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A Continuous Flow System for In-Situ XANES Measurements of Change in Oxidation State of Ce(III) to Ce(IV)

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To develop a microsystem for determining the oxidation state of actinides, we tested the performance of a mm-scale continuous-flow system in measuring the change in oxidation state of Ce(III) to Ce(IV) with time using X-ray absorption near-edge structure (XANES) analysis. A 1 mM Ce(III) solution mixed with a 1 mM desferrioximine B solution (DFO) was pumped into the system, and then the solution was carried through it at a constant flow rate to the point at which the XANES spectra were captured. The system revealed the distinct peaks of Ce(III) and Ce(IV) in L_{III} edge Ce XANES spectra. The peak intensity of Ce(IV) increased when the reaction time after mixing the two solutions was extended, reflecting the continued oxidation state change of Ce(III) by DFO. Five XANES spectra repeated taken during the test showed no changes in the spectra, indicating the constancy of the oxidation states of Ce throughout the duration of the measurements. Measurements of XANES spectrum over longer periods in the system revealed only low fluctuations in the spectrum around the Ce(III) and Ce(IV) peaks. These results indicate that the mm-scale continuous flow system with XANES analysis is suitable for measuring changes in the oxidation state of actinides with time.

1. Introduction

Actinides migration are of great concern in the environment because of their radioactivity and long half-lives.[1] Their migratory behavior depends on their oxidation states[2] that differ among the III, IV, V, and VI.

The amounts of actinides that can be used in experiments are limited by regulations. These state that the chemical states of actinides should be determined with limited amounts of actinides, thus requiring precise measurements on low concentrations. One resolution for this problem is to develop a micro-measurement system. Various microfluodic devices fabricated by micromachining technologies have been successfully applied in miniaturizing analytical and chemical systems.[3–5] Micro-reaction systems offer many advantages over the traditional large-scale systems: efficient mass transfer, highly effective heat management, a highly specific surface area, less waste and toxic materials generated in chemical reactions, and so on.[6]

X-ray absorption near-edge structure (XANES) is one of the methods that might be useful for analyzing oxidation states in chemicals at low concentrations,[7] and have applied to determine oxidation state of actinides.[8–10] Thus, combining the micro devices with XANES analysis opens the possibility of in-situ measurements of oxidation states of the actinides. However, before developing a microfluodic device for actinides, the performance of a larger continuous flow system, using non-actinides, should first be assessed.

For the present study, we developed a mm-scale continuous flow system for in-situ XANES measurements of the oxidation state of Cerium (Ce). Ce was selected because it is an analogue of trivalent actinides. Further, the oxidation state of Ce(III) changes to Ce(IV) after exposure a desferrioximine B (DFO) solution.[11]

2. Experimental

In-situ flow system for XANES measurement. Figure 1 is a diagram of the continuous-flow system to measure the in-situ XANES spectra. The system is installed at beam line 27B in the Photon Factory of the High Energy Research Organization (Tsukuba, Japan). It employs two micro-tube pumps controlling flow rate of the contained solutions. Each solution

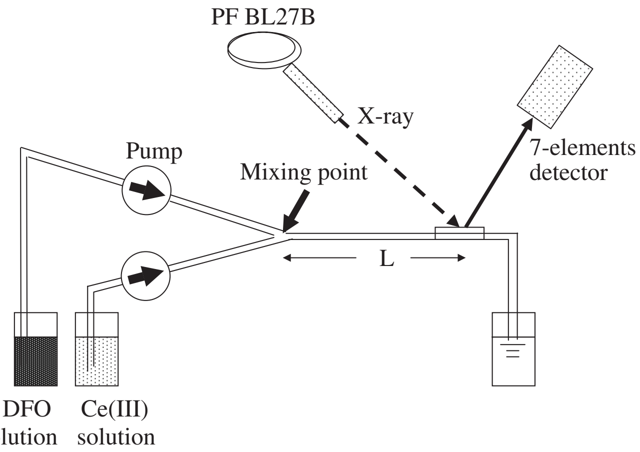

Figure 1. Conceptual diagram of the mm-scale continuous flow system for measuring the oxidation states of elements by in-situ XANES analysis. PF BL27B means KEK, PF beam line, and L in cm. See the details of the system shown in Experimental.

