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Decomposition of Oxalate in Low-level Liquid Waste Using UV Irradiation

Masanobu NOGAMI[1]*, Takeshi SAKASHITA[2], Kazunori SUZUKI[1], and Yasuhisa IKEDA[3]
[1]*Kashiwa Laboratory, Institute of Research and Innovation*
1201 Takada, Kashiwa, Chiba 277-0861, Japan
[2]*Nuclear Fuel Cycle Plant Engineering Department, Ishikawajima-Harima Heavy Industries Co., Ltd.*
1 Shin-nakahara-cho, Isogo-ku, Yokohama 235-8501, Japan
[3]*Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology*
O-okayama, Meguro-ku, Tokyo 152-8550, Japan

An application of ultraviolet ray (UV) irradiation for the decomposition of oxalate in low-level liquid waste's (LLLW's) including transuranium nuclide was investigated. The decomposition properties of oxalate are studied in various simulated LLLW's which basically contain U(VI) and 3M $NaNO_3$. Batch experiments have revealed that the decomposition rates were increased with a decrease in the concentration of HNO_3 in the sample solutions. It has been also found that U(VI) in LLLW's enhanced the decomposition, and that no decomposition was observed in a basic solution containing Na_2CO_3. An optimum solution condition to decompose oxalate in LLLW's is expected to be 0.05M HNO_3. UV was also irradiated in solutions containing 3M $NaNO_3$ without U(VI) and HNO_2 has been found to be a decomposing species of oxalate. UV irradiation will be a promising method for the decomposition of oxalate in LLLW's.

KEYWORDS: ultraviolet light irradiation, oxalate, decomposition, low-level liquid waste, nitrate, uranium

I. Introduction

Low-level liquid wastes (LLLW's) in the reprocessing plants contain mainly uranium, transuranium nuclides (TRU's), and $NaNO_3$. Various organic chelating agents used for chemical analysis of TRU's. The agents are able to form water-soluble complexes with the nuclides in LLLW's. It is difficult to separate nuclides in the liquid wastes or to reduce leaching of nuclides from solidified wastes. Therefore, the chelating agents should be decomposed.

Ozone, hydrogen peroxide, ultraviolet ray (UV) irradiation, or a combination of some or all of them is generally used for decomposition of organic compounds in aqueous solutions[1-3]. Radiolysis using gamma rays, nitric acid, or heating is also applied in some nuclear facilities[4-6]. However, there have been only a few studies for the decomposition of organic compounds in the solutions containing salts of high concentrations[7].

Oxalate ion is one of the representative chelating agents and is supposed to be a component of LLLW's. Under some conditions of LLLW's, oxalate is able to coordinate to U(VI). It is well-known that the U(VI)-oxalate complexes would strongly enhance the decomposition of oxalate by absorbing UV ray at 254nm, because U(VI) works as a catalyst[8] as;

$$\mathrm{U(VI)} + \mathrm{C_2H_2O_4} \xrightarrow{h\nu} \mathrm{U(IV)} + 2\mathrm{CO_2} + 2\mathrm{H^+}$$
$$\xrightarrow{+1/2\mathrm{O_2}} \mathrm{U(VI)} + 2\mathrm{CO_2} + \mathrm{H_2O} \qquad (1)$$

It is expected, therefore, that the complete decomposition of oxalate may be achieved only by using UV irradiation without other procedures. A simple apparatus in the UV irradiation system is another advantage. NO_3^- in the solution is known as an interference species against the decomposition of organic compounds[3].

In this paper, decomposition properties of oxalate by UV irradiation were investigated in the presence of U(VI) and high concentrations of $NaNO_3$ to find the appropriate solution conditions for treating LLLW's.

