Stability of pyrrolidone derivatives against γ-ray irradiation

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To evaluate the stability of *N*-alkylated pyrrolidone derivatives (NRPs), which are supposed to be used as precipitants for U(VI) and Pu(IV, VI) species in HNO_3 media, under irradiation environment, some candidate NRPs were irradiated by γ-ray. Irradiation to HNO_3 solutions up to 6 mol dm^{-3} (= M) containing 2 M *N*-*n*-butyl-2-pyrrolidone (NBP), one of NRPs with lower hydrophobicity, has revealed that the residual ratios of NBP in the samples of HNO_3 up to 3 M decreased identically and linearly. Approximately 20% of NBP was found to be degraded after the irradiation at 1 MGy. It was also found that the decrease in the precipitation ratio of UO_2^{2+} (P.R., %) was gentle and that the P.R. values were relatively in accordance with the residual ratios of NBP. On the other hand, the degradation of the samples irradiated in 6 M HNO_3 was found more distinguished. It was proposed from the analyses of degraded compounds that the degradation of NBP in HNO_3 by γ-ray irradiation started from the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from HNO_3, followed by the formation of chain compounds by the successive addition of oxygen, leading to the generation of oxalic acid and acetic acid. The stability of other NRPs in 3 M HNO_3 was evaluated to be nearly identical with that of NBP except lower P.R. values of the samples containing NRPs with higher hydrophobicity irradiated at more than 0.5 MGy.

pyrrolidone derivatives, precipitants, γ-ray irradiation, HNO_3, U(VI)

1   Introduction

Some of *N*-alkylated pyrrolidone derivatives (NRPs, Figure 1) are water-soluble and have precipitation ability to actinoid (An) (IV, VI) species in nitric acid media. The selectivity to both species is controlled by changing the structure of the side chain, R. We have been developing a novel reprocessing system for spent fuels of fast breeder reactors based on two precipitation processes using the above nature of NRPs [1–7]. In this system, only U(VI) species firstly precipitate in HNO_3 solutions dissolving spent fuels by using a water-soluble NRP with low hydrophobicity and donicity which bring lower precipitation ability. Secondly the residual U(VI) and Pu(IV, VI) precipitate simultaneously using another water-soluble NRP with higher precipitation ability. It is necessary to evaluate the stability of NRPs under irradiation environment for practical use in a reprocessing plant. A lot of irradiation studies in HNO_3 media have been carried out for chain-amide-type extractants. As the results, the effect of acid concentration, identification of degraded compounds, etc. have been reported [8–11]. On the other hand, irradiation studies for cyclic amides including NRPs are missing. In this study, stability of some candidate NRPs against γ-ray irradiation in HNO_3 and the mechanism for

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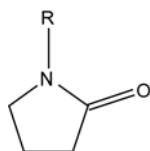
Figure 1 Chemical structure of NRP.

degradation were investigated.

2 Experimental

2.1 Irradiation of NRPs

HNO$_3$ solutions up to 6 mol dm^{-3} (= M) containing 2 M *N-n*-butyl-2-pyrrolidone (NBP), one of NRPs with lower hydrophobicity, were put into Pyrex glass tubes. γ-Ray irradiation from the ^{60}Co source was performed up to 1 MGy at room temperature under ambient atmosphere. As dose rate 13.0 kGy h^{-1} was applied unless otherwise noted. Similar irradiation experiments were carried out for 3 M HNO$_3$ solutions containing other NRPs (2 M), respectively, where NRPs were *N-n*-propyl-2-pyrrolidone (NProP), *N-iso*-butyl-2-pyrrolidone (NiBP), *N*-(1,2-dimethyl)propyl-2-pyrrolidone (NDMProP), *N*-neopentyl-2-pyrrolidone (NNpP), and *N*-cyclohexyl-2-pyrrolidone (NCP). Among the six examined NRPs, we have categorized NBP, NProP and NiBP into NRPs with lower hydrophobicity and the rest three into NRPs with higher hydrophobicity.

2.2 Evaluation of irradiated NRPs

The irradiated sample solutions of NRP were analyzed by a high performance liquid chromatograph (HPLC) to determine the residual ratio of NRP. *N-n*-octyl-2-pyrrolidone (NOP) was added to the irradiated sample as the internal standard material. For the analysis, a column (Phenomenex, Luna 5 μ C8(2), 4.6 mm dia. × 150 mmH) and a UV detector (214 nm) were used with a mobile phase consisting of methanol/H$_2$O = 80:20 (vol%) at a flow rate of 1 cm^3 min^{-1}. The residual ratio of NRP was evaluated by normalizing each peak area of NRP by that of NOP.

