

Photochemical Decomposition of Oxalate Precipitates in Nitric Acid Medium

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Abstract- This work has been performed as a part of the partitioning of minor actinides. Minor actinides can be recovered from high-level wastes as oxalate precipitates, but they tend to be co-precipitated together with lanthanide oxalates. This requires another partitioning step for mutual separation of actinide and lanthanide groups. Accordingly, the objective of this study was to decompose and dissolve oxalate precipitates into a dilute nitric acid solution by using a photochemical reaction. In order to do this, oxalic acid and neodymium oxalate precipitate were used in this study. Neodymium oxalate was chosen as a stand-in element representing americium, curium and lanthanides. As a result, decomposition characteristics of oxalic acid were first investigated and then on the basis of these results, the decomposition of neodymium oxalate precipitates was evaluated. From results using oxalic acid, the oxalate decomposition appeared to take place due to the reaction between the oxalate ion and hydroxyl radical generated from the nitric acid by photo-radiation. And the oxalate decomposition rate was measured in the experiments for various nitric acid contents when a mercury lamp ($\lambda=254$ nm) was used as a light source. The maximum decomposition rate was obtained when the nitric acid concentration was around 0.5 M, while the decomposition rate was reduced with an increase in the nitric acid concentration at more than 0.5 M. The photo-decomposition rate of neodymium oxalate precipitates was found to be 0.0034 M/h at the condition of 0.5 M HNO_3 .

Key words : Oxalic Acid, Photo-Decomposition, Nitric Acid, Oxalate Precipitate, Photochemical Reaction

INTRODUCTION

Until recently, various kinds of partitioning processes have been suggested for removing long-lived radionuclides from high-level liquid waste (HLLW) [IAEA, 1982; Forsberg, 1981]. Among them, the oxalate precipitation process permits the precipitation of transuranium (TRU) and lanthanide elements from HLLW [Forsberg, 1981; Kim et al., 1995; Rankin et al., 1977; Kim et al., 1997]. The TRU elements can be separated either by ion-exchange chromatography or by a solvent extraction method from the lanthanide elements. However, these processes require the filtration of solid precipitates from slurry, remote handling of radioactive solids at a high temperature for oxide formation and its dissolution for the next process, such as solvent extraction or ion-exchange chromatography. Due to these problems, the oxalate precipitation has generally been considered delicate for plant-scale operations. In order to solve these problems of the oxalate precipitation process, the authors have been developing a new simple technology by which oxalate precipitates can be directly decomposed on the filter by a wet process.

In this connection, recently, the authors have reported the decompositions of oxalic acid and oxalate precipitate by hydrogen peroxide in an aqueous solution [Kim, 1998a]. However, this method requires 3 M HNO_3 and temperature of above 90 °C to completely dissolve oxalate precipitates. In this case, a denitration process should additionally be needed because the next processes, such as solvent extraction or ion exchange,

should be operated under conditions where the nitric acid concentrations are less than 0.5 M. In order to decompose oxalate at room temperature, the authors [Kim et al., 1997] presented the experimental results on the decomposition of oxalic acid in hydrogen peroxide solution by photochemical reaction. On the basis of this result, the authors proposed a method to completely dissolve and decompose oxalate precipitates in 0.5 M nitric acid solution by using a photochemical method in this study. At first, photo-decomposition of oxalic acid was carried out to investigate the mechanism of the decomposition of an oxalate ion in the presence of nitric acid, and then the decomposition of neodymium oxalate precipitate was examined under the same conditions.

EXPERIMENT

1. Oxalate Precipitate and Reagents

Neodymium oxalate precipitate was prepared by adding the weighed solid of oxalic acid into 0.5 M nitric acid solution containing neodymium nitrate salt (0.3 M in the solution) with a total volume of 300 ml. The resulting precipitates were filtered by a filter paper (Whatman filter paper of No 40) and were washed twice with distilled water. Then, the precipitates were dried under the atmosphere. Nitric acid and oxalic acid used in this work were supplied from Merck and neodymium nitrate salt from Aldrich Co.

