

Structural effect of Zn^{2+} on biogenic Mn oxides: EXAFS analysis of solid residues after concomitant immobilization

QIANQIAN YU^{1*}, KEIKO SASAKI¹, TSUYOSHI HIRAJIMA¹, KAZUYA TANAKA² AND TOSHIHIKO OHNUKI²

¹Department of Earth Resources Engineering, Kyushu University, Fukuoka, Japan
(q-yu09@mine.kyushu-u.ac.jp)

²Advanced Science Research Center, Japan Atomic Energy Agency, Ibaraki, Japan

Manganese oxides which are thought to be the potential scavenger of trace metals are commonly believed to be biogenic origin. Zn^{2+} in aquatic phase can be immobilized in Mn oxide phase during the biotic oxidation of Mn^{2+} . The amounts of immobilized Zn^{2+} were around twice in microbial Mn^{2+} oxidation in the presence of Zn^{2+} than in simple sorption of Zn^{2+} on biogenic Mn oxides which was produced in advance (Fig. 1). Analysis of Zn K-edge EXAFS spectrum for the solid residue after the concomitant immobilization of Zn^{2+} suggests that Zn atoms are coordinated to O atoms via triple-corner sharing (TC) at Mn vacant site in tetrahedral coordination. The XRD patterns showed that it belongs to poorly crystalline birnessite, its crystal size was calculated to less than 100 nm by Scherrer equation, and there is a lack of stacking in c axis. The measurement of zeta potential for the solid residue after the concomitant immobilization of Zn^{2+} indicated that the surface charge was more negative compared with fresh biogenic birnessite. XAFS/EXAFS analysis revealed that it contains less Mn(III) contents and larger numbers of vacant sites than fresh biogenic birnessite. Co-existence of Zn^{2+} influences Mn oxide formation during bio-oxidation, resulting in poorly crystallized birnessite and other types of Mn oxides which can be commonly found in the natural environments.

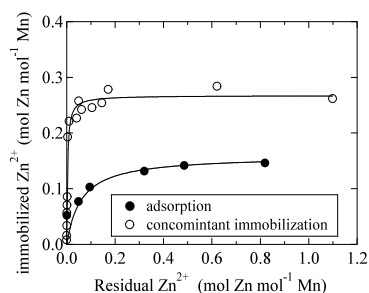


Figure 1: Sorption isotherms of Zn^{2+} on biogenic birnessite (●), and in concomitant immobilization with microbial oxidation of Mn^{2+} ions (○) at 25 °C and pH 6.5.

Metastable phase equilibria for the aqueous system containing lithium, rubidium and chloride at 298.15 K

X. D. YU¹, Y. ZENG^{1,2*}, J. Q. ZHANG¹, J. Y. YANG³

¹Department of Geochemistry, Chengdu University of Technology, Chengdu, 610059, China;

(*correspondence: zengyster@gmail.com)

²Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu, 610059, China;

³Development & Comprehensive Utilization of Marine Sedimentary Brine Sichuan Provincial Key Laboratory, Chengdu, 610059, China

The Pingluoba underground brine (Southwest China), belongs to the marine sedimentary deep brine. The components of the brines are sodium, potassium, lithium, borate, and the rare alkaline elements rubidium and cesium. However, the utilization of the underground brine scarcely has been reported because of a lack of relative solubilities and metastable phase diagram. The system containing lithium, rubidium and chloride is one of the subsystems of the underground brine and has not been reported. In this paper, the metastable equilibria of this system were studied at 298.15 K using an isothermal evaporation method.

Figure 1 is the metastable phase diagram of the system at 298.15 K. The diagram consists of one invariant point, two univariant curves and two crystallization fields. No double salt or solid solution is formed in this system at 298.15 K. The invariant point E is cosaturated with $LiCl \cdot H_2O$ and $RbCl$, and the mass fraction of its equilibrium solution is $w(LiCl)$ 29.74 % and $w(RbCl)$ 23.21 %. $LiCl \cdot H_2O$ is the only crystallization form of lithium chloride at 298.15 K.

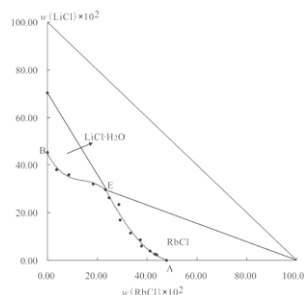


Figure 1: Metastable phase diagram of the system containing lithium, rubidium and chloride at 298.15 K

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