To examine the dependence of the precipitation ability to U(VI) (UO$_2^{2+}$) on dose, an aliquot of the irradiated sample solution was added to a 3 M HNO$_3$ solution containing 1 M UO$_2^{2+}$ at the ratio of [NRP]/[UO$_2^{2+}$] = 1.4, under which condition max. 70% of UO$_2^{2+}$ is supposed to precipitate, because two NRP molecules are necessary for precipitating one molecule of UO$_2^{2+}$ [2]. The mixture was stirred vigorously with a vortex mixer, followed by standing for 1 h at room temperature and centrifuging. The concentration of UO$_2^{2+}$ in the supernatant was determined by ICP-AES. The precipitation ratio of UO$_2^{2+}$ (P.R., %) was calculated based on the assumption that the sum of the volume of sample solution containing NRP and that of HNO$_3$ remains unchanged before and after mixing regardless of the nature of the degraded compounds, as,

$$\text{P.R.} = 100 \times ([U]_I - [U]_S)/[U]_I$$

where $[U]_I$ and $[U]_S$ are the concentrations of UO$_2^{2+}$ in the HNO$_3$ solution before precipitation and those in supernatant liquids after precipitation, respectively.

2.3 Investigation of degradation mechanism

To investigate the degradation mechanism of NRPs by γ-ray irradiation, some instrumental analyses were performed for the irradiated samples. The samples of NBP irradiated in 3 M HNO$_3$ were analyzed by ion chromatography (IC) to identify and quantify anionic degraded compounds using a column (Dionex AS12A) and an eluent consisting of 0.3 mM NaHNO$_3$ and 2.7 mM Na$_2$CO$_3$. Potassium hydrogen phthalate (KHP) was added as the internal standard material to the irradiated sample at the time of dilution.

The irradiated samples of NNpP and NCP were analyzed by liquid chromatography mass spectrometry (LC-MS: Waters micromass ZQ) without using the fractionation function of LC. Two 6 M HNO$_3$ solutions containing 2 M NNpP or NCP were used as the sample solutions. They were irradiated for 43 h (0.35 and 0.21 MGy, respectively) under heating at 50 °C. The heating was added with expectation that the degradation might be enhanced. As the results of the treatment, the two samples split into two phases, respectively. For the analysis, the "organic-rich" phase of NNpP and NCP was sampled and diluted with 50% aqueous acetonitrile solution. Aqueous methanol solution (50%) was used as the mobile phase at a flow rate of 1 cm^3 min^{-1}. Temperatures of the source and the desolvation were 70 and 200 °C, respectively, with APCI for the ionization mode.

The irradiated sample solutions of NBP were also analyzed by ^{1}H and ^{13}C NMR (JEOL 400 MHz, solvent: dimethyl sulfoxide-d6) mainly to identify water-soluble degraded compounds. A 6 M HNO$_3$ solutions containing 2 M NBP was used as the sample solution. It was irradiated for 43 h (0.28 MGy) under heating at 50 °C. It was expected that the resulting sample still had undegraded NBP. It is known that NRPs work as extractants in liquid-liquid extraction systems using organohalide diluents such as dichloromethane [12]. Therefore, most of NBP was removed using CDCl$_3$ in order to avoid the overlap of the peaks of water-soluble degraded compounds with those of NBP.

3 Results and discussion

3.1 Evaluation of irradiated NRPs

For NBP, oily drops were observed in the samples irradiated in 6 M HNO$_3$ at 0.48 MGy and more. The drops disappeared during standing for a few days after the end of irradiation. Also, a gas continued to generate from all samples

irradiated in 6 M HNO$_3$. On the other hand, almost no changes in the appearance were observed for NBP samples except coloration in the samples of HNO$_3$ of lower concentrations. The dependence of the residual ratio of NBP on dose is shown in Figure 2. It is found that the residual ratios of the samples for HNO$_3$ solutions up to 3 M decrease identically and linearly with increasing dose. This indicates that the coloration in the samples of HNO$_3$ of lower concentrations has very little influence on the residual ratios. Approximately 20% of NBP is found to be degraded after the irradiation at 1 MGy. Applying the above results to the first precipitation process using a NRP with lower hydrophobicity in our reprocessing system, e.g. 10 kGy h^{-1} of dose rate and 1 h of retention time, it was estimated that only 0.2% of NRP is decomposed. On the other hand, the degradation of the samples irradiated in 6 M HNO$_3$ is found to be more distinguished. The residual ratios at the irradiation from 0.1 to 0.85 MGy are ca. 70% regardless of dose in those regions. The reason of the distinguished difference in the residual ratio of the concentration of HNO$_3$ during irradiation between up to 3 M and 6 M still remains unknown. There may be some thresholds. Further investigations are necessary.

