BIO-MINERAL PROCESSING OF DOUBLE REFRACTORY GOLD ORES USING LACCASE-MEDIATOR SYSTEM

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（ラッカーゼメディエーター酵素系を用いた超難処理金鉱石のバイオミネラルプロセシング)

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論 文 内 容 の 要 旨

Gold ores in which gold particles are trapped within sulfide minerals are called "refractory gold ores," and the ores associated with carbonaceous shale are classified as "double refractory gold ores (DRGO)." Since $Au(CN)_2^-$ complexes are adsorbed on the carbonaceous matter (CM) in cyanidation, the conventional extraction makes gold recovery loss of 30 to 70% (preg-robbing effect). In addition, DRGO is not suitable for general flotation beneficiation due to the poor separation of carbonaceous and sulfide minerals, despite its higher gold grade than ordinary gold ores, making it unsuitable for economic exploitation. However, DRGOs are distributed over five continents, and the gold resources are estimated to be equivalent to a fraction of the world's total gold production. It is no exaggeration to say that there is now a global demand for hydrometallurgy to recover gold from DRGOs without causing environmental impacts.

The present work reports on a (bio)hydrometallurgy for graphitic gold ores that avoids roasting, which releases toxic gases, and achieves the necessary mineral degradation at ambient temperature and pressure with a low environmental impact and proposes a new direction that uses the laccase (Lcc) reaction among ligninolytic enzymes, which has never been attempted before, to recover gold from DRGO with different degrees of graphitization. This provides a new guideline for the sequential DRGO treatment process for each ore, through a molecular-level study of degraded products by laccase reaction.

First, **Chapter 1** reviews the occurrence of DRGO, the troubles encountered in DRGO, and the importance of overcoming their pre-treatment to improve gold beneficiation. The overview of conventional and novel pre-treatments is listed, focusing on DRGO sequential bio-treatment as a continuous effort to decrease air pollution from conventional processes. Next, Lcc was compared with lignin-degrading enzymes like lignin peroxidase (LiP) and manganese peroxidase (MnP), pointing out the advantages of laccase over the peroxidases. Finally, the objectives of this thesis were proposed.

The methodology to approach the above objectives was summarized in **Chapter 2**, where biochemical approaches (enzyme assay), elemental and mineralogical characterization (X-ray fluorescence spectroscopy and X-ray diffraction), solution analysis (inductive coupled plasma-optical emission spectroscopy, ICP-OES and inductive coupled plasma-mass spectroscopy, ICP-MS), and several unique characterizations for

carbonaceous matter (Raman spectroscopy, thermos-gravimetric analysis, three-dimensional fluorescence spectrometry) are included. In particular, gas chromatography-mass spectrometry (GC-MS) played an essential role in the molecular-level characterization of CM and its by-products derived from enzyme reactions.

First of all, the analytical and preparation problems behind the trace analysis of Au in DRGO were pointed out and overcome in **Chapter 3**. In determining Au by ICP-OES, the coexisting Fe strongly interfered with the 1st dominant Au optical emission peak at 242 nm. After the matrix normalization by adding the same Fe concentrations as in unknown samples to the Au standard solutions, the accuracy of Au determination was improved. In acid digestion of gold ore samples, the acid ratio from normal aqua regia (HCl: HNO_3 =3:1) was modified to highly reverse aqua regia (HCl: HNO_3 =1:5) to increase the oxidizing ability. The optimized conditions were applied to three different DRGOs, where the detection limit was 20 ppb in ICP-OES. As for ICP-MS, the memory effect derived from the reduction of Au(III) to Au(0), and the consequent deposition was overcome by adding 1% L-cysteine as a sacrificing oxidant and ligand.

Chapter 4 elucidated the superiority of Lcc over LiP and MnP in the degradation of powder activated carbon (PAC) as a carbon surrogate. Lcc treatment largely decreased the gold robbing index than the mixture of LiP and MnP under the same enzymatic activity. As such, in **Chapter 5**, the supplemented electron mediator of 1-hydroxybenzotriazole (HBT) improved the degradation efficiency with some direct evidence of bio-degraded products by GC-MS. Laccase-mediator system (LMS) treatment for 7 days physically and chemically altered the surface of PAC with the reduction of specific surface area and pore volume. The disruption of aromatic moieties into aliphatic compounds and the formation of oxygen-containing functional groups, mainly carbonyl groups, were revealed by GC-MS. Subsequently, the adsorption density of $Au(CN)_2^-$ on the surface-degraded PAC was dramatically decreased from 46.0 to 7.36 μmol/g. These experimental conditions were applied to natural DRGO.

In **Chapter 6**, the organic carbon from three carbonaceous gold ores: PXX and SYM (flotation concentrates), and BOG (after bio-oxidation of flotation concentrate), were characterized. There was an extreme contrast between PXX and SYM as poorly and highly preg-robbing ores. As for BOG (moderately), the surface property was influenced by the presence of extracellular polymeric substances (EPS) formed during intensive bio-oxidation of sulfides. LMS pre-treatment was applied to the above three ores to decompose CM. Almost 100% of Au was recovered from PXX by cyanidation without any pretreatments. Meanwhile, its Ag recovery reached only 33.7%, and it improved to almost 100% after LMS treatment. Au recovery in BOG yielded 77% after sulfide decomposition and further improved to >90% after removing jarosite by oxalic acid washing. However, the presence of EPS layers on CM interfered with laccase reaction by enzyme activity consumption, resulting in a slight increase to 92%. Therefore, for SYM, $FeCl_3$ leaching was applied for the decomposition of sulfides avoiding the formation of jarosite and EPS**.** GC-MS results for the LMS-treated SYM confirmed the presence and increment of fatty acids and aliphatic hydrocarbon, indicating LMS degradation went through the disturbance of the benzene rings from the defective sites of CM and made the CM surface became more hydrophilic. Finally, sequential treatment of SYM improved Au recovery in cyanidation as shown in 44% (original) →77% ($FeCl_3$ leaching) →86% (LMS), which is the most refractory gold ore in the present work.

In **Chapter 7**, the main conclusions of the present thesis were summarized, including a general direction for the pretreatment of DRGO and the applicability of LMS treatment.