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ARTICLE

Temperature-swing gelification recovery of U recovery from leaching solution of U wastes

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The fabrication of nuclear fuel has led to a wide variety of solid wastes being contaminated by enriched uranium (U), and a considerable proportion of these wastes are being accumulated in facilities. A treatment procedure comprising leaching by nitric acid solution and the selective recovery of U from the acid is proposed, facilitating a reduction in the load of waste management. Temperature-swing gelification recovery is a potential technology for efficient U recovery from the leaching solution, which contains metal ions such as Fe^{3+}, Al^{3+}, and Ba^{2+} in 3 M HNO_3. The technology utilizes the principle of solvent extraction and gel formation for phase separation. This study examined the applicability of the technology for waste treatment by investigating materials for the operation, U-recovery performance from a simulated leaching solution, and characterizing residue after heating the temperature-swing gelification products. Poly(N-isopropyl methacrylamide) (PNIPMAAm) and *N*,*N*-di(2-ethylhexyl)decanamide (C10-BAMA) were selected as an appropriate polymer and extractant for the technology, respectively. U in the simulated solution was successfully recovered from the simulated solution, and the heating operation decomposed the organic in the product.

Keywords: U recovery; temperature swing extraction; monoamide

1. Introduction

Nuclear fuel fabrication comprises several physical and chemical procedures and generates wastes contaminated with enriched uranium (U), such as scrap metals, concrete debris, miscellaneous solid wastes, and sludge from chemical treatments on the effluent. Approximately 20% of the wastes are sludge, and wastes with relatively high U concentrations (10^2~10^4 Bq/g) are involved in them. The chemical state and U concentration of the wastes depends on the chemical treatment procedure, such as iron coprecipitation, carbonate coprecipitation, ion exchange, and combustion, and more than hundreds of tons of the wastes containing at least 2 tons of uranium have been accumulating over a long period in Japan. Therefore, an appropriate waste disposal scenario must be discussed to reduce the waste management load. Geologic disposal might be promising, and disposal depth must be as shallow as possible to achieve economic efficiency. However, the U concentration of some wastes is not small enough for geologic disposal in the near field region. Therefore, to establish practical waste disposal protocols, reducing the contamination level of the waste is indispensable.

The Japan Atomic Energy Agency is developing a practical technology for U recovery from leaching solution of U-contaminated wastes. A nitric acid solution is a candidate for the leaching solution, and a substantial proportion of U in the wastes should be transferred into the solution. For example, the composition of the leaching solution of the iron coprecipitation sludge, which is the major part of the sludge, is shown in **Table 1**. Where U as well as other elements are dissolved in a 3 M nitric acid solution. The efficient recovery of U from the leaching solution releasing a small amount of secondary wastes is required. The U-recovery ratio should be as large as possible to adopt regulations for geologic disposal, and the required purity of the recovered U depends on the usage of the product. The development assumes the tentative target uranium recovery to be 95%. Target purity will be discussed by considering possible applications of the product.

Solvent extraction with tributyl phosphate (TBP) is an established U-recovery procedure, utilizing a nitric acid medium to reprocess spent nuclear fuel [1]. U may be recovered from wastes in existing reprocessing plants. However, the U concentration in the leaching solution is far smaller than the dissolved solutions of spent nuclear fuel, and U recovery from the leaching solution with solvent extraction might be less efficient than the

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Table 1. Composition of a leaching solution of the iron coprecipitation waste.

Specie	UO_2	Na	Al	Si	Fe	Ba	P	HNO_3
Concentration	210 ppm	24 ppm	64 ppm	33 ppm	3800 ppm	2400 ppm	120 ppm	3 mol/L