Stability against γ-ray irradiation for chain monoamide compounds, e.g., *N,N*-dioctylhexanamide, which are developed as extractants with selectivity to U(VI) in HNO$_3$, has been investigated. As the results, it has been clarified that the residual ratios decreased identically and linearly with increasing dose and reached 85% to 90% at 0.5 MGy [11]. Direct comparison on the stability between the extraction and our precipitation systems is impossible because the experimental conditions are different. For example, NBP and extractants are dissolved in an aqueous solution and organic diluents such as dodecane, respectively, during irradiation. Nevertheless, the stability of the two systems would be comparable as far as the residual ratio is concerned.

For the other NRPs irradiated in 3 M HNO$_3$, almost no changes were observed in the appearances of the sample solutions of NRPs with lower hydrophobicity such as NProP and NiBP. However, those of NNpP and NCP which

have higher hydrophobicity were found to be split into two phases before the irradiation at 1 MGy and 0.2 MGy, respectively. The two phases then were merged by standing at room temperature for several weeks or months after the end of irradiation. The ease of the splitting was in accordance with the hydrophobicity of NRPs. This means that some degraded compounds generated in the earlier stage of irradiation are more hydrophobic than the corresponding NRP. It was also found that the upper layer was the "organic-rich" phase for NNpP and the opposite for NCP. The changes in the residual ratio of NProP and NiBP as a function of dose are shown with that of NBP in Figure 3. As can be seen, the tendency of degradation is nearly identical among the three NRPs. The residual ratios of NRPs with higher hydrophobicity have not been analyzed due to the splitting behavior of NNpP and NCP.

Dependence of P.R. of NRPs with lower hydrophobicity irradiated in 3 M HNO$_3$ on dose is shown in Figure 4. It is found that the decrease in P.R. values is gentle and that each P.R. value is in accordance with the residual ratio of NRP within the error of ca. 10%. This may indicate that the degraded compounds hardly affect the P.R. values under these conditions and that all these precipitants have nearly equiv-
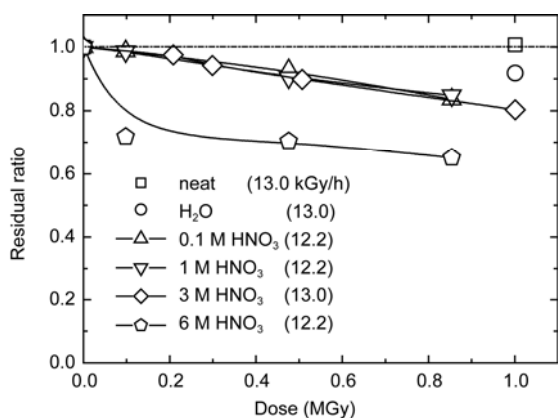
Figure 3 Change in residual ratio of NRPs with lower hydrophobicity irradiated in 3 M HNO$_3$ versus dose.

Figure 2 Change in residual ratio of NBP irradiated in HNO$_3$ of various concentrations versus dose.
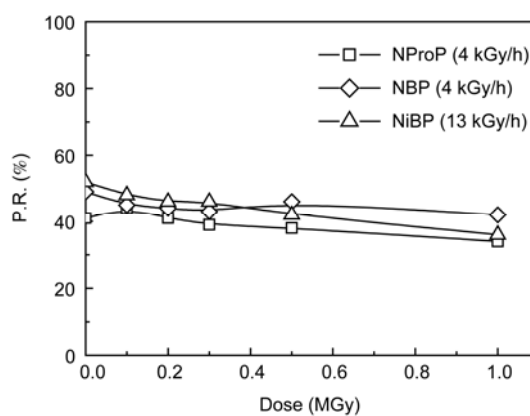
Figure 4 Dependence of P.R. of NRPs with lower hydrophobicity irradiated in 3 M HNO$_3$ on dose.

alent stability enough to be used for multiple precipitation cycles by an appropriate recovery method. The effect of the changes in P.R. values of NRPs with lower hydrophobicity irradiated at 0.5 MGy as a function of dose rate from 2 to 13 kGy h^{-1} is shown in Figure 5. It would be evaluated that all P.R. values are nearly identical and, therefore, that dose rate is independent of the degradation of NRPs under the examined conditions, although we have not examined the dependence of the residual ratio of NRP on the dose rate.