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pumped up from a polyethylene bottle is mixed at the system's mixing point. The hand-made mixer consisted of a silicon tube of 5 mm internal diameter. Through this tube, the mixed solution is introduced to the measurement cell made of a silicon plate with 5 × 5 mm trench. The reaction time, t, in seconds was determined by $t = L{\cdot}A{\cdot}r^{-1}$, where r is flow rate (cm^3/s), L length between the mixing point and the measurement point (cm), and A is a cross section of the silicon tube (cm^2). Note that the mixer is simply a tube, and nothing inside the tube to ensure that the two solutions were mixed.

Solution. Desferrioxamine B (DFO), purchased from Sigma Co. Ltd., was used as received. The chemicals employed were analytical grade. 1 mM solutions of $Ce(III)(NO_3)_3$ and DFO were prepared by dissolving them in deionized water. The pHs of the resulting solutions were adjusted to 7.0 by adding 1 M HCl and NaOH solution.

Measurement of XANES spectra. XANES spectra were measured in the fluorescence mode for the mixed solutions using a 7-element Ge array detector interfaced to single-channel analyzers. XANES spectra for the Ce L_{III} edge were obtained at the measurement point by changing the energy of the induced X-ray that was scanned at intervals of 0.2 eV. The fluorescent X-ray of the mixed solution was measured for 5 s at each energy interval of the induced X-ray. To obtain the XANES spectra at different reaction times, the flow rate was changed to 3, 8, 18, or 180 s. The flow rate of the Ce and DFO solutions was the same.

XANES spectra were measured at different reaction times for the Ce L_{III} edge in the Ce(III) solution alone, and after the Ce solution was mixed with DFO solution. $Cerium(III)(NO_3)_3$ and $Ce(IV)O_2$ were used as the standard materials for trivalent and tetravalent Ce, respectively. Energy calibration was performed based on the energy of the first peak of $Ce(IV)O_2$ at 5731 eV.

Constancy and stability of XANES spectrum. Since the change in the oxidation state change of Ce(III) to Ce(IV) took place in the silicon tube after mixing the solutions, the performance of the in-situ XANES measurement system was rated by the constancy and stability of XANES spectrum. Five repetitive XANES spectra were captured to verify constancy. Each XANES spectrum was obtained by measuring the Ce-DFO solution at the measurement point for 5 s at each energy interval of the induced X-ray. The reaction time was 18 s after mixing. Measuring at 1- and 5- s at each energy interval of the induced X-ray assessed the stability of the XANES spectrum.

3. Results and Discussion

XANES spectra measurements of Ce-DFO mixtures. The L_{III} edge Ce XANES spectra of a 1 mM Ce solution without DFO (Figure 2: Without DFO) showed one strong peak at 5726 eV. The peak energy was the same as that in the spectrum of the Ce(III) standard, denoting that Ce was present as Ce(III) in the solution. Three seconds after mixing with a 1 mM DFO solution, the spectrum was the same as that in the unmodified Ce solution.

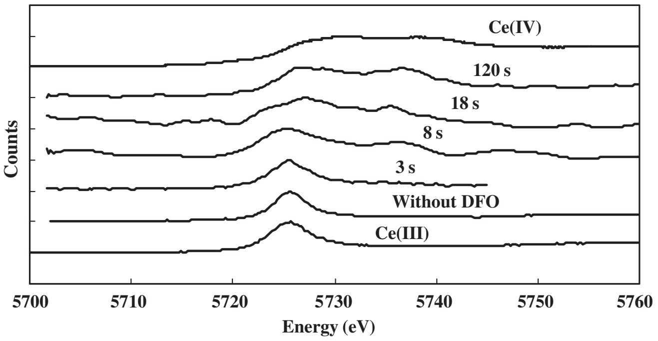

Figure 2. The L_{III} edge Ce XANES spectra of a 1 mM Ce solution alone (Without DFO), at 3, 8, 18, and 120 s after mixing a 1 mM Ce(III) solution with a 1mM DFO solution. The spectra shown by Ce(III) and Ce(IV) are obtained from the standard solutions for $Ce(III)(NO_3)_3$ and $Ce(IV)O_2$.