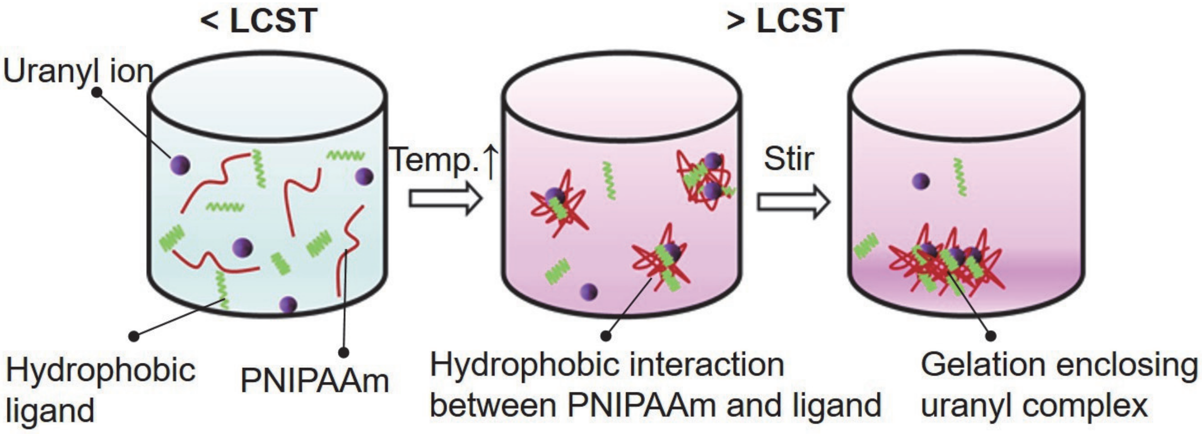

Figure 1. Uranium recovery concept by the temperature swing gelification technology.

reprocessing procedure. The concentration of the leaching solution requires a dedicated apparatus. The U-recovery operation generates several secondary wastes, such as spent solvents, although the technology easily achieves a high recovery ratio and purity. Thus, solvent extraction might be unsuitable for waste treatment.

Extraction chromatography applies to U recovery from a nitric acid medium, and fewer secondary organic liquid wastes are expected to be released [2-4]. The extraction chromatography uses the principle of solvent extraction, and chemical separation can be achieved through adsorption/desorption reactions on the adsorbent packed in a column. Although the technology is promising for efficient U recovery, the treatment and disposal of spent adsorbent is a crucial drawback.

Currently, we focus on temperature-swing gelification separation as an alternative technology to solvent extraction and extraction chromatography [5]. In this technology, a hydrophobic ligand and a polymer with reversible hydrophilic–hydrophobic properties, such as poly(*N*-isopropylacrylamide) (PNIPAAm), are used for the formation of complexes with target metal ions in the solution and the formation of polymer gel precipitation, respectively. When the PNIPAAm and the ligand are mixed in an aqueous solution containing target metal ions below Lower Critical Solution Temperature (LCST), the hydrophobic ligand can disperse into the solution due to hydrophobic interaction with isopropyl groups of PNIPAAm, resulting in the complexation of the target metal ions with the ligand. With increasing temperature above the LCST, the hydrophobic aggregation of PNIPAAm capturing the complexes is induced, and the complex-enclosing gel can be recovered (**Figure 1**) [6, 7]. Consequently, all organic compounds added into the solution and the target metal ions are recovered as precipitation. This procedure does not require organic diluent, and the ligand can be effectively separated from aqueous solutions. As the amount of the ligand and the polymer are easily adjusted for processing solutions, the technology can be flexibly applied to solutions with various compositions; therefore, the technology is promising to treat the leaching solution of the various U wastes.

In the previous studies, trivalent rare earth metals were effectively recovered from simulated high-level liquid waste containing several metal ions in nitric acid solution by the temperature swing gelification using a combination of the PNIPAAm and hydrophobic diglycolamide-type ligands [8]. Recovery performance depended on the coordination ability of the ligands toward rare earth ions, and the gelification procedure scarcely influenced the extraction behavior. The selection of an appropriate ligand is an important factor in achieving a promising treatment procedure for the U wastes.