Dependence of P.R. of NRPs with higher hydrophobicity irradiated in 3 M HNO$_3$ on dose is shown in Figure 6. It is found that all three NRPs have similar P.R. values with those of NRPs with lower hydrophobicity up to ca. 0.5 MGy. But the decrease is more distinguished over 0.5 MGy, particularly those of NNpP and NCP. It can also be seen that the variabilities of P.R. values are greater than those for NRPs with lower hydrophobicity. The above trend would mainly result from the splitting behavior of the sample solutions. Namely, some samples were heterogeneous and the sample taken might not reflect the real components in spite of sufficient stirring before sampling.

The above results indicate that max.ca. 3 M may be desirable as the concentration of HNO$_3$ for the precipitation operation from the viewpoint of the stability of NRPs. In the present study, the stability was evaluated by the residual ratio and P.R., i.e., the precipitation ratio of UO$_2^{2+}$. However, changes in the precipitation ability of irradiated NRPs to Pu(IV, VI) species are also important, and they should be investigated in the future.

3.2   Investigation of degradation mechanism

The results of IC are shown in Figure 7. A distinguished peak assigned as oxalic acid (OX) is identified at around 12.5 min and the peak height is found to increase with increasing dose, which indicates that OX is a major final degraded product of irradiated NBP. It can also be seen from the chromatograms that the concentration of HNO$_3$ decreases with increasing dose. Other smaller peaks are observed in the retention time ranging from 2 to 4 min but the identification has not been made. The change in the concentration of OX calculated from Figure 7 is shown in Figure 8. By combining the results of Figure 8 with those of the above HPLC (Figure 2), it was evaluated that ca. one fourth to one third of the degraded NBP turned into OX, meaning that the rest is other degraded products.
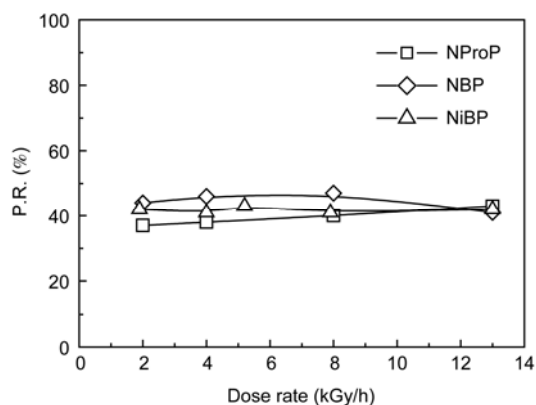

Figure 5   Dependence of P.R. of NRPs with lower hydrophobicity irradiated in 3 M HNO$_3$ for 0.5 MGy on dose rate.
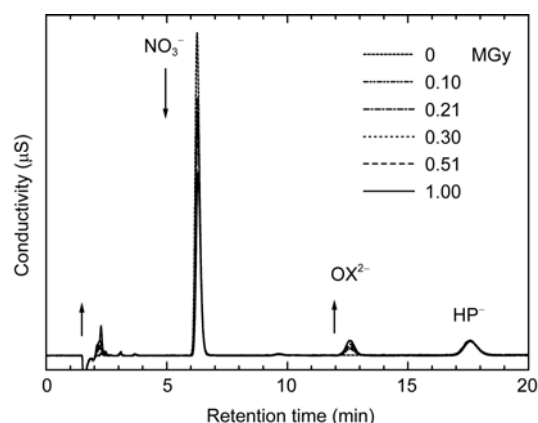

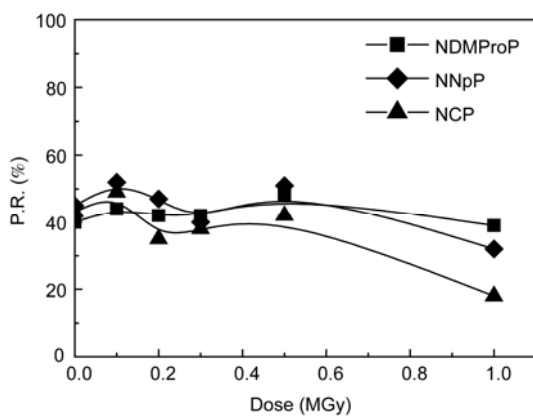**Figure 7**   Change in ion chromatogram of NBP irradiated in 3 M HNO$_3$.

