

DECOMPOSITION OF OXALATE PRECIPITATES BY PHOTOCHEMICAL REACTION

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Abstract

A photo-radiation method was applied to decompose oxalate precipitates so that it can be dissolved into dilute nitric acid. This work has been studied as a part of 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. In this study, therefore, some experimental work of photochemical decomposition of oxalate was carried out to prove its feasibility as a step of partitioning process. The decomposition of oxalic acid in the presence of nitric acid was performed in advance in order to understand the mechanistic behaviour of oxalate destruction, and then the decomposition of neodymium oxalate, which was chosen as a stand-in compound representing minor actinide and lanthanide oxalates, was examined. The decomposition rate of neodymium oxalate was found as 0.003 mole/hr at the conditions of 0.5 M HNO_3 and room temperature when a mercury lamp was used as a light source.

Introduction

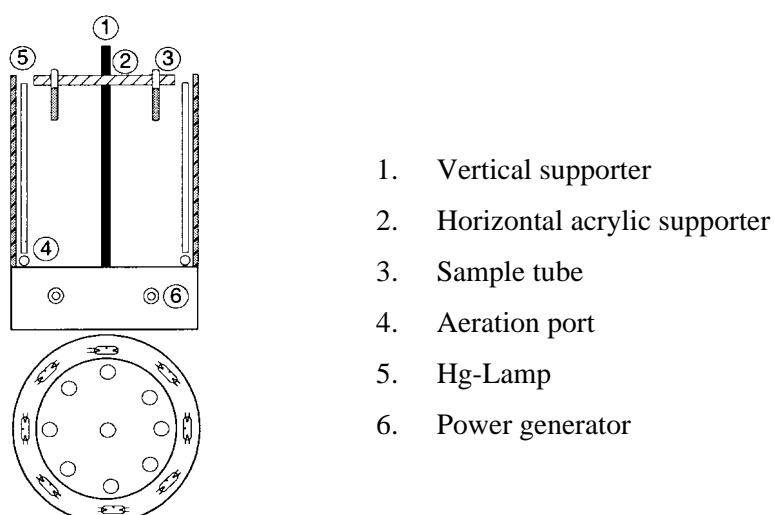
Since minor actinides such as americium and curium, and lanthanides, in general, have similar chemical properties in long-lived radionuclide partitioning processes, it is not so easy to separate minor actinides selectively from other elements. Instead, it is a typical way to separate both of them from other elements in the first step and then to separate them from each other in the next step. Oxalate precipitation, therefore, is an applicable way for the first step because minor actinide oxalates can be coprecipitated with lanthanide oxalates (Forsberg , 1980). The mixture of minor actinides and lanthanides should then be processed for mutual separation, requiring that the oxalates precipitated should be dissolved into a solution for subsequent processing. In this study, the photochemical method was used to test the feasibility of oxalate decomposition and its dissolution in nitric acid. At first, photo-decomposition of oxalic acid was carried out to investigate the mechanistic behaviours of the oxalate ion decomposition in the presence of nitric acid, and then the decomposition of neodymium oxalate was examined under the same conditions.

Experimental

Experimental equipment and procedure

The photo-radiation equipment (Model : RPR-208) with eight 15 ml reaction tubes made of quartz and eight mercury lamps (120 W, 2573 Å of wavelength) was used in the experiments. As shown in Figure 1, mercury lamps are located around reaction tubes, emitting UV light toward the tubes which were placed at the circumference of the circular horizontal acrylic supporter so that simultaneous irradiation for the tubes can be achieved. In order to suppress the temperature increase in the solution of reaction tubes during irradiation, cooling air is blown up into the air-ports installed at the bottom of reactor. In every run of experiments, the volume of working solution in the reaction tubes was set to 10 ml and 0.01-0.1 ml of a sample was periodically taken to determine the oxalic acid concentration of the solution during the photolysis.

Figure 1. Schematic diagram of the photolysis system



Chemical analysis

The light absorptions of pure nitric acid and oxalic acid in 0.5M 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 determined by measuring COD (Chemical Oxygen Demand) of the solution by means of Hack 2000 DR-type COD analyser, and the concentration of NO_2^- ion produced from nitric acid was determined by reflectometry (Reflectoquant, Merck).

Result and discussion

Photo-decomposition of oxalic acid

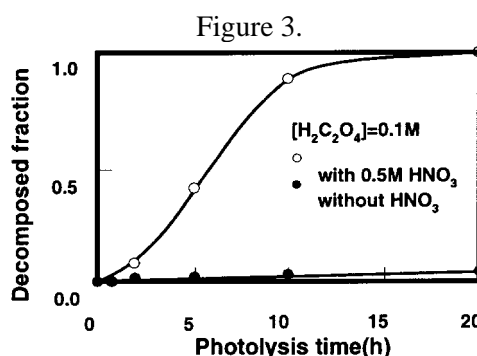
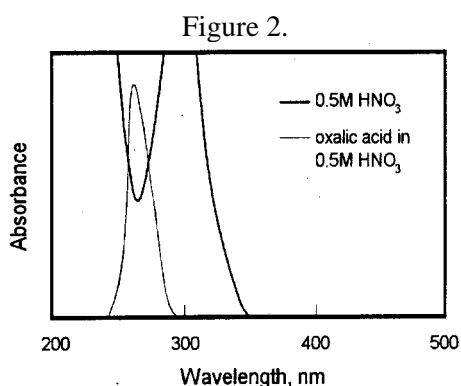


