

A kinetic experiments of oxidation of arsenopyrite in $\text{Fe}_2(\text{SO}_4)_3$ solutions

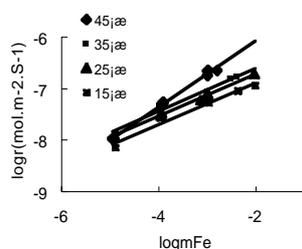
YU YUNMEI AND ZHU YONGXUAN

Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, China (yum@public.gz.cn)

Arsenopyrite is a moderately stable mineral and it can stably exist only in strongly alkaline and reducing environments. Oxygen-rich, acidic surface waters are favorable to the oxidation and dissolution of arsenopyrite and the release of As, Fe and S from it.

In this paper kinetic experiments were made on the oxidation of arsenopyrite in $\text{Fe}_2(\text{SO}_4)_3$ solutions (pH=1.8) with a concentration of 110^{-2} — 110^{-5} mol.kg⁻¹ at the temperatures of 45°C, 35°C, 25°C and 15°C in a mixed flow reactor.

The results have shown that the rates of oxidation of arsenopyrite increase with increasing concentrations of $\text{Fe}_2(\text{SO}_4)_3$ solutions and the rise of reaction temperature as shown in the Figure;



Arsenic released during oxidation of arsenopyrite is present dominantly as hydrous compounds of As(III); As(V) is present in subordinate concentrations and is derived mainly from the outermost layer of oxidized arsenopyrite at the beginning of an experiment while As(III) is the product of oxidation of arsenopyrite. In $\text{Fe}_2(\text{SO}_4)_3$ solutions the oxidation of As(III) to As(V) proceeds very slowly allowing As(III) to predominate in the solution. The stability of As(III) tends to increase with decreasing oxidant concentration and increasing reaction temperature;

The existence of Cl^- in the solutions is favorable to the oxidation of arsenopyrite and the acceleration of conversion of As(III) to As(V).

References

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X-ray Study of Actinide Host-Phases Formation

S.V. YUDINTSEV¹, S.V. STEFANOVSKY², Y.N. JANG³,
AND R.C. EWING⁴

- 1 Institute of Geology of Ore Deposits, Moscow, Russia
(syud@igem.ru)
 2 SIA "Radon", Moscow, Russia (profstef@radon.ru)
 3 Korean Institute of Geology, Taejeon, Korea
(crystal@kis.kigam.re.kr)
 4 University of Michigan, Ann Arbor, USA (rodewing@umich.edu)

Crystalline phases with fluorite-derived structure (zirconolite, pyrochlore) are the promising hosts for long-lived actinide immobilization. These waste forms are usually produced by solid state synthesis – cold pressing at 100-200 MPa followed by sintering at 1300 – 1500 °C for 3-4 hours (CPS). Duration of synthesis required for a single-phase product fabrication depends on chemical composition of the target host-phase. In order to determine optimal parameters of CPS method of actinide waste forms fabrication we have studied rate of phase formation in four systems of different composition: Ca-Zr-Ti-O (the target phase is zirconolite, $\text{CaZrTi}_2\text{O}_7$); Ca-Ce-Ti-O (pyrochlore, $\text{CaCeTi}_2\text{O}_7$); Gd-Ti-O (pyrochlore, $\text{Gd}_2\text{Ti}_2\text{O}_7$), and Gd-Zr-O (pyrochlore, $\text{Gd}_2\text{Zr}_2\text{O}_7$). Synthesis was performed using initial oxide precursor powdered up to grains dimension of about 20 μm . Runs were carried out in air or pure oxygen (for Ce-batch only) in temperature range from 800 to 1600 °C and period of sintering from 5 to 100 hours. Products of the experiments were examined using XRD analysis. The rate of target phase formation is the fastest in titanate systems (Ca-Ce-Ti-O and Gd-Ti-O) and the lowest in the Gd-Zr-O system. Rate of zirconolite formation has intermediate value. Formation of titanate pyrochlore-based matrix takes 3-4 hours at 1400 °C and 0.5-1 hour at 1500 °C. To obtain the single phase zirconate pyrochlore for actinide immobilization too long time of sintering exceeding 40 hours at 1600 °C is required. Zirconate-based pyrochlore is a promising waste forms due to its very high chemical durability and stability to radiation damages induced by α -decay events. To produce this matrix some other methods may be employed instead of the CPS route, for example inductive melting in a cold crucible or self-sustaining high-temperature synthesis.