By 8 s, a small peak at approximately 5738 eV was distinguishable in the spectrum. The first peak energy was nearly the same as that of the Ce(III) standard solution, but its half-value width was broader than that of the standard. The energy of the first peak shifted to higher energy in the spectra collected at 18 and 180 s after mixing. Yoshida et al. indicated that the energy of the first peak shifts with a change in the fraction of Ce(III) to Ce(IV).[11] This finding showed that Ce(IV) oxidized by the reaction with DFO. Our results indicated that the in-situ continuous flow system detected the change of the oxidation states of Ce in the Ce-DFO complex.

Performance of the system. Figure 3 depicts the XANES spectra of Ce measured repetitively five times at 18 s after mixing a 1 mM Ce(III) solution with 1 mM DFO solution. Two peaks around 5727 and 5737 eV were distinguished in all the spectra with energies different from that of Ce(III) or Ce(IV). This result indicated that some fractions of Ce were present as Ce(III) and Ce(IV). The peaks energies were constant in all the spectra, demonstrating that the XANES spectrum was invariant with time, showing constant oxidation states of Ce at the measurement point.

Figure 4 gives the XANES spectra of Ce measured for 1 and 5 s at each energy interval of the induced X-ray. The reaction time of a Ce(III) solution with a DFO solution was 18 s. Both spectra showed two peaks around 5727 and 5737 eV that did not changed with time. Thus, measuring the spectra for longer periods lowered fluctuations in the peaks' intensity, rendering them more distinct.

These results clearly affirmed the sufficiency of the system's performance in measuring the changes in oxidation states with

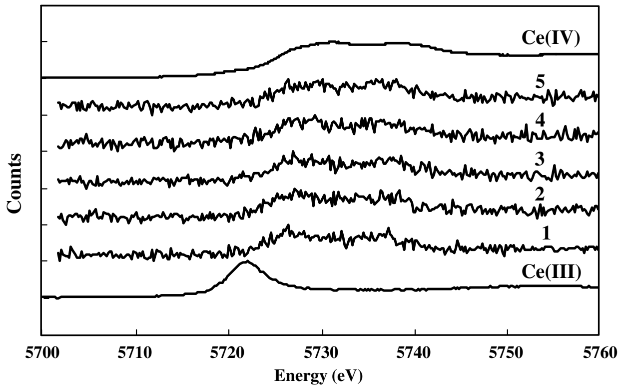

Figure 3. The XANES spectra of Ce collected 18 s after mixing a 1 mM Ce(III) solution with a 1 mM DFO solution and repeating the measurements 5 times. The reference spectra of Ce(III) and Ce(IV) are shown. The small numbers denote the sequential order of the measurements.

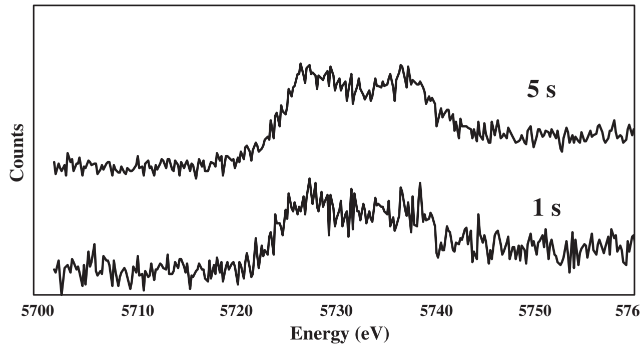

Figure 4. The XANES spectra of Ce measured at 18 s after mixing a 1 mM Ce(III) solution with a 1 mM DFO solution for 1s and for 5 s at each energy interval of the induced X-ray.

time. Therefore, we conclude that the mm-scale continuous flow system with XANES analysis is applicable for measuring such changes in the actinides.

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