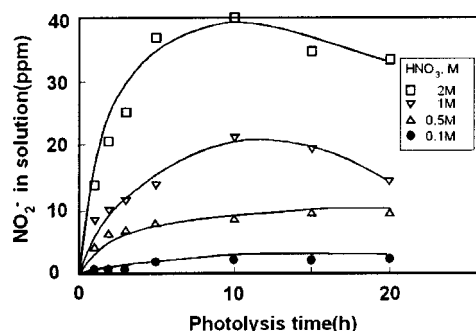
Figure 2 shows UV spectrums of two solutions; one for 0.5 M nitric acid and the other for the mixture of 0.1 M oxalic acid and 0.5 M nitric acid. It illustrates that oxalic acid has an absorption peak around the wavelength of the mercury lamp. However, as shown in Figure 3, the decomposition rate of 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 be enormous in the decomposition of oxalic acid. Experimental results show that the decomposition yield of oxalic acid without nitric acid is less than 5% even after 20 hrs irradiation, whereas 0.1 M oxalic acid in 0.5 M nitric acid was completely decomposed within 20 hr. In order to search the role of nitric acid, a solution containing only nitric acid was first irradiated in the photochemical reactor. The results, as illustrated in Figure 4 gives that the content of nitrite ion increases with nitric acid concentration and also with irradiation time. According to F. Barat et al (1970) and P. Warneck et al (1988), the photolysis of nitrate ions involves two pathways as illustrated in Eqn (1)-(3). On the basis of these phenomena, the photolysis mechanism of nitric acid has been known as:

1. $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}$
2. $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^\cdot + \text{O}^{\cdot-}$
3. $\text{O}^{\cdot-} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{OH}^-$
4. $\text{NO}_2^\cdot \rightarrow \text{N}_2\text{O}_4$
5. $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2 \text{H}^+$
6. $\text{NO}_2^- + h\nu \rightarrow \text{NO}^\cdot + \text{O}^{\cdot-}$
7. $\text{NO}_2^- + \cdot\text{OH} \rightarrow \text{NO}_2 + \text{OH}^-$

Accordingly, it can be inferred that the photo-decomposition of oxalate in a nitric acid medium will be induced by the oxidants such as NO_2^- ion and $\cdot\text{OH}$ radical as follows:

8. $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{NO}_2^- \rightarrow 2 \text{NO} + 2 \text{CO}_2 + 2 \text{OH}^-$
9. $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{OH} \rightarrow 2 \text{H}_2\text{O} + 2 \text{CO}_2$

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



Warneck and Wurzinger (1988) ,however, reported that the quantum yield of $\cdot\text{OH}$ formation from nitric acid is much higher than that of the other pathway, and therefore oxidations are generally attributed to hydroxyl radicals which are more reactive than atomic oxygen.

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 is around 0.5 M and the decomposition fraction was rather decreased above 0.5 M as shown in Figure 5. This result indicates that the major contributor to the destruction of oxalate ion is not the nitrite ion because more nitrite ions are generated as the nitrate concentration becomes higher, as shown in Figure 4 and Figure 6. The results in Figure 4 are obtained when there is no oxalic acid contained in the nitric acid whereas those results in Figure 6 are gained when 0.1 M oxalic acid is put into the nitric acid. In this study, therefore, it was considered that the reaction in Eqn (9) would be more dominant than that in Eqn (8) in the photo-decomposition of oxalic acid, that is, the following phenomena would be expected: if more $\cdot\text{OH}$ is consumed by the oxalic acid, then its content will be reduced, resulting in less consumption of NO_2^- ion in the reaction of Eqn (7), and therefore the NO_2^- concentration will grow as more oxalic acid is added into the nitric acid. Finally, this inference was proved by the experimental results in Figure 7. When the nitric acid concentration increases above 0.5 M, then the reaction in Eqn (7) will become more active because more nitrite ions generated from the nitric acid consume hydroxyl radicals, which will certainly reduce the oxalate decomposition yield. Figure 8 shows the whole pathways of the photolysis of nitrate ion in the decomposition procedure of oxalic acid.