II. Experimental

Experiments were carried out by batch method. The configuration of the apparatus is illustrated in **Fig. 1**. A highly stable mercury-xenon lamp (L2570, Hamamatsu Photonics K.K.; 200W) and a reflector for focusing UV (E4169-02, Hamamatsu Photonics K.K.) were used. The reflection property of the reflector measured by Hamamatsu is shown in **Fig. 2**. The reflector completely eliminates the wavelength under 220nm in order to prevent the generation of O_3 by UV irradiation. The irradiation intensity

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*Corresponding author, tel. +81-4-7146-0011, fax. +81-4-7144-7602, e-mail nogami@iri.or.jp

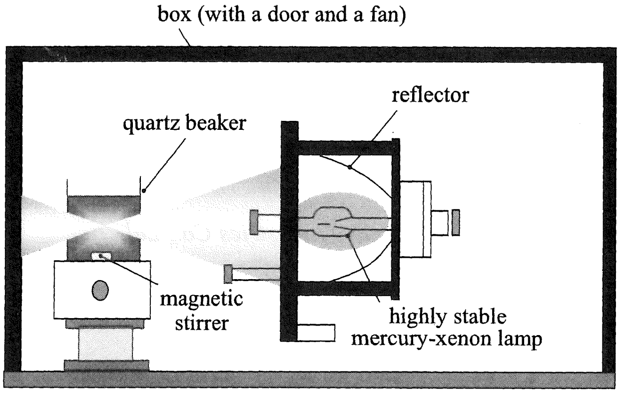

Fig. 1 Configuration of experimental apparatus

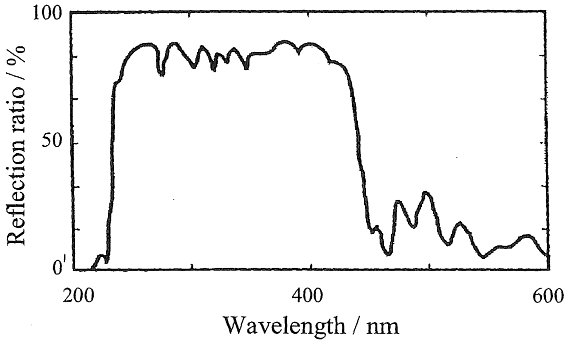

Fig. 2 Reflection property of reflector

measured by a radiometer (C6080-02, Hamamatsu Photonics K.K.) was 1200mW/cm^2 at the focus.

250cm^3 of solutions which basically contain 3M $NaNO_3$, 2.2mM oxalate and various concentrations of U(VI) were prepared as the simulated LLLW's. Acidity of the solutions was adjusted with HNO_3 or NaOH. Fe(III) was added in some cases. Fe(III) is a component of LLLW's and produced by dissolution of the plumbing made of stainless steal. $H_2C_2O_4 \cdot 2H_2O$ or $Na_2C_2O_4$ was used as oxalate compound.

The sample solution was put into quartz beaker and was set so that UV was focused in the center of the sample. During irradiation the solution was stirred with a magnetic stirrer. The initial temperature of the solutions was adjusted to 25℃ and the temperature was not controlled any more during irradiation. The sample solutions were not degassed before and during irradiation. Aliquots of the sample solutions were taken at appropriate intervals. The concentrations of oxalate were measured by ion chromatography. The concentrations of NO_2^- in the sample solutions were analyzed by the color reaction using 4-aminobenzenesulfonamide and *N*-1-naphthylethylenediamine dihydrochloride.

III. Results and Discussion

1. Influence of acidity of simulated LLLW's

Influence of acidity of simulated LLLW's on the decomposition properties of oxalate was examined by using 3M $NaNO_3$ solutions containing 0.38mM U(VI). **Fig. 3** shows that the decomposition is increased with a decrease in the concentrations of HNO_3 and that almost all of the oxalate is decomposed within 10 min in the case of 0.05M HNO_3. Almost no decomposition was observed in case of the solution containing 0.1M Na_2CO_3. These results indicate that oxalate in LLLW's is decomposed completely by adjusting the acidity, in spite of the presence of NO_3^- which interferes the decomposition.