2. Experimental Equipment and Procedure

Concentration ranges of oxalic acid and nitric acid used in this study were from 0.05 M to 0.1 M and 0 M to 2 M, respectively. The amounts of neodymium oxalate precipitates

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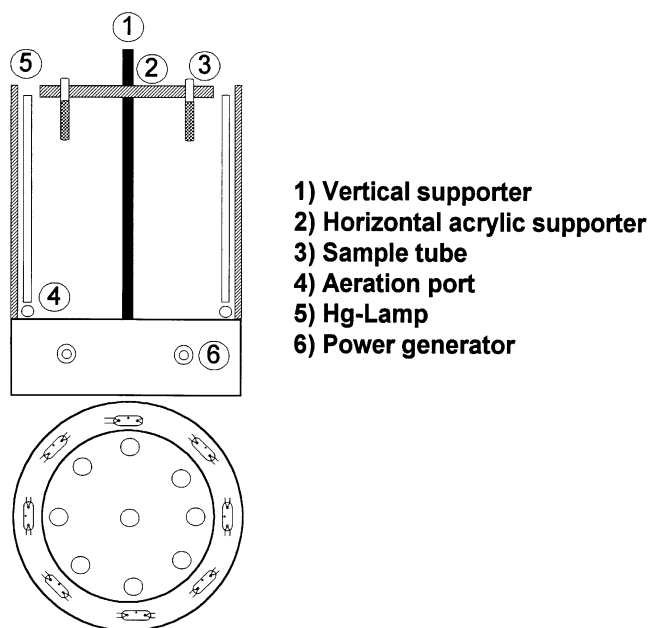


Fig. 1. Schematic diagram of the photoreactor.

used were from 0.122 g to 0.488 g. Equipment used for photo-destruction of oxalate was supplied from Rayonet Co (Model: RPR-208). This consisted of Hg-lamp with 120 W, emitting 2,537 Å wavelength. A schematic diagram of the experiment is shown in Fig. 1. The photo-reactor is a cylinder-type (40 cm in diameter and 60 cm in height). Eight mercury lamps are located at the circumference of the reactor, from which UV light travels in the direction of the core of the reactor. The material of the reaction tube is quartz and its capacity is 15 ml. As seen in Fig. 1, the reaction tubes are located on the circumference of the circular-type horizontal supporter, which is made of acrylic resin and is designed so that eight reaction tubes can run simultaneously. In order to control an increase of temperature in the reaction tube during irradiation of UV on the reacting solution, air-circulation ports are installed at the bottom of the reactor for air cooling, from which air flows up. However, during UV irradiation, the temperature of the working solution was increased from room temperature ($19 \pm 2^\circ\text{C}$) to $41 \pm 2^\circ\text{C}$ within 30 min and then was kept stable all the time during photolysis. As it was not easy to cool down the photoreactor used in this study to room temperature, all the experiments were carried out at approximately 41°C to be stable temperature. Thus, when the temperature of the solution approached about 41°C and became stable, the concentrated nitric acid (14.4 M) was added to the working solution as much as the amounts required in the experiments. The amount of working volume used in all experiments was 10 ml. Sample ranges of 10 to 100 μl were taken to determine the decomposition fraction of oxalate in the solution during photolysis.

3. Analysis

The light absorptions of nitric acid and oxalic acid in 0.5 M nitric acid were scanned by UV spectrophotometer (Model; Shimadzu UV-160A) in order to confirm the applicability of the mercury lamp to our workscope of photolysis. During the photolysis, the decomposed fraction of oxalic acid was deter-