Only U oxide can be obtained as a final product without releasing organic waste, given the organic compounds in the precipitation are completely decomposed into inorganic gas by heating. The polymer comprises C, H, O, and N and is expected to decompose completely into CO_2, NO_x, and H_2O by heating. Monoamides (**Figure 2**) comprising only C, H, O, and N are ideal extractants [9, 10]. The

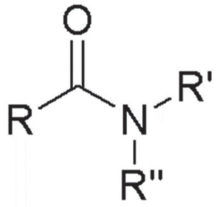

Figure 2. General structure of monoamides.
R, R′ and R″ are alkyl chains.

monoamides exhibit affinity toward tetravalent and hexavalent cations, and the U-recovery performance of the monoamides from a nitric acid medium has been widely studied for reprocessing applications. This study examines the feasibility of the temperature-swing gelification recovery employing monoamides to treat U-contained wastes through fundamental experiments on a simulated leaching solution. Batch-wise experiments with various polymers and extractants on a simulated solution containing Ce(IV) were performed to find appropriate operation conditions, and the U-recovery performance was demonstrated using the optimized conditions. Where Ce(IV) was used to determine general operation conditions through inactive experiments. The applicability of the technology to the U waste treatment was examined on a simulated liquid waste, which was prepared based on a composition of genuine leaching solution of the iron coprecipitation waste (Table 1). The heating of the U product and characterization of the final product were also conducted. Based on the experimental results, the applicability of the technology and future challenges for practical application are discussed.

2. Experimental

2.1. Selection of polymers

Poly(*N*-isopropyl acrylamide) (PNIPAAm), poly(*N*-isopropyl methacrylamide) (PNIPMAAm), poly(*N*, *N*-diethyl acrylamide) (PNDEAAm), and poly(*N*-ethyl acrylamide) (PNEAAm) were synthesized by radical polymerization (**Figure 3**). The LCST of those polymers in water and nitric acid solution were evaluated to be 308–318 K and 263–267 K for PNIPAAm, PNDEAAm, and PNIPMAAm in water and in 3 M HNO_3, respectively. For PNEAAm, the temperature was 361 K and 228 K in water and 3 M HNO_3, respectively. The LCST was determined by the light transmittance of polymer solutions at 500 nm measured using a UV–Vis spectrophotometer (V-630, JASCO Co.) equipped with a Peltier thermostatic cell holder (control accuracy: ±0.1 °C). The aqueous solution of the polymer was prepared by dissolving a given amount of polymer into each concentration of acid solution. The LCST in each solution was determined from the temperature-dependent plot of optical transmittance. The hydrophobic property of the polymers in acid is stronger than in water; thus, the temperatures in the acid are lower than in water.

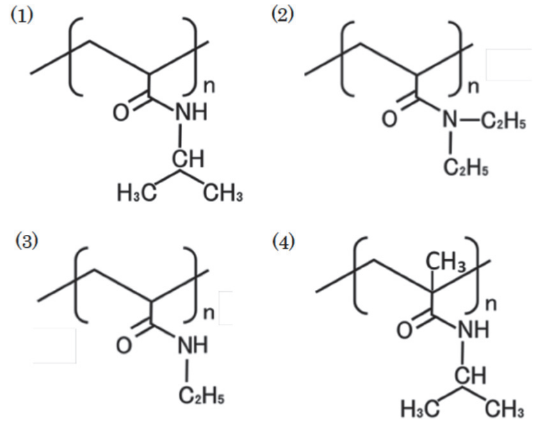

Figure 3. Polymers for the temperature swing extraction.
(1) PNIPAAm, (2) PNDEAAm, (3) PNEAAm, (4) PNIPMAAm

Temperature-swing gelification experiments with these polymers and a monoamide (N,N-di(2-ethylhexyl) decanamide; C10-BAMA) on the Ce(IV) solution were performed to evaluate the operability and gel formation performance, and 0.5 mmol of C10-BAMA was added in 50 mL of 3 M nitric acid solution containing 0.05 M Ce(IV) and mixed 30 min at room temperature to facilitate Ce(IV) extraction. The polymer dissolved in 2 mL of water with 1.25 mmol equivalent amount of the monomer was placed in the mixture and heated until precipitation formation was observed. The precipitation was recovered by filtering with a Poly-Prep® column. The Ce(IV) concentration in the filtered solution was determined by UV-Vis spectrum at 350 nm.