These results can be reasonably explained by the fact that dissociation of oxalate increases with lower acidity and produces more amount of U(VI)-oxalate complexes. According to a previous paper$^{9)}$, no complex formation between U(VI) and oxalate was confirmed in the range of pH<0 ($[H]^+>1M$), and only a 1:2 complex between U(VI) and hydrogenoxalate, $HC_2O_4^-$, is formed at pH=1.7 ($[H]^+=0.02M$). Acidity of sample solutions in our study is ranged from 0.05M to 1.0M, thus only the U(VI)-hydrogenoxalato complex is considered except the sample of 1.0M HNO_3.

In the Na_2CO_3 solution, on the other hand, oxalate is present as free $C_2O_4^{2-}$ ion because CO_3^{2-} forms much more stable complexes with U(VI). Therefore, the UV absorption of U(VI)-oxalato complexes does not occur in this case. An optimum solution condition to decompose oxalate in LLLW's will be lower acidic without CO_3^{2-}, i.e. pH~4. In order to avoid hydrolysis of U(VI) after the decomposition of oxalate, a little more acidic solution, e.g., 0.05M HNO_3 will be appropriate.

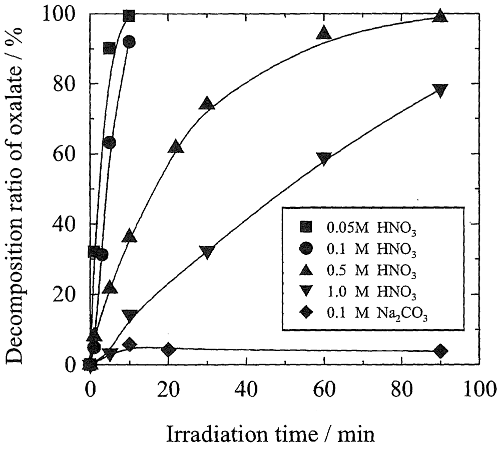

Fig. 3 Decomposition of oxalate in simulate LLLW's of various acidities as a function of irradiation time

2. Influence of U(VI) and/or Fe(III) addition

Influence of U(VI) concentration in the simulated LLLW's on the decomposition of oxalate was investigated under solution conditions containing 3M $NaNO_3$ and 0.05M HNO_3. The most effective decomposition property was observed in the conditions, as examined in the previous section. In addition, the influence of Fe(III) was also examined. The results are shown in **Fig. 4**. The decomposition rate is increased with an increase in the concentration of U(VI). The rate of the solution containing Fe(III) shows the same tendency. In the case of the solutions with U(VI), initial molar ratio of [U(VI)] to [$HC_2O_4^-$] is smaller than stoichiometric 1 to 2. The results, therefore, indicate that an increase in the concentration of U(VI)-hydrogenoxalato complexes enhances the decomposition of oxalate and that U(VI) works as a catalyst. Faster decomposition rates in the solutions with higher concentration of [U(VI)] are attributed to a decrease in the excess of free $HC_2O_4^-$[10]. The results of the solutions containing Fe(III) can be explained as well by the catalytic behavior of Fe(III) in Fe(III)-hydrogenoxalato complexes.

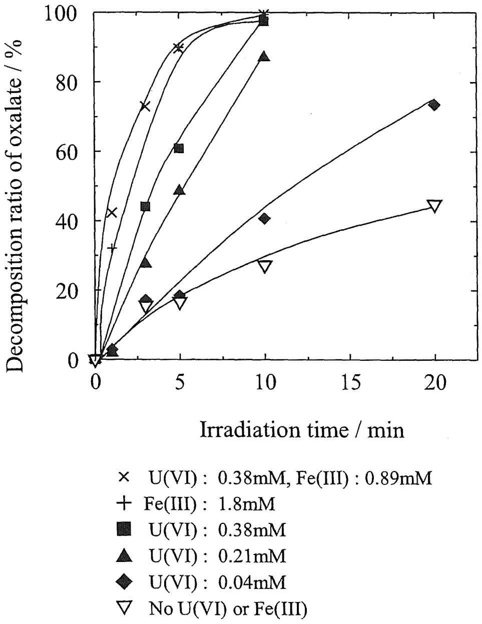

Fig. 4 Decomposition of oxalate in simulated LLLW's containing various U(VI) and/or Fe(III) concentrations as a function of irradiation time (oxalate : 2.2mM)