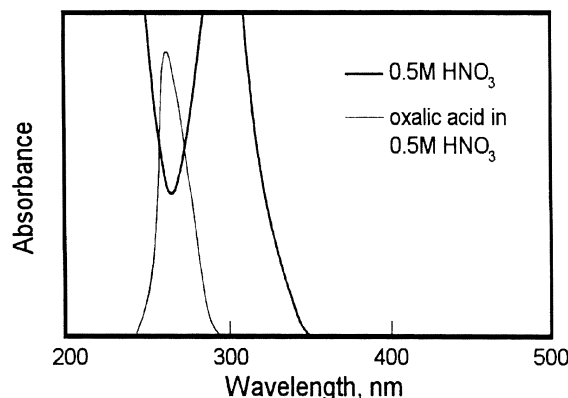


Fig. 2. UV absorption spectra of nitric acid and oxalic acid.

mined by measuring COD (Chemical Oxygen Demand) in the solution by means of the Hach 2000 DR-type COD analyzer. However, the decomposed fraction of neodymium oxalate precipitate could not be determined by measuring the COD because the neodymium oxalate precipitate was dissolved as much as the corresponding solubility in the solution. Accordingly, the decomposition fraction of neodymium oxalate precipitate could be determined by measuring the neodymium ion concentration by means of the inductively coupled plasma atomic emission spectrophotometer (ISA Jobin-Yvon JY50P). The concentration of NO_2^- ion produced during photolysis of nitric acid was determined by reflectometry (Reflectoquant, Merck).

RESULTS AND DISCUSSION

1. Photo-Decomposition of Oxalic Acid

Fig. 2 shows the UV spectrums of two solutions; one for 0.5 M nitric acid and the other for 0.1 M oxalic acid in 0.5 M nitric acid solution. This illustrates that the solutions commonly absorb lights of a wavelength below 350 nm. In particular, it appeared that the oxalic acid absorbs the lights around 254 nm of wavelength. Accordingly, the mercury lamp emitting a beam with 254 nm wavelength was used for photo-decomposition of oxalic acid in this study. However, as shown in Fig. 3, the decomposition rate of oxalic acid in the absence of nitric acid was very low compared with that in the presence of nitric acid, indicating that the role of nitric acid should

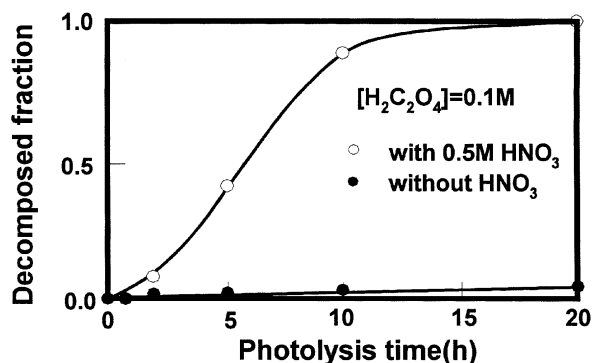


Fig. 3. Decomposed fraction of oxalic acids with and without nitric acid.

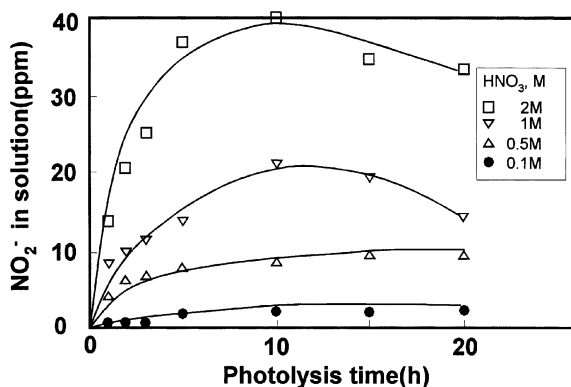


Fig. 4. Effect of nitrate concentration on nitrite formation during photolysis.