2.2. Selection of ligand

The hydrophobic property of the ligand is essential for efficient gel formation, and hydrophobic side chains in the monoamide are crucial. Here, the influence of the length of the side chain on phase separation was investigated through temperature-swing gelification experiments using monoamides with different side chain lengths (*N*,*N*-di(2-ethylhexyl)decanamide (C10-BAMA) and N,N-di(2-ethylhexyl)tetradecanamide (C14-BAMA)) on the Ce(IV) solution. Experiments with trihexylphenylphosphate (THHP), designed to possess longer side chains than TBP, were also conducted. TBP is unsuitable for gel formation due to its tendency to exhibit minute hydrophobicity. For the THHP, benzene rings were introduced at side chains of TBP, and hexyl chains were attached to the rings to enhance their hydrophobic nature. **Figure 4** shows the structure of the ligands used in the experiments. Temperature-swing gelification experiments with an appropriate polymer selected in previous experiments were conducted using the procedure shown in the previous section.

2.3. Uranium recovery test

Temperature-swing gelification of U from a simulated leaching solution was conducted by combining an appropriate polymer selected in 3.1 and an extractant selected in 3.2. The composition of the simulated solution based on a genuine leaching solution of iron coprecipitation sludge is the same as that shown in Table 1. The experimental procedure was the same as in 2.1, and cation concentrations in the solution were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4. Heating of the uranium product

For the organic compound decomposition of the U product via heating, appropriate operation conditions are

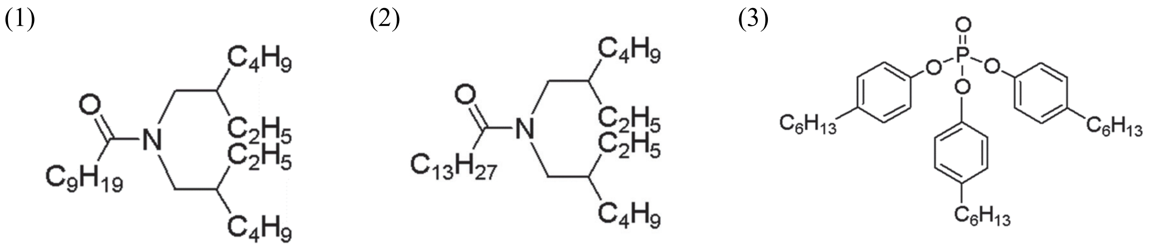

Figure 4. Extractants used in the experiments.
(1) C10-BAMA, (2) C14-BAMA, (3) THHP

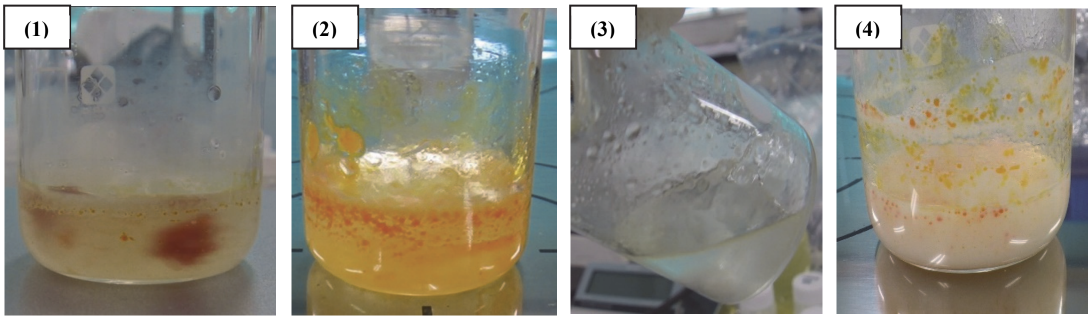

Figure 5. Appearances of the gel.
(1) PNIPAAm, (2) PNDEAAm, (3) PNEAAm, (4) PNIPMAAm

discussed based on thermogravimetry (TG)/differential thermal analysis (DTA) on the product obtained in 3.3. In this analysis, 10 mg of the sample was heated to 1073 K at 10K/min under an atmospheric environment. Then, 5 mL of the gelification product in an Al_2O_3 crucible was heated with the determined appropriate operation conditions. X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) analyses were conducted on the heated product to elucidate the chemical form of the product. EXAFS was performed at the BL27B beamline of the Photon Factory in the High Energy Accelerator Research Organization, Japan.