3. Decomposition properties of oxalate without U(VI)

As shown in Fig. 4, it has been found that oxalate is decomposed to some extent even in the solution without U(VI). In order to discuss the mechanisms of the decomposition of oxalate in the solutions with high concentrations of $NaNO_3$ without U(VI), experiments were carried out in both basic and acidic solutions. The results are shown in **Fig. 5**. In the solution containing only oxalic acid, ca. 60% of oxalate is decomposed after 90 min of irradiation time.

The decomposition ratio in the solution with 3M $NaNO_3$ is ca. one third of the ratio in the solution containing only oxalic acid, although both solutions have almost the same pH value (pH~3). The decrease in the ratio is due to the presence of NO_3^- as mentioned above.

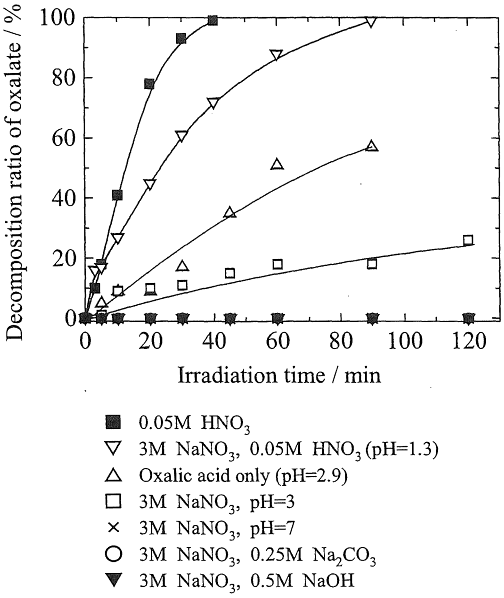

Fig. 5 Decomposition of oxalate in various solutions without U(VI) as a function of irradiation time

The decomposition rates are decreased with decreasing pH in the solutions containing 3M $NaNO_3$. No decomposition is found in pH $\geqq$ 7, while complete decomposition within 90 min is found in the 3M $NaNO_3$ solution with 0.05M HNO_3 (pH=1.3).

Generally, when 180nm of UV ray is irradiated, hydroxyl radical ($\cdot$ OH) are generated from some oxidants such as O_3 or H_2O_2 in the solutions or even from H_2O. It is also known that NO_3^- is reduced to NO_2^- by vacuum-UV irradiation. Although the wavelength under 220nm was eliminated in our study, no proof to completely deny the generation of $\cdot$ OH is available so far. For the generation of NO_2^-, concentrations of HNO_2 were measured in the solution of pH=1.3. For comparison, concentrations of HNO_2 in the corresponding solution without oxalate were also measured.

The results are shown in **Fig. 6**. A small and constant amount of HNO_2 was generated in the solution without oxalate. On the other hand, a large peak is found in the solution with oxalate. The concentration is increased with irradiation time and reaches the maximum value after 40 to 50 min of irradiation time. The concentration of HNO_2 is decreased to the low level after ca. 100 min. Oxalate in the solution containing 3M $NaNO_3$ and 0.05M HNO_3 was decomposed completely at 100 min (See Fig. 5). The agreement strongly indicates that HNO_2 generated by UV irradiation works as an oxidant of oxalate. HNO_2 becomes more stable as the dissociated form, NO_2^-, with an increase in pH. Therefore, the decomposition of oxalate will be decreased with an increase in pH.