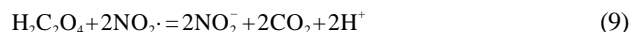
be enormous in the decomposition of oxalic acid. Experimental results showed that the decomposition yield of oxalic acid without nitric acid was less than 5 % even after 20 h irradiation, whereas 0.1 M oxalic acid in 0.5 M nitric acid was completely decomposed within 20 h. In order to determine the role of nitric acid, a solution containing only nitric acid was first irradiated in the photochemical reactor. The results, as illustrated in Fig. 4, show that the content of nitrite ion increases with the nitric acid concentration and also with irradiation time. Daniels et al. [1968] suggested two possible decomposition pathways for the photolysis of nitrate ion can be given as follows :



Where the O^- radical ion subsequently combines with a proton to form an OH radical. Two pathways ultimately produce NO_2^- ion as a final product, while the former does oxygen radical and the latter hydroxyl and nitrite radicals as the intermediate products. However, the evidence of intermediate species was not confirmed in this study. At any rate, it is considered that NO_2^- ion obtained from photolysis of NO_3^- follows the photo-decomposition mechanism as suggested by Daniels et al. [1968]. More recently, it was discovered that the quantum yield in the formation of the hydroxyl radical is far higher than that of the oxygen radical and OH radicals are more reactive than atomic oxygen for decomposing organic substances [Sarakha et al., 1993]. Accordingly, it can be expected that the photo-decomposition of NO_3^- ion will follow the mechanisms below :



From this result, we can easily infer that the decomposition of oxalate in the nitric acid medium will be induced by oxidants such as NO_2^- ion, OH radical and NO_2 radical. However, reactivity of radicals is generally known to be much higher than that of ion species toward organic substances. Accordingly, either the NO_2 radical or OH radical will decompose the oxalate in the nitric acid solution. Therefore, it is important to examine which chemical species plays a more positive role in decomposing oxalic acid. Possible decomposition mechanisms of oxalic acid by two radicals can be expressed as follows :



In our experiments, the effect of nitric acid concentration on the destruction of oxalic acid was examined at first. The maximum decomposition fraction was obtained when the nitric acid concentration was around 0.5 M and the decomposition fraction was rather decreased with the increase of the nitric acid concentration, as shown in Fig. 5. This result indicates that the major contributor to the destruction of oxalate ion may be not the nitrite radical because more nitrite radicals are produced as the nitric acid concentration becomes higher. As a matter of course, OH radical as well as NO_2 radical will increase with nitric acid concentration. Unlike NO_2 radical, however, OH radical decreases with an increase of nitric acid concentration by Eq. (6). Fig. 6 demonstrates these facts. The results in Fig. 6 were obtained when 0.1 M oxalic acid was initially contained in the nitric acid. As nitric acid concentration increase, the increase in NO_2^- ion concentration indicates that NO_2^- ion generation is from Eqs. (3), (4) and (5), not from Eq. (9). If NO_2^- ion was obtained through Eq. (9), oxalate should be more rapidly decomposed at a high concentration of HNO_3 . As mentioned in Fig. 5, the decrease in decomposition rate of oxalate at nitric acid concentration of above 0.5 M is con-

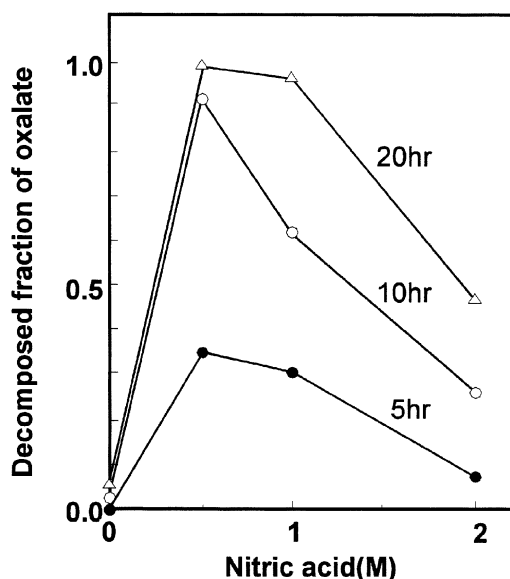


Fig. 5. Effect of nitrate concentration on photodestruction of oxalic acid.

