



## 微生物由来のマンガン沈殿物に含まれる マンガンの化学形態の推定

TUM Sereyroith<sup>1</sup>, 西方美羽<sup>1, 2</sup>, 橋本洋平<sup>2</sup>

1 産業技術総合研究所, 2 東京農工大学

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### 1. 背景と研究目的

The chemical treatment of acid mine drainage (AMD) continues to operate even though the legacy mine was closed decades ago. Therefore, sustainable treatment methods such as passive treatment need is necessary to reduce the treatment costs and environmental impact. A pilot-scale passive-treatment system was constructed in the study area, successfully treating manganese (Mn) and zinc (Zn). However, the mechanisms involved in Mn and Zn removal from AMD remain uncertain. This research aims to determine the Mn and Zn removal mechanisms in the pilot-scale passive-treatment plant at circumneutral pH (6.5-7.5) using X-ray absorption fine structure (XAFS).

### 2. 実験内容

XAFS analysis was conducted for both Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) at Aichi Synchrotron Radiation Center, Aichi, Japan, Beamline BL5S1. The Mn K-edge XAS spectra was obtained from 6392-7316 eV,  $E_0 = 6546$  eV by transmission method using silica (111) monochromator crystal and was calibrated by Mn foil. The reference materials for Mn K-edge analysis are MnO ( $Mn^{2+}$ ),  $Mn_2O_3$  ( $Mn^{3+}$ ),  $Mn_3O_4$  ( $Mn^{2+,3+}$ ),  $MnO_2$  ( $Mn^{4+}$ ), and  $KMnO_4$  ( $Mn^{7+}$ ), rhodochrosite ( $MnCO_3$ ),  $MnSO_4$ , birnessite, co-precipitation Zn and birnessite, and adsorption Zn on birnessite. The measurement Zn K-edges XAS spectra was obtained at 9363-10163 eV,  $E_0 = 9659$  eV: by transmission method using silica (111) monochromator crystal and was calibrated by Zn foil. The reference material samples are ZnO ( $Zn^{2+}$ ), ZnS ( $Zn^{2+}$ ),  $ZnCO_3$  ( $Zn^{2+}$ ), adsorption  $Zn^{2+}$  on birnessite, and  $Zn^{2+}$  coprecipitation with birnessite.

### 3. 結果および考察

XANES data shows MD, A-1, and A-2 were at same of the photon energy at 6562.345 eV, is identical to  $MnO_2$ . Liner combination fitting (LCF) model reveal that up to 80% of Mn species in the sludge samples are  $Mn^{4+}$ , which indicate the  $Mn^{2+}$  quickly oxidized to  $Mn^{4+}$  in the study area. Fig.1 shows the radial distribution function  $R$  of Zn with a reference samples. The  $Zn^{2+}$  ( $R = 1.5 \text{ \AA}$ ) was incorporated with birnessite as coprecipitation at  $R = 2.67 \text{ \AA}$  and adsorption at  $R = 3.07 \text{ \AA}$ . LCF shows that the Zn coprecipitation was 39.8% while Zn adsorption 60.2% in MD, but in contrast Zn coprecipitation increased to 59.9% while Zn adsorption was 40.1% in A-1. In A-2 was similar to A-1, 57.9% Zn coprecipitation, 40.8% Zn adsorption, but there was  $ZnCO_3$  about 1.3%. Mn and Zn removal mechanisms in the pilot-scale passive-treatment plant at circumneutral pH; (1) Mn oxidation due to presence of Mn oxidizing bacteria, and (2) Zn co-precipitation during oxidation processes, and (3) Zn adsorption on birnessite surface.

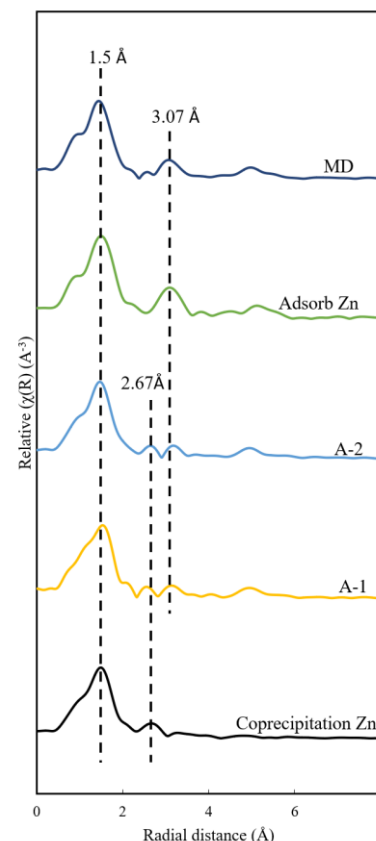


Fig.1 : The radial distribution functions for Zn of standard samples and sludge samples