Figure 6   Dependence of P.R. of NRPs with higher hydrophobicity irradiated in 3 M HNO$_3$ on dose.
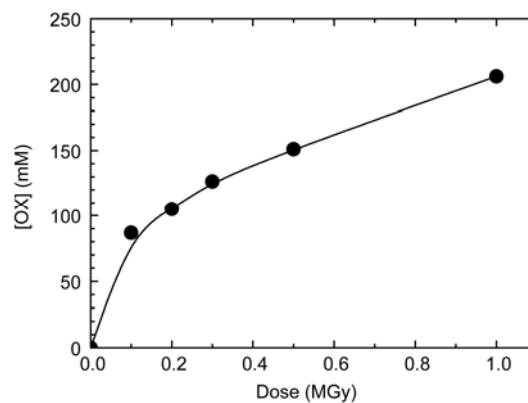

Figure 8   Change in concentration of OX generated from NBP irradiated in 3 M HNO$_3$ versus dose.

Decomposition behavior of OX by γ-ray irradiation in HNO₃ was then examined. A HNO₃ solution of various concentrations containing 180 mM OX was irradiated in a similar manner at room temperature and analyzed by IC. The change in the concentration of OX as a function of dose is shown in Figure 9. It can be seen that, contrary to the results for NRPs, decomposition of OX proceeds more rapidly with decreasing concentration of HNO₃ and more slowly than the generation of OX by degradation of NBP irradiated in 3 or 6 M HNO₃. This suggests that OX may accumulate in many irradiated samples with increasing dose in our system. In fact, colorless and transparent crystals were observed in some irradiated samples by standing at room temperature for several weeks or months after the end of irradiation, and they were identified as OX.

The MS spectra of organic-rich phase in the irradiated samples of NNpP and NCP are shown in Figure 10, respectively. The lower limit of determination for *m/z* is set to 120, because the detection of relatively hydrophobic compounds was intended. These spectra clearly show that the peaks appear at nearly identical *m/z* values for both samples. In addition, as the corresponding *m/z* values are underlined in the figure, almost all peak intervals of *m/z* are found to be the multiples of 16. These results suggest that major degraded compounds of NRPs with higher molecule possess plural oxygen atoms regardless of the structure of the side chain of pyrrolidone ring.

The ¹³C and ¹H NMR spectra are shown in Figures 11 and 12, respectively. For Figure 11, the signal which should be attributed to the carbon atom of OX is detected at ca. 161 ppm. Other new peaks appear at around 85 and 170–175 ppm. They would be assigned to carbon atoms bonded to hydroxyl group and those attributed to carboxyl or aldehyde groups, respectively. Figure 12 suggests that *n*-butylamine, acetic acid, and propionic acid are included and butyric acid is not included in water-soluble degraded compounds of NBP. The signal of acetic acid was found to increase with increasing dose as the results of the analyses for other irradiated samples of NBP.

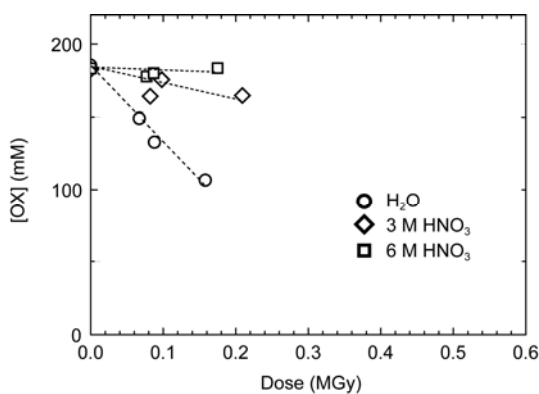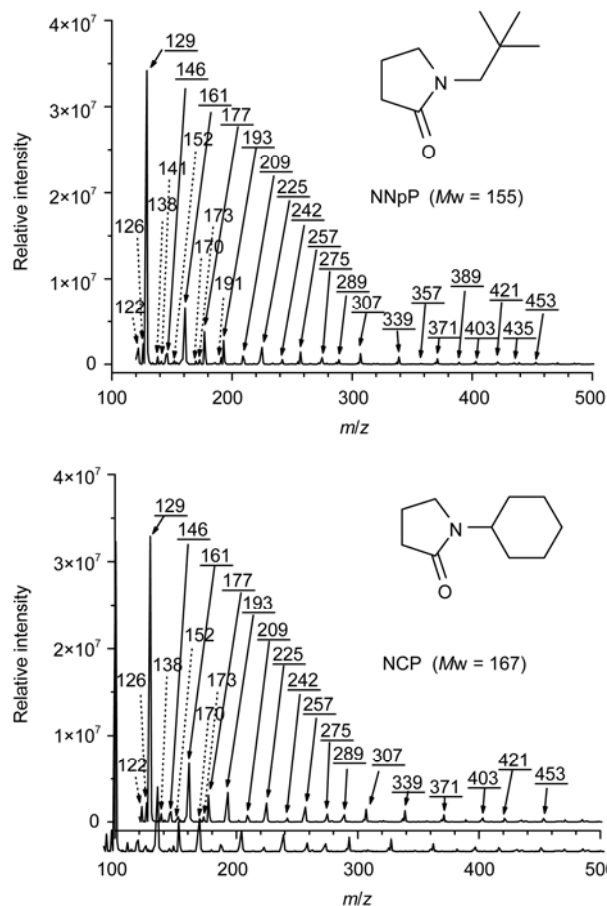From the above results, the degradation route of NBP in