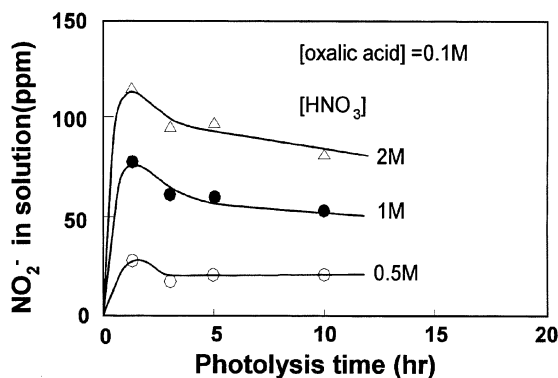


Fig. 6. Effect of nitrate concentration on nitrite formation in the presence of oxalic acid.

sidered to be due to the disappearance of OH radicals by the reaction of Eq. (6). Therefore, it was considered that the reaction of Eq. (10) would be more dominant than that of Eq. (9) in the photo-decomposition of oxalic acid, that is, the following phenomena would be expected: if more OH radicals are consumed by oxalic acid, then the content of OH radicals will be reduced, resulting in less consumption of NO_2^- ion in the reaction of Eq. (6), and thus the NO_2^- ion concentration will grow as the concentration of oxalic acid increases. This inference proved to be correct by the experimental results in Fig. 7. And also, the authors [Kim et al., 1997] reported in the previous work that oxalic acid could be easily decomposed by OH radicals obtained from photo-decomposition of H_2O_2 .

In the meantime, it is very important to search the reason why the decomposition rate of the oxalate was at a maximum around 0.5 M nitric acid. Daniels et al. [1968] have predicted that a quantum yield of nitrite ion could be increased by the reaction of an oxygen ion radical with a nitrate ion as follows:



As seen in Fig. 4, at a high concentration of nitric acid, it was observed that NO_2^- ion concentration reached a maximum and then gradually decreased during photolysis. Recently, it was

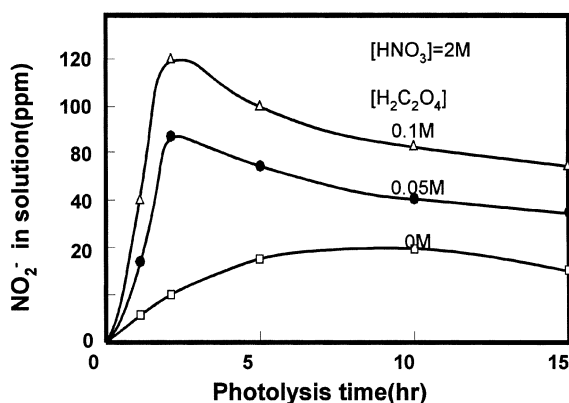


Fig. 7. Effect of oxalic acid concentration on the rate of nitrite formation during Photolysis.

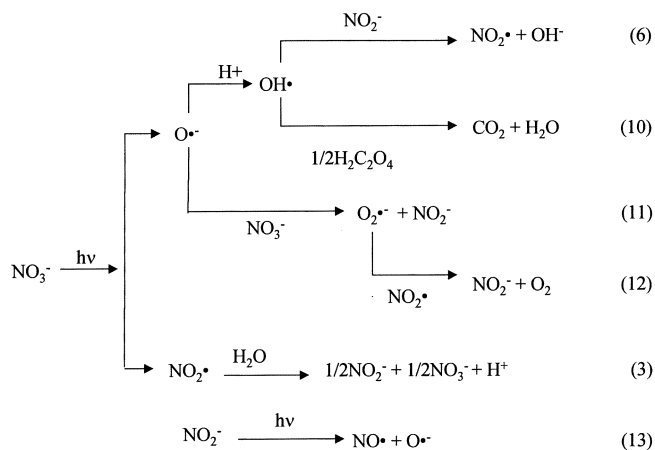


Fig. 8. Pathways for photolysis of nitrate and nitrite.