The decomposition mechanism of oxalate in the simulated LLLW's is very complicated because various species participate in the decomposition as oxidants. Direct decomposition by UV irradiation is also possible[3]. More detailed investigation is necessary for more understanding of the mechanism.

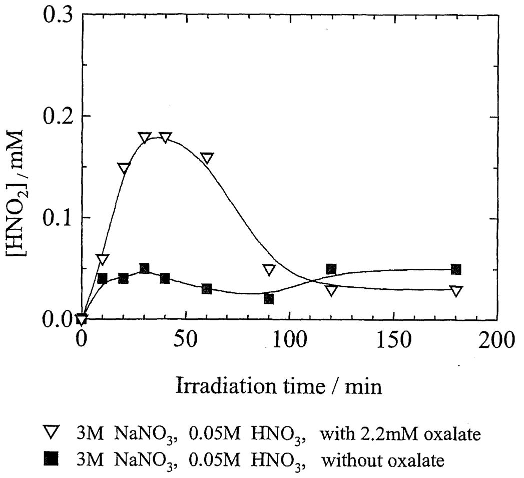

Fig. 6 Generation of HNO_2 during UV irradiation

IV. Conclusions

The decomposition properties of oxalate in the simulated LLLW's were investigated. The decomposition rate was increased with a decrease in the concentration of HNO_3. The result was explained by the concentration of U(VI)-hydrogenoxalato complex in the LLLW's. An optimum solution condition to decompose oxalate in LLLW's is expected to be 0.05M HNO_3. UV ray was also irradiated in the solutions containing 3M $NaNO_3$ without U(VI) and HNO_2 has been found to be a decomposing species of oxalate. This study has indicated that UV irradiation will be a promising method for the decomposition of oxalate in LLLW's from the viewpoint of solution conditions.

References

1) I. Nicole, J. D. Laat, M. Dore, et al., "Use of U.V. radiation in water treatment : measurement of photonic flux by hydrogen peroxide actinometry," Wat. Res. 24[2], 157 (1990)

2) R. Brunet, M. M. Bourbigot, M. Dore, "Oxidation of organic compounds through the combination ozone - hydrogen peroxide," Ozone Sci. Eng., 6, 163 (1984)

3) S. Echigo, K. Kosaka, H. Yamada, et al., "Study on the characteristics of ozone / vacuum ultraviolet treatment," Environ. Sanit. Eng. Res. 11[3], 227 (1997), [in Japanese]

4) B. K. Sharma, P. Saran, "^{60}Co-gamma radiolysis of the trisoxalato cobalt(III) ions in deoxygenated neutral aqueous solution," Radiation Eff. Let., 87, 141 (1985)

5) M. Kubota, "Decomposition of oxalic acid with nitric acid," J. Radioanal. Chem., 75[1-2], 39 (1982)

6) S. I. Nikitenko, V. I. Dzyubenko, N. N. Malkova, et al., 'Kinetics of intermolecular oxidation of the oxalate ion in a monooxalate complex with plutonium(IV) in nitric acid solutions,' Radiokhimiya, 30[5], 664 (1988)

7) S. K. Nayak, T. G. Srinivasan, P. R. V. Rao, et al. "Photochemical destruction of organic compounds formed during dissolution of uranium carbide in nitric acid," Sep. Sci. Technol., 23[12-13], 1551(1988)

8) E. Rabinowitch, R. L. Belfold, Spectroscopy and Photochemistry of Uranyl Comppounds, Pergamon Press, Oxford, 264 (1964)

9) A. G. Brits, R. Eldik, J. A. Berg, "Equilibrium studies of the uranyl oxalate system in acidic Aqueous Solution," Zeit. Physikal. Chem. Neue Folge, 99, 107 (1976)

10) A. G. Brits, R. Eldik, J. A. Berg, "The photolysis of the uranyl oxalate system; I. Photochemical Behaviour in strongly acidic aqueous solution," Zeit. Physikal. Chem. Neue Folge, 102, 203 (1976)