Figure 5. Effect of nitrate concentration on photo-destruction of oxalic acid

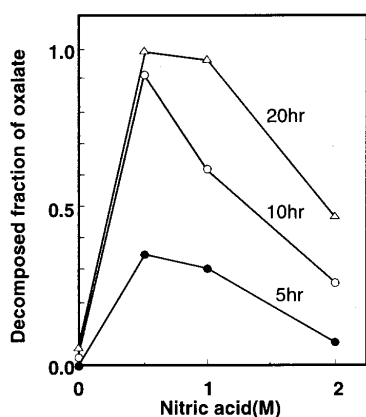


Figure 6. Effect of nitrate concentration on nitrite formation in the presence of oxalic acid

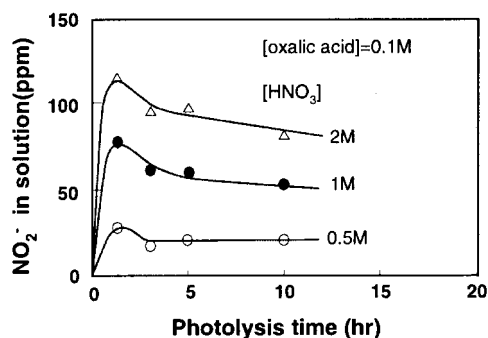


Figure 7. Effect of oxalic acid concentration on the rate of nitrite formation during photolysis

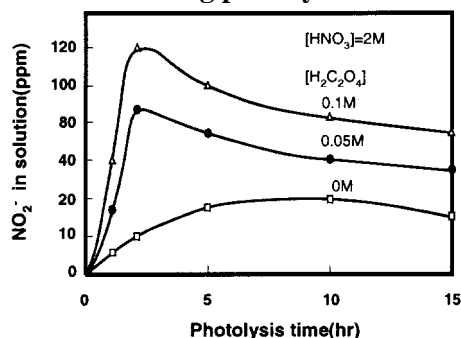


Figure 8. Pathways for photolysis of nitrate and nitrite

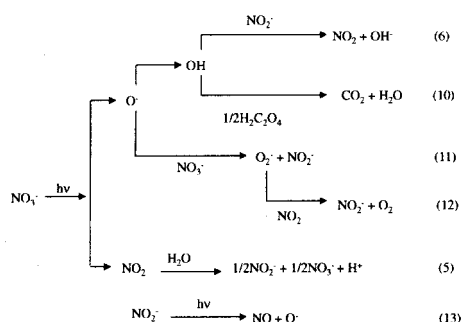


Photo-decomposition of oxalate salt

Since the decomposition of oxalic acid is mainly induced by a hydroxyl radical, oxalate salts are also inferred to be destroyed by the same mechanism, that is, neodymium oxalate will be decomposed by the following mechanism:



In our experiments, the decomposition rates were compared between oxalic acid and neodymium oxalate for the same content of oxalate. The result in Figure 9 shows that the decomposition rate of oxalate salt is slightly slower than that of oxalic acid. This is due to the fact that oxalate salt, which exists as a solid, needs additional time to dissolve into the solution, retarding the destruction process. In order to obtain the decomposition rate, various contents of neodymium oxalate were dissolved in 0.5 M nitric acid and duration times for complete dissolution were measured. As a result, the time increases linearly with the quantity of initial neodymium oxalate, as shown in Figure 10, giving the dissolution rate of 0.003 mole/hr at the condition of 0.5 M nitric acid and room temperature. Consequently, the final concentration of nitric acid can be diminished to less than 0.1 M in the solution due to the destruction of the nitrate ion, which would then give an appropriate condition to separate minor actinides and lanthanides from each other. Such partitioning processes as ion exchange and solvent extraction, which require very low acidity of feed solution, can be applied for the purpose of mutual separation.

Figure 9. Decomposition rates of oxalic acid and neodymium oxalate during photolysis

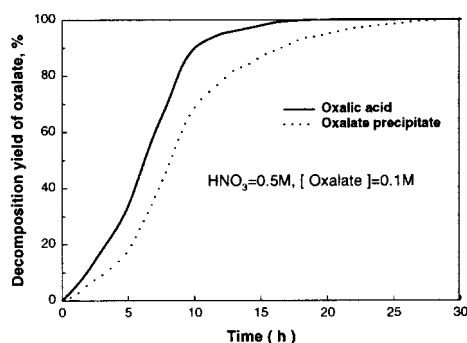
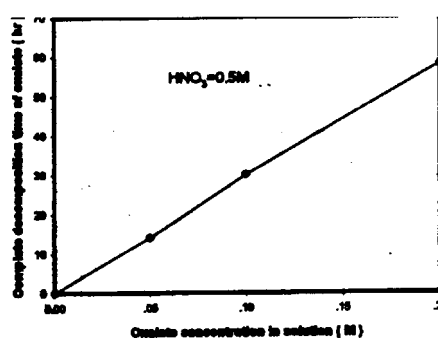


Figure 10. Complete decomposition time of neodymium oxalate with its initial concentration



Conclusion

The mechanism of oxalate decomposition in nitric acid was experimentally investigated in this study and it was elucidated that the decomposition reaction is dominated by the reaction of oxalic acid with hydroxyl radical generated from the nitric acid, rather than with the nitrite ion which is also produced from the nitric acid. The maximum decomposition rate of oxalic acid with the mercury lamp ($\lambda = 254$ nm) was obtained when the nitric acid concentration is about 0.5 M in the initial solution. This phenomenon is interpreted as that, at lower nitric acidity, less hydroxyl radical is generated from nitric acid, reducing the oxalate destruction yield, however, a larger quantity of the nitrite ion forms at higher acidity, consuming more hydroxyl radicals and thus diminishing the oxalate decomposition yield.

Acknowledgements

This project has been carried out under the nuclear R&D program of the Korean MOST.

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