reported that the excitation of a nitrite ion leads to the formation of nitrogen monoxide and hydroxyl radicals as follows:

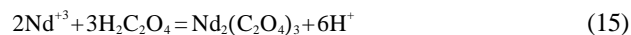


Rearranging the chemical reactions presented above, we can express again the whole mechanisms. The result is shown in Fig. 8. When the concentrations of nitrate ion and the acidity increase together in the solution, Eqs. (6), (10), (11) and (12) will compete with each other. Thus, it is expected that the decomposition of oxalic acid as well as the formation of nitrite ion will increase during photolysis. However, if the concentration of nitrate ion is low and, in opposition, the acidity is relatively high, Eqs. (6) and (10) will be dominant. In particular, Eq. (10) will be more favorable. Based on this assumption, we can consider that decomposition of oxalic acid will be more dominant when an appropriate nitric acid concentration is kept during photolysis. In this respect, the decomposition rate of oxalic acid seems to be at a maximum around 0.5 M of nitric acid as presented in this work.

2. Photo-Decomposition of Oxalate Precipitate

2-1. Characterization of Neodymium Oxalate Precipitate

It was well known that the oxalate precipitation for lanthanide elements takes place easily because of an exceedingly low solubility in the oxalate solution. The chemical reaction of the oxalate precipitation for neodymium ion is generally expressed as the following:

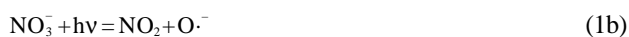


However, the oxalate precipitate obtained thereby is known to have several water molecules as a crystalline form. Jenkins et al. [1965] reported that neodymium oxalate contains ten water molecules. Accordingly, it is very important to know the exact chemical formula of the oxalate precipitate because the real composition of Nd^{+3} and oxalate ion in the solution should be understood during the photo-dissolution of neodymium oxalate precipitate. The result of the X-ray diffraction pattern of the neodymium oxalate precipitate obtained from this work was identical to the chemical formula $(\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O})$ of JCPDS card No. 200764. From this result, therefore, we can confirm

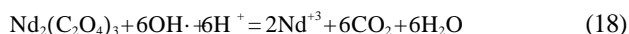
the fact that the oxalate precipitate obtained from this work has ten water molecules.

2-2. Photo-Decomposition of Oxalate in Precipitate

We knew that the photo-decomposition rate of oxalic acid was at a maximum at 0.5 M nitric acid and at the 254 nm wavelength. In other words, we can imagine that a quantum yield of OH radicals may be the highest under the above condition although some more experiments are needed. Accordingly, dissolution experiments of oxalate precipitates were also carried out under the same condition. The dissolution of oxalate precipitate in the nitric acid solution is inferred to proceed as follows. At a temperature of approximately 41 °C and 0.5 M nitric acid, the solubility of oxalate precipitate is very low, 0.006 M as oxalate concentration [Kim, 1998b]. Therefore, most oxalate precipitates are settled at the bottom of the reaction vessel and only a very little amount corresponding to the solubility will exist in the supernatant. Thus, as if the decomposition of oxalic acid was mainly induced by the hydroxyl radical, the oxalate precipitate is also expected to be decomposed by the reaction with hydroxyl radical, which is produced from NO_3^- ion by absorbing the light of 254 nm. During the decomposition of oxalate by the OH radical, the concentration of oxalate in the solution will decrease, and simultaneously oxalate precipitates will be dissolved from the oxalate slurry at the bottom of the reacting vessel. Then the oxalate and Nd^{+3} ions will diffuse up to the solution region. A decomposition mechanism is suggested as follows :



Overall the decomposition reaction of neodymium oxalate can be expressed by :