3. Results and discussion

3.1. Selection of polymer

The gels formed in the experiments were separated from the aqueous phase by filtering, and oil droplets on the surface of the solution were visually checked. A considerable amount of Ce(IV) was not observed in any filtered solutions. The monoamide must sufficiently extract the Ce(IV). **Figure 5** shows the appearance of the gel formed during the experiments. Gel formation was observed for PNIPAAm and PNIPMAAm at approximately 323 K, whereas gel formation was limited for PNDEAAm and PNEAAm at temperatures exceeding 355 K. The interaction of the polymer with the hydrophobic part of the ligand is crucial for gel formation, and different polymer structures influence the gel formation behavior. PNDEAAm lacks an amide bond in the molecule, and PNEAAm exhibits an anisotropic structure around the N atom. These properties could potentially explain the poor affinity to the ligand.

The gel formed in the PNIPAAm system was lodged against the stirring bar, tendering it unable to encompass all ligands, and a part of the extractant remained in the aqueous phase. However, no extractant remained in the PNIPMAAm system, and the precipitation was easily collected by filtration. Regarding operability, PNIPMAAm is deemed suitable for temperature swing gelification.

3.2. Selection of ligand

Based on the results of the previous section, PNIPMAAm was selected as the appropriate polymer. All extractants successfully formed gels with PNIPMAAm at approximately 323 K, as seen in previous experiments, and organic compounds did not remain in the aqueous phase following gel separation. However, it was observed that the ligands did not exhibit a high degree of dependence on the phase separation performance. C10-BAMA exhibits hydrophobic properties conducive to gel formation, and further elongation in the side chain does not yield explicit benefits. However, elongation in the side chain in TBP succeeded in temperature-swing gelification. Modifying the structure of ligands enhances the phase separation performance. Therefore, the most appropriate monoamide structure should be selected based on the gel formation performance with monoamides with shorter side chains. C10-BAMA is more cost-effective than C14-BAMA owing to the lower price of raw materials. Herein, C10-BAMA was selected as the superior ligand. The subsequent step will explore the optimization of the structure.

Table 2. Distribution coefficient obtained by the temperature swing extraction experiment.

U	Na	Al	Si	Fe	Ba	P
1.1×10^{1}	8.6×10^{-1}	9.2×10^{-1}	2.0×10^{1}	9.8×10^{-1}	9.9×10^{-1}	6.9×10^{-1}

3.3. U-recovery test

Temperature-swing gelification recovery experiments employing C10-BAMA with PNIPMAAm successfully recovered 70% of U. At least three operation stages are required to achieve the target recovery ratio (95%). **Table 2** shows the distribution ratios K_d of the elements in the simulated solution obtained by the following equation,

$$K_\mathrm{d} = \frac{[\mathrm{M}]_\mathrm{gel}}{[\mathrm{M}]_\mathrm{aq}} \qquad (1)$$

$[\mathrm{M}]_\mathrm{gel}$: Concentration of element M in gel phase [mol/L]
$[\mathrm{M}]_\mathrm{aq}$: Concentration of element M in the aqueous phase [mol/L]

where the volume of the gel and the concentration of metals in the gel were measured with a graduated cylinder and calculated from the concentrations in the aqueous solution, respectively.