Figure 10 MS spectra of organic-rich phase of degraded NNpP (up) and NCP (down), positive charge.

HNO₃ by γ-ray irradiation shown in Figure 13 may be proposed. Namely, the degradation of NBP starts from the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from HNO₃, followed by the formation of chain compounds by the successive addition of oxygen, leading to the generation of OX and acetic acid. Some of the OX further decompose to CO₂. The rate, however, is slower than that of the generation of OX and it accumulates in the sample as mentioned above. Acetic acid would be produced from the side butyl group through propionic acid. The decrease in the concentration of HNO₃ with increasing dose seen in the IC analysis is consistent with the above explanation. A lot of compounds are described in Figure 13, but it does not mean all of them are stable. For Figure 10, not a few *m/z* values are larger than the molecular weights of NNpP (*M*w: 155) or NCP (*M*w: 167) for each sample, ranging to several hundreds. This may result from, e.g., the formation of the trimer (trioxane) by polycondensation of compound (A) in Figure 10. This reaction accompanies dehydration and, therefore, is more likely to occur during heating and desolvation of the sample in the MS analysis than during irradiation of the aqueous sample solution. The explanation of the large *m/z* values remains as a task.
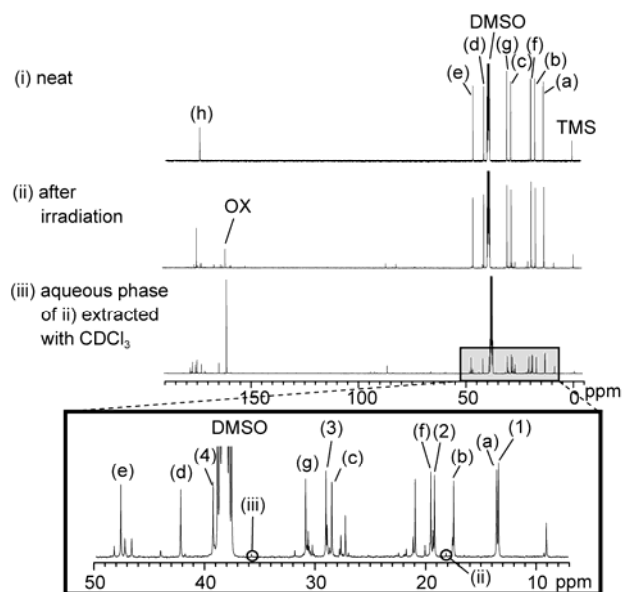
Figure 9 Change in concentration of OX irradiated in HNO₃ of various concentrations versus dose.

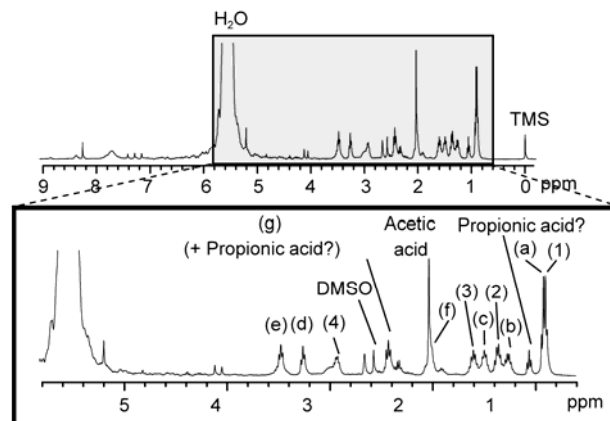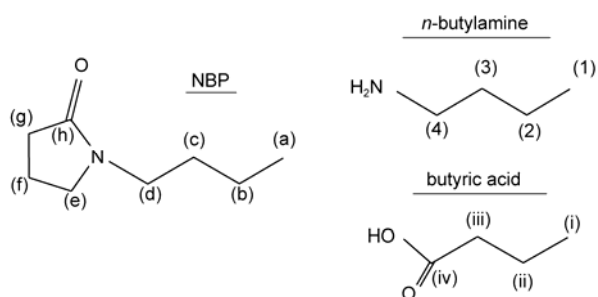**Figure 11** ^{13}C NMR spectra of NBP irradiated in 6 M HNO$_3$, 50 °C, 0.35 MGy, 43 h.