By the above reaction mechanisms, the neodymium ion will remain dissolved in the solution. Fig. 9 shows the decomposition of oxalate in the solution containing oxalate precipitates. In Fig. 9, the solid line indicates the decomposition of oxalic acid and the dotted line represents that of the oxalate precipitate. In fact, the title on the Y-axis for the dissolution of oxalate precipitate in Fig. 9 should be expressed as “ Nd^{+3} ion concentration in the solution.” However, in order to compare decomposition behaviors of oxalic acid and oxalate precipitate, the title on the Y-axis in Fig. 9 was described as “Decomposition yield of oxalate.” Accordingly, Nd^{+3} concentration generated during the photolysis of oxalate precipitates was converted into the corresponding oxalate concentration which was calculated on the basis of the chemical formula, $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. It appeared that the decomposition rate of oxalate precipitate was somewhat lower than that of oxalic acid. Probably, it is considered to be due to the low dissolution rate of oxalate because the disso-

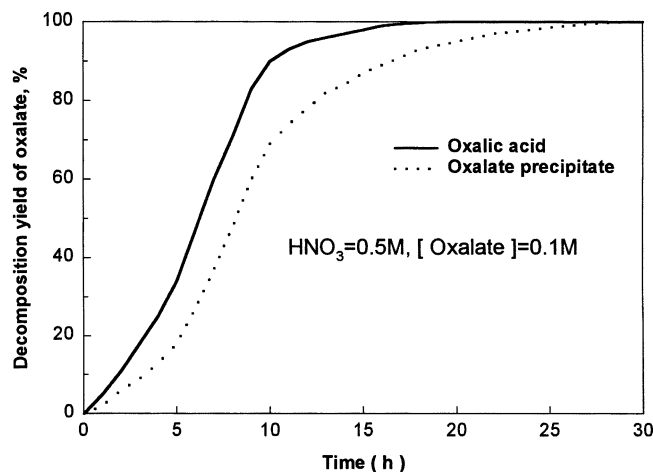


Fig. 9. Decomposition rates of oxalic acid neodymium oxalate during photolysis

lution rate of oxalate precipitate depends on the solubility in a nitric acid concentration at a given temperature. However, on the whole, oxalate precipitate was completely dissolved and decomposed after the irradiation time of 30 h. Fig. 10 shows that as the amount of oxalate precipitates added into the solution increases, the time required for the complete dissolution and decomposition of oxalate precipitate increases. It follows that this time increases with an increase of slurry content in the solution. From the linear relation of Fig. 10, the rate of decomposition of oxalate precipitate is estimated to be about 0.0034 M/h at a given wavelength and irradiation power of the lamp. However, this rate can generally increase by increasing the irradiation power of the lamp and by increasing the mixing effect of the slurry. This means that the dissolved oxalate ions can be homogeneously distributed in the entire reaction volume within a short time, and then can be rapidly decomposed with an increase of lamp power. At any rate, we can find it to be an important fact that 0.2 M of oxalate is equivalent to about 0.067 M on the base of neodymium oxalate precipitate and also cor-

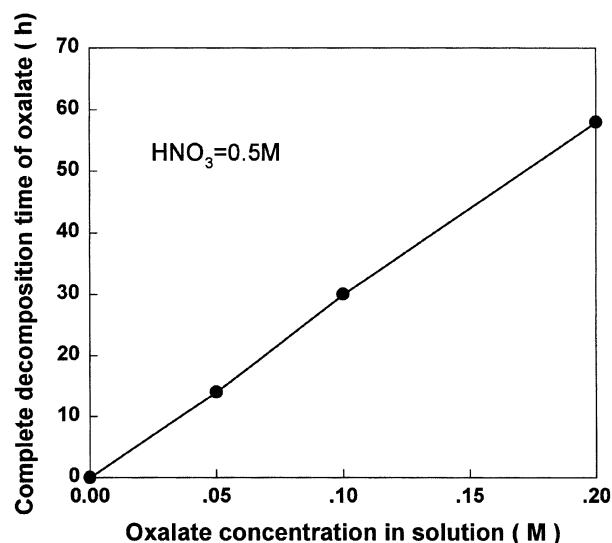


Fig. 10. Variation of complete decomposition time of neodymium oxalate according to oxalate concentration.