Except for Si and U, the distribution coefficients of the coexisting elements were approximately 1. These results suggest that those elements were incorporated into the product in the form of an aqueous phase rather than being complexed with the monoamide. The elemental compositions, except for Si and U, in the solution obtained via centrifugal separation of the product precipitation were similar to that of the initial solution; therefore, water removal from the temperature-swing extraction product should be incorporated to achieve the target U purity. Because monoamides do not exhibit affinity to Si, interaction with the polymer may influence the behavior of Si. Optimization in the polymer, additional Si decontamination, or modifications in the process should be considered to improve the purity of U. Detailed interaction of Si with the polymer is required to be investigated for the optimization. Information obtained by this experiment will contribute to the design of practical instruments for industrial applications. Scale-up studies, engineering-scale apparatus design, and process optimization will be conducted for the required throughput and U-recovery performance.

3.4. Heating of the U product

Figure 6 shows the TG/DTA curves of the gel precipitations obtained in 3.3, where curves of gel precipitations prepared using a pure nitric acid solution were also shown as a reference. In the temperature range of 373-473 K, an endothermal and an exothermal peak were observed for the organic compounds, and approximately 50% of the weight was lost within this temperature range. The weight loss continued to persist up to 773 K, accompanying small exothermal peaks, and no sample remained after the analysis. This weight-loss behavior is attributed to the vaporization of water and thermal decomposition of the organic compounds. Distinct endothermal peaks were observed at 298–473 and 573–673 K for the gel containing U. The former peak was also observed in the organic compounds, whereas the latter peak might be attributed to nitrate ion decomposition and/or U oxidation. The weight changes were completed at 873 K, and all oxidation reactions are regarded as fully completed. Therefore, the heating temperature was set at 873 K.

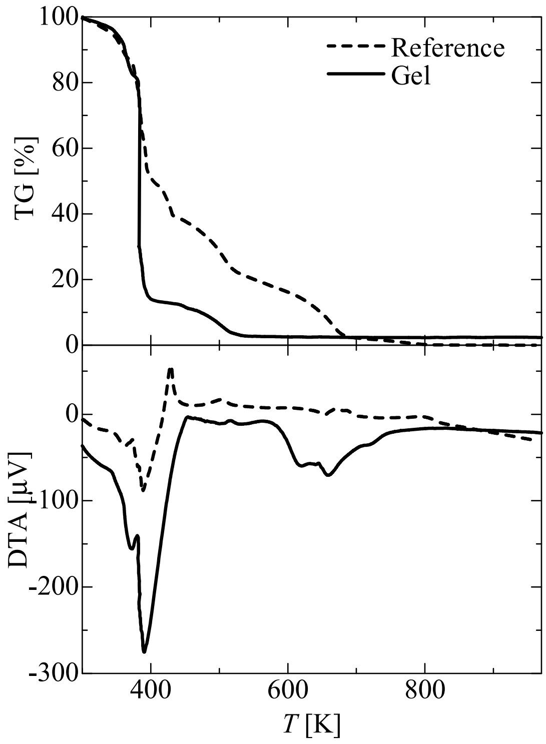

Figure 6. TG/DTA curves of the gels and organic compounds.

The U product obtained by temperature-swing gelification operation was heated to 873 K at 30 K/min under an atmospheric environment and maintained for 4 h. The heated product was a brown-black powder (**Figure 7**). **Figure 8** shows the XRD patterns of the products. Some characteristic XRD peaks were assigned to be uranium oxide products. These results indicate that the heating oxidized all uranium in the gel. However, some XRD peaks could not be assigned to the uranium compounds, and those might be attributed to impurities such as Si. **Figure 9** shows the EXAFS oscillations extracted from the X-ray absorption spectrum using the cubic spline method, where the k^3 weight was multiplied by the oscillation to emphasize the oscillations at the high k region. Data analysis was carried out using WinXAS 2.3 software [11]. The EXAFS oscillation of the heated gel

Figure 7. Appearance of the calcination product.

