

SEARCH FOR IRON REDOX ABILITIES IN EXTREMELY ACIDOPHILIC MICROORGANISMS AND THEIR USE IN MINERAL PROCESSING

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論 文 名 : SEARCH FOR IRON REDOX ABILITIES IN EXTREMELY ACIDOPHILIC
MICROORGANISMS AND THEIR USE IN MINERAL PROCESSING
(超好酸性微生物における鉄酸化/還元能の探索及びそれらを利用した鉱物処理
に関する研究)

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論 文 内 容 の 要 旨

The thesis consists of investigations of iron redox abilities of extremely acidophilic microorganisms as fundamental studies (chapter 3 and 4) and their utilization to mineral processing as application studies (chapter 5 to 8). The latter includes reductive bioleaching of Indonesian Ni-limonite ore and chalcopyrite concentrate, and oxidative bioleaching of chalcopyrite concentrate in silver catalyzed or redox potential-controlled systems.

In chapter 1, background and objectives of this work are provided especially focusing on importance of microbiological iron redox transformation and its utilization to mineral processing. Previous studies related to the present work were reviewed and discussed in this chapter.

In chapter 2, methodologies used in this work are described.

In chapter 3, for the purpose of utilizing microbial Fe(III) reduction for reductive bioleaching of Fe(III)-containing minerals and for bioremediation of heavy metal polluted-environments, useful Fe(III)-reducing acidophiles were searched from Chinoike Jigoku ("Blood Pond Hell") hot spring located in Beppu, on Kyushu Island of Japan. This is because the hot spring features acidic pHs and a large amount of ferric mineral in sedimentary layers. The presence of Fe metabolizing acidophiles was implied based on the 16S rRNA gene analysis. Successive enrichment cultivation with Fe(III) under micro-aerobic conditions resulted in isolation of an acidophilic archaeon, *Sulfolobus* (*S.*) sp. GA1 (with 99.7% 16S rRNA gene sequence identity with *S. shibatae* B12^T). Strain GA1 showed unique characteristics (unlike other *Sulfolobus* spp.), capable of reducing Fe(III), and incapable of oxidizing S⁰. The strain was found to reduce extremely toxic Cr(VI) to less toxic/soluble Cr(III).

The facts revealed in chapter 3 lead to further investigation of general trend of Fe redox transformation abilities in six representative *Sulfolobus* spp. **in chapter 4**. The degree of Fe(II)-oxidizing abilities were found to differ largely between the strains tested. Four strains (*S. tokodaii* 7, *S. solfataricus* P1, *S. shibatae* B12 and *Sulfolobus* sp. GA1) were capable of anaerobic growth via Fe(III) respiration. All strains other than *Sulfolobus* sp. GA1 displayed Fe(III)-reducing abilities in growth-uncoupled cell suspensions. Nonetheless, Fe(III)-reducing ability in each strain responded significantly differently to the oxygen level. The trend of Fe(III) reduction in six strains did not correspond to that of Cr(VI), implying different mechanisms being involved in Fe(III) and Cr(VI) reduction in *Sulfolobus* spp. tested. The information on Fe redox

transformation abilities by *Sulfolobus* spp. contributed to better understanding of Fe redox cycles in natural environments, and provided its potential applicability to mineral processing such as biohydrometallurgical approaches.

In chapter 5, screening of useful Fe(III)-reducing acidophiles was carried out based on their effectiveness in soluble Fe(III) reduction and subsequent dissolution of chemically synthesized goethite. The selected Fe(III)-reducing acidophiles were then tested for reductive bioleaching of Indonesian Ni-limonite ore (mainly consisting of goethite). Dissolution behaviors of Ni and Fe from the limonite ore were linearly correlated and Ni extraction was found to be sensitive to solution redox potentials, total soluble Fe concentrations, and solution pHs. Ni extraction continued by refreshing bioleaching media to remove dissolved metals: The maximum Ni extraction of 55 or 41% were marked at the end of the 3rd step (30 days in total) using cell suspensions of *S. tokodaii* 7 or *Sb. acidophilus* YTF1, respectively.

In chapter 6, applicability of the reductive bioleaching approach to refractory primary copper sulfides, chalcopyrite (CuFeS_2), was investigated. However, no noticeable improvement in Cu recovery was observed. This was likely caused by higher refractoriness of chalcopyrite than Fe(III) oxides (such as goethite), hindering its acid dissolution.

In chapter 7, catalytic effect of silver on chalcopyrite bioleaching was investigated. When tested with silver sulfate, microbial oxidizing capabilities of Fe(II) and S^0 were both inhibited by the presence of silver catalyst. Unexpectedly, after silver sulfate was added at day 10, sterile controls showed higher Cu recovery (52% at day 42) than that in mixed cultures (43% at day 42). This was likely caused by passivation layer of S^0 accumulation that formed at higher solution redox potentials before the addition of silver sulfate to mixed cultures.

In chapter 8, potential utility of the microbiological solution redox potential control during chalcopyrite bioleaching was investigated using mixed cultures of moderately thermophilic acidophiles. Utilization of different mixed cultures showing different degrees of Fe(II)-oxidizing capability resulted in different levels of E_{normal} and Cu leaching rate. Final Cu recovery in mixed cultures of *Acidithiobacillus* (*At.*) *calvus* KU plus *Sb. acidophilus* YTF1 marked 75% by day 70, while that in mixed cultures of *At. calvus* KU plus *Acidiplasma* sp. Fv-Ap was 49%. The above difference in Cu recovery was attributed to the E_{normal} level: $0 < E_{\text{normal}} < 1$ was maintained throughout the bioleaching test in the former, whereas E_{normal} rapidly exceeded 1 in the latter. Effectiveness of chalcopyrite dissolution during the test was discussed based on the kinetic study. Chalcopyrite bioleaching was found to be controlled by “surface reaction” at $0 < E_{\text{normal}} < 1$, while that was controlled by “diffusion through product layers” (e.g., jarosite) at $E_{\text{normal}} > 1$. Consequently, different kinetics involved in chalcopyrite bioleaching were found to lead to either facilitation ($0 < E_{\text{normal}} < 1$; using “weak” Fe(II)-oxidizing microbes) or hindrance ($E_{\text{normal}} > 1$; using “strong” Fe(II)-oxidizing microbes) of the mineral dissolution. The Cu leaching rate was shown to be maximized at the E_{normal} value of approx. 0.3.

In chapter 9, conclusions and recommendations for future work are provided.