Figure 12 ^{1}H NMR spectra of aqueous phase of NBP extracted with CDCl$_3$ after irradiation in 6 M HNO$_3$, 50 °C, 0.35 MGy, 43 h

It is expected that the similar degradation routes apply to the other NRPs. The formation of oily drops and the split of the sample solutions into two phases seen in NBP, NNpP and NCP, respectively, suggests the high possibility that the degraded compounds generated in the earlier stage shown in Figure 13 are more hydrophobic than the corresponding initial NRPs.

It is known that the decomposition behavior of chain-amide-type extractants in HNO$_3$ by γ-ray irradiation is relatively simple, because the cleavage of the amide bond mainly occurs [8, 9]. Besides, it has been reported that the resulting main degradation products of carboxylic acids and secondary amines hardly affect the separation of U(VI) and
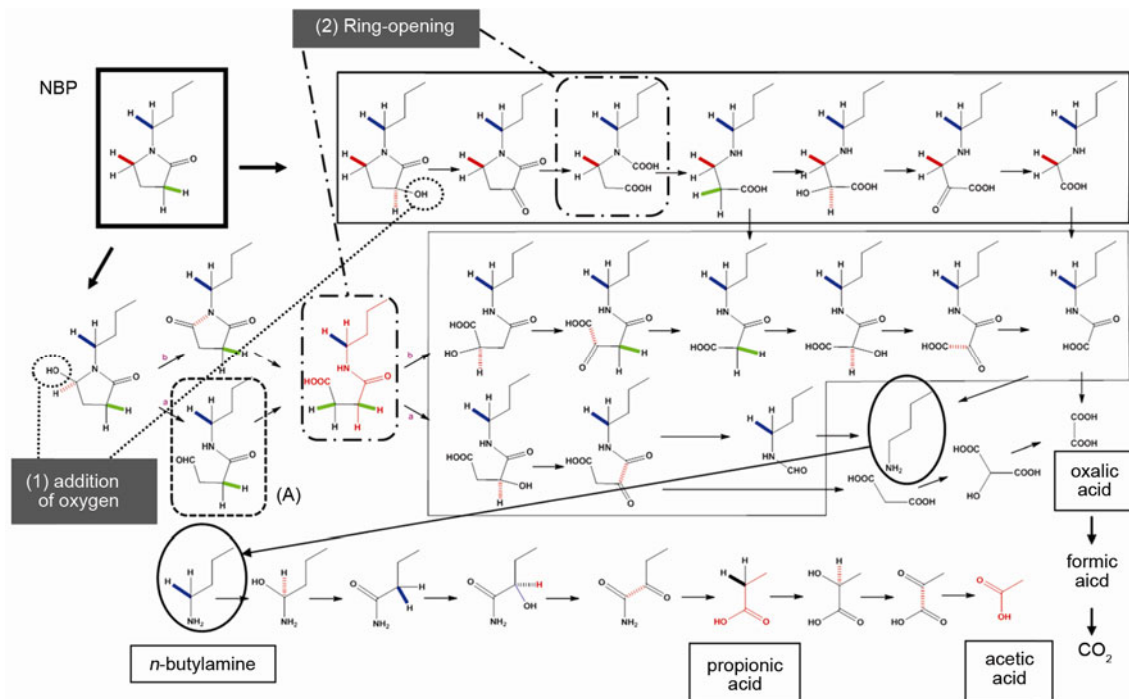

Figure 13 Expected degradation routes of NBP by γ-ray irradiation in HNO$_3$

Pu(IV) [8, 11]. While, it was clarified that the decomposition of NRPs is more complicated as explained above. Many of the degraded compounds may coordinate U(VI), Pu(IV, VI), other actinoid species, and some fission products in HNO_3, considering the chemical structure including oxygen atoms. This would lead to the decrease in the selectivity to U(VI) and Pu(IV, VI) species and, therefore, should be investigated in the future.

