite (+ 50 mV at pH 2), enabled effective bioscorodite crystallization, owing to their property as absorbent of anionic As(V) ($H_2AsO_4^-$) and less positively charged *Ac. brierleyi* cells (+ 5 mV at pH 2).

In **chapter 6**, behavior of SO_4^{2-} ions during bioscorodite formation was investigated by liquid/solid characterization analyses, and the mechanism of bioscorodite crystallization process (2-stage process consisting of precursor formation and transformation into crystalline scorodite) was elucidated. During the 1st-stage As-removal, brown-colored amorphous precursors were formed by precipitation of mixture of ferric hydroxysulfate ($MFe_x(SO_4)_y(OH)_z$) and ferric arsenate ($FeAsO_4 \cdot nH_2O$). During the following equilibrium state (induction period), the cycle of dissolution and recrystallization of the above precursors likely proceeded: As a result, ferric hydroxysulfate particles having higher solubility mostly dissolved and released Fe(III), which were able to further react with the remaining As(V) ions in bulk solution. This supported the coarsening of ferric arsenate ($FeAsO_4 \cdot nH_2O$) particles, followed by scorodite crystallization (2nd-stage As-removal; Ostwald ripening). Since the above bioscorodite crystallization process was made possible only in the presence of SO_4^{2-} ions, formation of intermediate ferric hydroxysulfate was thought to be the key trigger for effective As removal.

In **chapter 7**, the alternative archaeal strains were tested for bioscorodite crystallization; *S. metallicus* Kra23, *S. tokodaii* 7, *S. acidocaldarius* 98-3 and *M. sedula* TH2. Partial As(III) oxidation was observed only in *M. sedula* TH2 culture in the presence of Fe(II) and elemental sulfur. Bioscorodite was successfully crystallized in *M. sedula* culture containing 6.5 mM As(III), 9 mM Fe(II) and 0.1% (w/v) elemental sulfur at pH 1.5 on day 23. In the absence of Fe(II), microbial As(III) oxidation was not observed regardless of the presence/absence of elemental sulfur and yeast extract. This result implied that the presence of Fe(II) induced microbial As(III) oxidation ability of *M. sedula* TH2.

In **chapter 8**, the main conclusions of this work were summarized.