responds to 0.133 M of Nd^{+3} in the solution, and then the concentration of Nd^{+3} combines with approximately 0.4 M of NO_3^- to form a nitrate salt in the solution. Consequently, the concentration of free nitrate ion becomes below 0.1 M in the solution because of the loss by photo-decomposition of NO_3^- . Therefore, this condition is considered to be a very appropriate one for the next process, such as ion exchange chromatography or solvent extraction processes, to separate minor actinide and lanthanide from each other, because these following processes require the acidity below 0.2 M. Additionally, 0.2 M of oxalate is almost equivalent to the oxalate content in metallic oxalate precipitates obtained after the oxalate precipitation of a real HLLW.

CONCLUSION

The results of oxalate decomposition obtained in nitric acid media by using mercury-lamp ($I=254$ nm) are as follows. The oxalate decomposition appeared to take place by the reaction between oxalate and hydroxyl radical generated from the nitric acid by photo-radiation, and the maximum decomposition rate was obtained when the nitric acid concentration was around 0.5 M. Neodymium oxalate precipitate of 0.067 M was completely decomposed and dissolved at 0.5 M nitric acid in 60 h of irradiation time.

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REFERENCES

- Daniels, M., Meyers, R. V. and Belardo, E. V., "Photochemistry of the Aqueous Nitrate System I. Excitation in the 300- μm Band," *J. Phys. Chem.*, **72**(2), 389 (1968).
- Forsberg, C. W., "Separation of Americium, Curium, and Trivalent Lanthanides from High-Level Wastes by Oxalate Precipitation: Experiments with Synthetic Waste Solutions," *Nucl. Tech.*, **49**, 243 (1980).
- IAEA Technical Reports Series No. 214, "Evaluation of Actinide Partitioning and Transmutation," IAEA, Vienna (1982).
- Jenkins, I. L., Moore, F. H. and Waterman, M. J., "X-ray Powder Crystallographic Data on Plutonium and Other Oxalates-I," *J. Inorg. Nucl. Chem.*, **27**, 77 (1965).
- Kim, E. H., "Application of New Oxalate Precipitation Process to Partitioning of Long-Lived Nuclides from High Level Liquid Waste," Submitted to *Nucl. Tech.* (1998b).
- Kim, E. H., Chung, D. Y., Kim, W. H., Shin, Y. J., Lee, E. H., Yoo, J. H. and Choi, C. S., "Neptunium Oxalate Precipitation from the Simulated Radioactive Liquid Waste," *J. Nucl. Sci. and Tech.*, **34**, 283 (1997).
- Kim, E. H., "Dissolution of Oxalate Precipitate and Destruction of Oxalate Ion by Hydrogen Peroxide in Nitric Acid Solution," Submitted to *J. Nucl. Sci. and Tech.* (1998a).
- Kim, E. H., Kim, Y. H., Chung, D. Y., Yoo, J. H. and Choi, C. S., "Effect of H_2O_2 on Photodestruction of Oxalic Acid," *HWAHAK KONGHAK*, **35**, 440 (1997).
- Kim, E. H., Shin, Y. J., Kim, W. H., Chung, D. Y., Kim, S. S., Yoo, J. H. and Choi, C. S., "Partitioning of Neodymium and Americium in the Liquid Radioactive Waste by Oxalate Precipitation," *Korean J. Chem. Eng.*, **12**, 557 (1995).
- Rankin, D. T., Burney, G. A., Smith, P. K. and Sisson, R. D. Jr., "Preparation and Characterization of Oxalate-Based $^{237}\text{NpO}_2$ Powder," *Ceramic Bulletin*, **56**, 478 (1977).
- Sarakha, M., Boule, P. and Lenoir, D., "Phototransformation of 2-Phenylphenol Induced in Aqueous Solution by Excitation of Nitrate Ions," *J. Photochem. Photobiol. A: Chem.*, **75**, 61 (1993).