

## Chemical states change of heavy elements by interaction with microorganisms

Toshihiko OHNUKI\*<sup>1</sup>, Naofumi KOZAI<sup>1</sup>, Takuo OZAKI<sup>1</sup>,  
Takuya NANKAWA<sup>1</sup>, Yoshinori SUZUKI<sup>1</sup>, Hiroshi ISOBE<sup>2</sup>

<sup>1</sup>JAEA, Toaki, Ibaraki 319-1195, Japan

<sup>2</sup>Kumamoto Univ., Kumamoto, Kumamoto 860-8555, Japan

### Introduction

Actinides migrations are of great concern in the environment because of their radioactivity and long half-lives. Their migratory behavior depends on their oxidation states [1] that differ among the III, IV, V, and VI. We have investigated chemical states change of actinides and lanthanides by the interaction with microorganisms. So far, we have elucidated the arsenic behavior around acid mine [2] by the contact with Mn oxidizing bacteria [3], adsorption of U(VI) by the mixture of microorganism and kaolinite clay [4], chemical states change of Ce(IV)-desferrioximine B (DFO) complex by the adsorption to microorganism [5] by the XAFS study at BL-27A and B. In 2006, we have conducted the following investigations:

- i) Oxidation states change of Cu(II) with lichen mycobiont.
- ii) Precipitation of uranium by reduction on indium-tin-oxide electrode.

### Oxidation states change of Cu(II) with lichen mycobiont

We have been studying the tolerant mechanisms to Cu in a Cu tolerant mycobiont from *Tremolecia atrata* (rusty-rock lichen). *T. atrata* mycobiont-cell aggregate, whose shape is almost spherical, showed higher growth in the presence of 0.4 mmol dm<sup>-3</sup> Cu(II)SO<sub>4</sub> compared to that in its absence but the growth was deteriorated at 1.6 mmol dm<sup>-3</sup> Cu(II)SO<sub>4</sub>. To clarify the chemical states change of Cu(II) by the mycobiont, the XANES analysis was carried out. Approximately 1 g of fresh *T. atrata* mycobiont-cell aggregates were inoculated into a 25-cm<sup>3</sup> MY medium with 1.2 mmol dm<sup>-3</sup> Cu(II)SO<sub>4</sub> in a 100-ml Erlenmeyer flask. The pH of the medium was approximately 4.7 before inoculation. The cell aggregates were incubated on a rotary shaker at 120 rpm in the dark at 20 °C for 336 hours. The cell aggregates were harvested by centrifugation and washed with purified water and then with 1 mmol dm<sup>-3</sup> HCl. The resulting cells were freeze-dried and sealed three-fold in polypropylene bags after exchanging the air in the bags with Ar gas. Zeolite antioxidants were put in the second bag to prevent oxidation reactions in the aggregates. As the reference for the oxidation states of Cu from 0 to II, a metal foil (Cu(0)), Cu(I)<sub>2</sub>O, Cu(I)Cl, Cu(I)<sub>2</sub>S, Cu(II)S, Cu(II)(NH<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>, Cu(II)Cl<sub>2</sub>, Cu(II)(OH)<sub>2</sub>, (COO)<sub>2</sub>Cu(II), Cu(II)(NO<sub>3</sub>)<sub>2</sub>, Cu(II)SO<sub>4</sub> were measured. The antioxidants were put in the polypropylene bags to

prevent the alteration of the oxidation states of Cu in the reference substances. Oxidation states of Cu in the cell aggregates and reference substances were examined by X-ray absorption near edge structure (XANES) spectroscopy of the Cu K $\alpha$ 1.

XANES spectra of the samples revealed that the Cu absorbed in the *T. atrata* mycobiont was predominantly divalent and the oxidation state was maintained through stable complexation of Cu(II) with cell-wall components, such as melanins. Some fraction of Cu(II) was reduced by glutathione (GSH), which was induced in *T. atrata* mycobiont by exposure to Cu(II)SO<sub>4</sub>.

### Precipitation of uranium by reduction on indium-tin-oxide electrode

We observed accumulation of uranium caused by reduction of U(VI) on indium-tin-oxide (ITO) electrode surface using the XANES spectroscopy at L<sub>III</sub>-edge absorption spectra of the uranium on ITO electrode after the reduction at -0.3 V for 1200 s and found that U(IV) on ITO surface. This result indicated that U(VI) was reduced to U(IV) and accumulated on ITO electrode surface. We also obtained time-resolved optical waveguide (OWG) spectra. At present, precipitation mechanism is in consideration.

### References

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\* ohnuki.toshihiko@jaea.go.jp