Leaching of heavy metals from sulfide ores under oxic environment: An experimental approach by using hydrogen peroxide
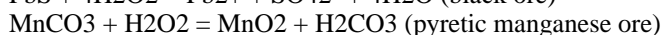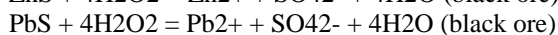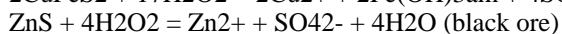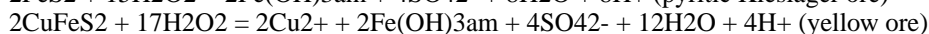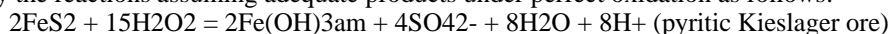
Shinya Suzuki[1]; Kosei Komuro[2]

[1] Life and Environmental Sci., Tsukuba Univ; [2] Life Environment. Sci., Univ. Tsukuba
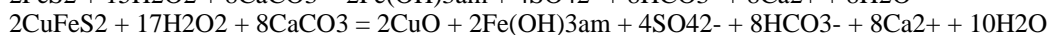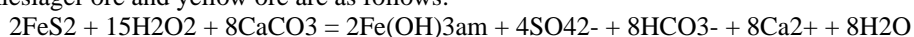
In order to understand the leaching of heavy metals and change in pH in solution during oxidation of sulfide ores under natural hydrogeological environment, oxidative dissolution experiment of sulfide ores was carried out by using hydrogen peroxide.

In the oxidative dissolution experiment, 25mg or 1000mg of powdered sulfide ore was sealed in the polypropylene bottle with 50ml solution containing oxidizing agent, and left for about 50 days at room temperature and pressure. Four types of the sulfide ores with limestone for neutralization reaction were used: black ore from the Toya-Takarada Kuroko deposit composed mainly of sphalerite and galena, yellow ore from the Shakanai Kuroko deposit mainly of chalcopyrite, pyritic Kieslager ore from the Yanahara Kieslager deposit mainly of pyrite, pyretic manganese ore from the Oe epithermal vein-type deposit mainly of rhodochrosite and pyrite, and limestone from Hiiragiyama mainly of calcite and dolomite. For each ore and their composite (1:3), series of experiments were carried out with changing the concentration of the H_2O_2 as oxidizing agent from 0 to $1.5*10-2$ mol/l. The run products were filtered by 0.20 micrometer membrane filters, and were analyzed pH and concentrations of heavy metals of the filtrated solutions.

The pH of the solutions are: 2.6 to 3.8 for pyritic Kieslager ore, 3.7 to 5.2 for yellow ore, 5.6 to 6.3 for black ore, 6.7 to 7.1 for pyretic manganese ore and 8.4 to 9.4 for limestone. The solutions are also acidic for the composites mainly of pyritic kieslager ore and yellow ore, and basic for those of pyretic manganese ore and limestone. Strong acidification with the increase of amount of hydrogen peroxide is found in the results for the series of pyritic Kieslager ore and yellow ore. These results are well explained by the reactions assuming adequate products under perfect oxidation as follows:

$2FeS_2 + 15H_2O_2 = 2Fe(OH)_3am + 4SO_4^{2-} + 8H_2O + 8H^+$ (pyritic Kieslager ore)

$2CuFeS_2 + 17H_2O_2 = 2Cu^{2+} + 2Fe(OH)_3am + 4SO_4^{2-} + 12H_2O + 4H^+$ (yellow ore)

$ZnS + 4H_2O_2 = Zn^{2+} + SO_4^{2-} + 4H_2O$ (black ore)

$PbS + 4H_2O_2 = Pb^{2+} + SO_4^{2-} + 4H_2O$ (black ore)

$MnCO_3 + H_2O_2 = MnO_2 + H_2CO_3$ (pyretic manganese ore)

The addition or mixing of limestone is highly effective for neutralization of these acids. The neutralization reactions for pyritic Kieslager ore and yellow ore are as follows:

$2FeS_2 + 15H_2O_2 + 8CaCO_3 = 2Fe(OH)_3am + 4SO_4^{2-} + 8HCO_3^- + 8Ca^{2+} + 8H_2O$

$2CuFeS_2 + 17H_2O_2 + 8CaCO_3 = 2CuO + 2Fe(OH)_3am + 4SO_4^{2-} + 8HCO_3^- + 8Ca^{2+} + 10H_2O$

The concentrations of the main constituent metals such as Fe, Cu, Pb and Zn in solutions increase with the increase of amount of hydrogen peroxide. The concentrations are high in lower pH conditions and are low in higher pH conditions, threshold pH values of which are: 4 for Fe and Pb, and 6 for Cu and Zn. The neutralization of these acids by adding or mixing of limestone is also conspicuously successful in reducing the concentrations of the main metals in the solutions, and is proved to be one of the most important controlling factors for metal leaching.

Thermodynamic calculation indicates that the concentrations of Fe under acidic pH conditions and those of Pb under neutral pH conditions can well be explained by the equilibrium with amorphous $Fe(OH)_3$ and $Pb(OH)_2$, respectively. Cu and Zn in the solutions are estimated to be under saturation for each solids in the system.