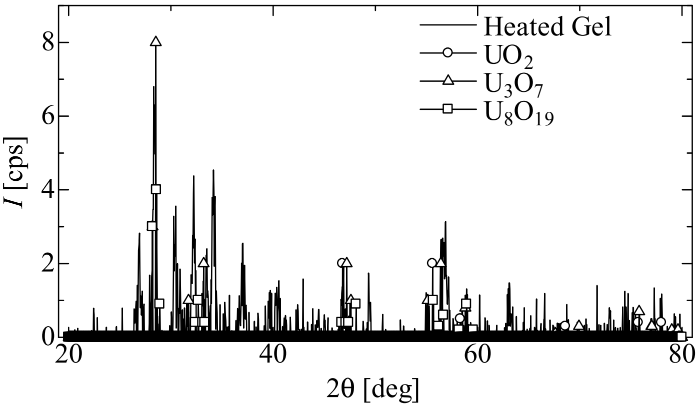

Figure 8. XRD pattern of the calcination product.

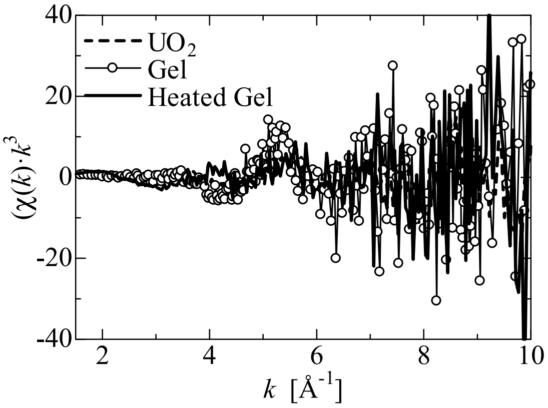

Figure 9. EXAFS oscillations of the gel and the heated gel.

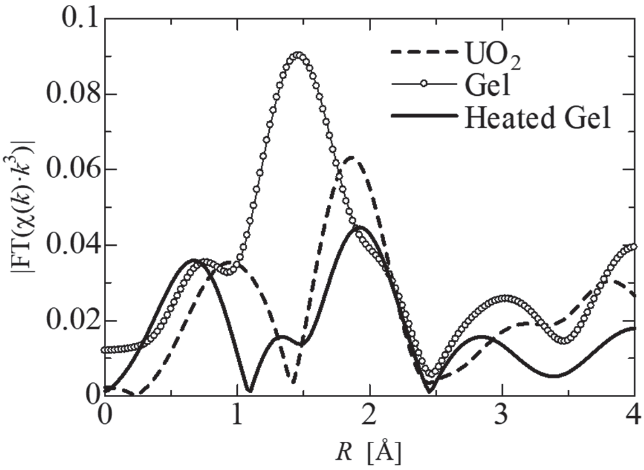

Figure 10. Radial distribution functions obtained by EXAFS.

slightly differs from other oscillations in its phase. The result suggests the difference in interatomic distance between a uranium atom and the nearest nonboring atom. The heating treatment influenced the local structure around uranium. Radial functions around uranium obtained by Fourier transformation of the EXAFS oscillations are shown in **Figure 10**. The difference in the oscillation leads to different peak positions of the radial structure functions. An UO_2^{2+} ion forms a complex with the monoamide and nitrate ions as $UO_2(NO_3)_2$(C-10BAMA)$_2$ form in nitric acid solution [12, 13]; thus, a dominant peak at 1.5 Å in the radial structural function is U–O interaction inside the UO_2^{2+} ion. Whereas, the radial structure function of the heated gel is similar to that of UO_2. The heat treatment must progress the decomposition of the complex. Further detailed investigations on these compounds must be done for a more detailed characterization of the product. Consequently, the gel produced by the temperature-swing gelification product can be transformed to U oxides by heating through organic compound decomposition and nitrate and metal ion oxidation.

4. Summary

The feasibility of temperature-swing gelification separation technology employing a monoamide extractant to treat U-contaminated waste was experimentally investigated. Regarding operability, PNIPMAAm was selected as an appropriate polymer for effective gel formation and separation from the aqueous phase. Monoamides exhibiting sufficient hydrophobic properties successfully extracted U from a nitric acid medium, and the complex was separated from the aqueous phase as precipitation. The gel product could be transformed into oxide by heating. The results showed that temperature-swing gelification is a potential technology for the waste treatment procedure, although some improvements or modifications in the process conditions are required.

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