4 Conclusion

γ-Ray irradiation to NRPs in max. 6 M HNO_3 revealed that the residual ratios of NBP, one of NRPs, in the samples of HNO_3 up to 3 M decreased identically and linearly. Approximately 20% of NBP was found to be degraded after the irradiation at 1 MGy, and the stability was evaluated as the same level as that of monoamide extractants. It was also found that the decrease in the precipitation ratios of UO_2^{2+} were relatively in accordance with the residual ratios of NBP. On the other hand, the degradation of the samples irradiated in 6 M HNO_3 was found more distinguished. It was proposed from the analyses of degraded compounds that the degradation of NBP in HNO_3 by γ-ray irradiation starts from the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from HNO_3, followed by the formation of chain compounds by the successive addition of oxygen, leading to the generation of oxalic acid and acetic acid. The stability of other NRPs in 3 M HNO_3 was found to be nearly identical with that of NBP.

1 Varga TR, Sato M, Fazekas Z, Ikeda Y, Tomiyasu H. New uranyl nitrate complex with *N*-cyclohexyl-2-pyrrolidone: A promising candidate for nuclear fuel reprocessing. *Inorg Chem Commun*, 2000, 3: 637–639

2 Varga TR, Benyei AC, Fazekas Z, Tomiyasu, H, Ikeda Y. Molecular and crystal structure of bis(*N*-cyclohexyl-2-pyrrolidone)dioxouranium(VI) nitrate. *Inorg Chim Acta*, 2003, 342: 291–294

3 Ikeda Y, Wada E, Harada M, Chikazawa T, Kikuchi T, Mineo H, Morita Y, Nogami M, Suzuki K. A study on pyrrolidone derivatives as selective precipitant for uranyl ion in HNO_3. *J Alloys Compd*, 2004, 374: 420–425

4 Koshino N, Harada M, Morita Y, Kikuchi T, Ikeda Y. Development of a simple reprocessing process using selective precipitant for uranyl ions–Fundamental studies for evaluating the precipitant performance. *Prog Nucl Energy*, 2005, 47: 406–413

5 Morita Y, Kawata Y, Mineo H, Koshino N, Asanuma N, Ikeda Y, Yamasaki K, Chikazawa T, Tamaki Y, Kikuchi T. A study on precipitation behavior of plutonium and other transuranium elements with *N*-cyclohexyl-2-pyrrolidone for development of a simple reprocessing process. *J Nucl Sci Technol*, 2007, 44: 354–360

6 Takao K, Noda K, Nogami M, Sugiyama Y, Harada M, Morita Y, Nishimura K, Ikeda Y. Solubility of uranyl nitrate precipitates with *N*-alkyl-2-pyrrolidone derivatives (Alkyl = *n*-propyl, *n*-butyl, *iso*-butyl, and cyclohexyl). *J Nucl Sci Technol*, 2009, 46: 995–999

7 Morita Y, Takao K, Kim SY, Kawata Y, Harada M, Nogami M, Nishimura K, Ikeda Y. Development of advanced reprocessing system based on precipitation method using pyrrolidone derivatives as precipitants Precipitation behavior of U(VI), Pu(IV), and Pu(VI) by pyrrolidone derivatives with low hydrophobicity. *J Nucl Sci Technol,* 2009, 46: 1129–1136

8 Thiollet G, Musikas C. Synthesis and uses of the amides extractants. *Solv Extr Ion Exch*, 1989, 7: 813–827

9 Ruikar PB, Nagar MS, Subramanian MS. Extraction of uranium, plutonium and some fission products with γ-irradiated unsymmetrical and branched chain dialkylamides. *J Radioanal Nucl Chem Letters*, 1993, 176: 103–111

10 Mowafy EA, Ali HF. Extraction of actinides and selected fission products from nitric acid medium using long chain monoamides. *Solv Extr Ion Exch*, 2001, 19: 629–641

11 Suzuki S, Yaita T, Sugo Y, Kimura T. Study on selective separation of uranium(VI) by new *N,N*-dialkyl carboxyamides. Proceedings of International Conference on Advanced Nuclear Fuel Cycles and Systems (GLOBAL2007), Boise, USA, 2007, 1137–1141

12 Takahashi Y, Hotokezaka H, Noda K, Nogami M, Ikeda Y. Extraction of uranium(VI) from nitric acid using pyrrolidone derivatives. *J Nucl Sci Technol*, 2009, 46: 787–792