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Photochemical Oxidation of Americium in Dilute Nitric Acid Solution with the Addition of Ozone

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ABSTRACT

A trial to oxidize americium (Am) from the trivalent to the hexavalent form in dilute nitric acid solution was undertaken by emitting light from a deuterium lamp as well as by blowing ozone into the solution. It was found out that trivalent Am in dilute nitric acid solution (~0.1 N) can be photooxidized to its hexavalent form by a deuterium lamp which emits lines below 170 nm. Photooxidation, however, cannot be effected unless the oxidation rate exceeds the rate of autoreduction of Am which is caused by radicals and ions formed by alpha radiolysis. Ozone was introduced into the solution to maintain Am in its hexavalent form because ozone, which does not oxidize Am^{3+} to Am^{6+} in acid media, readily oxidizes Am^{5+} to Am^{6+} in HNO_3 solution. Photooxidation can be effectively carried out by a combination of photolysis and ozone. Its oxidation rate was about 5%/h in 0.1 N nitric acid solution at 65°C. The oxidation rate decreased with increasing nitric acid concentration.

INTRODUCTION

Actinide elements are produced artificially by the irradiation of reactor fuels such as uranium and plutonium. It is necessary to isolate these elements because of their long half-life radioactivity as well as their toxicity. In the process of isolating actinide elements, it is necessary to separate

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microamounts of actinide elements from macroamounts of other radioactive and nonradioactive elements. Because of their chemical similarity, however, it is quite difficult to separate the elements of lanthanide and actinide groups. The most promising approach to the isolation and separation of lanthanide and actinide elements is based on using the differences in the behavior of these elements in different valence states.

Elements of lanthanide and actinide groups display considerable different absorption lines in solutions, and this characteristic is applicable to separation processes (1). The effective separations of mixtures of lanthanide or actinide elements by the photochemical method have been demonstrated recently (2, 3). The photochemical method is considered to be applicable to the rationalization of high-level radioactive waste management. The Talspeak method is a well-known way to separate lanthanide and actinide (Am, Cm) elements from high-level radioactive waste by the use of di-2-ethylhexyl-phosphoric acid (HDEHP) and diethylene triamine pentaacetic acid (DTPA). However, it requires the use of large amounts of chemical reagents. The most significant advantage of photochemical techniques compared with conventional methods is that photons can replace chemical reagents. This feature is of particular importance in nuclear fuel reprocessing where a reduction in the amount of chemicals reduces the amount of radioactive wastes.

Friedman et al. succeeded in the oxidation and reduction of Np in $HClO_4$ solution by using mercury lamps (4). Wada et al. reported that under the irradiation of a mercury lamp (0.015 W) in 3 N HNO_3 solution containing Pu^{3+} and Np^{5+}, more than 95% of Pu^{3+} was oxidized to Pu^{4+} within 10 minutes irradiation, while Np^{5+} did not change its valence state (3).

Am, which has the characteristics of Pu and Np, may photolyze, but probably not as well as either Pu and Np because the redox potential is greater for Am (5). The redox potentials are 1.69 V for Am (Am^{3+} to Am O_2^{2+}), 1.04 V for Pu (Pu^{4+} to PuO_2^{2+}), and 0.74 V for Np (Np^{4+} to Np O_2^{2+}).

In previous work we performed experiments to determine the likelihood of the oxidation of Am^{3+} in nitric acid solution to a higher valence state by photolysis for possible use in the separation processes of Am from the lanthanides or from Cm (6). The distribution ratio of Am in nitric acid solution mixed with 100% tri-*n*-butyl phosphate (TBP) slightly increased with the irradiation time, but was much smaller than a desired value.

Species produced by alpha radiolysis of water reduces the higher oxidation states of Am eventually to stable Am^{3+}. Because of its lower specific activity, the rate of autoreduction of ^{243}Am is much less than that of ^{241}Am. Most investigators concur that autoreductions of Am^{5+} and Am^{6+} are kinetically zero order with respect to the AmO_2^{+} and the AmO_2^{2+} ions, respectively, and first order with respect to total Am concentration (7). The rate of autoreduction of Am^{6+} to Am^{5+} amounts to ~4%/h, and the rate of autoreduction of Am^{5+} to Am^{3+} is ~2%/h (7).

Thus Am^{3+} may be photooxidized, but oxidation cannot be effected unless the oxidation rate exceeds the rate of autoreduction. For this reason, ozone was introduced into the solution to make the oxidation effective. Ozone readily oxidizes Am^{5+} to Am^{6+} in heated HNO_3 or $HClO_4$ solution (8), but will not oxidize Am^{3+} to Am^{6+} in acid media even when heated (7).

Photolysis was performed using a deuterium lamp which emits lines between 110 and 170 nm. The chances of photolysis of Am^{3+} by radiation lower than 240 nm would be better because the extinction coefficient increases dramatically below this wavelength (9, 10). A cell which would pass light in the vacant UV region is needed. Ozone was blown into the solution throughout the irradiation period to the limit of its solubility. The likelihood of Am^{3+} oxidation was evaluated.

EXPERIMENTAL

Sample Solutions and Experimental Instruments

A 2.5-mL HNO_3 solution containing 2.0×10^{-9} M ^{241}Am was prepared in a cell for each experiment. ^{241}Am in 0.5 N HNO_3 solution was supplied from Amersham, and its concentration was adjusted for each experiment. Am (tetra-, penta-, and hexavalent) in HNO_3 solution is negligibly small, and almost all the Am in a HNO_3 solution is considered to exist as the trivalent form. All other chemicals used in this study were of analytical grade and were supplied by Wako Pure Chemical Industries.

Figure 1 shows a schematic view of the experimental system. The system consists of a deuterium lamp (Hamamatsu Model L879), an ozonizer (Ishikawajima Heavy Industries), a hot magnetic stirrer, and a sample solution cell. The experiments were carried out at 25°C (room temperature) to 75°C by adjusting the solution temperature with the hot magnetic stirrer. The solution was continuously homogenized with the stirrer.

The output power of the deuterium lamp was 30 W. The lamp emits lines in the vacant UV region. Figure 2 shows the relative spectra of the energy distribution curve from the deuterium lamp. The cell used in this study was made of synthetic quartz.

Ozone was created from pure oxygen gas with the ozonizer, and was blown into the solution. The fraction of ozone in the product (O_3/O_2) depends on the electric current of the ozonizer as well as the oxygen flow rate. All experiments were carried out under an electric current of 200 mA and a 20-mL/min oxygen flow rate, which corresponds to an O_3/O_2

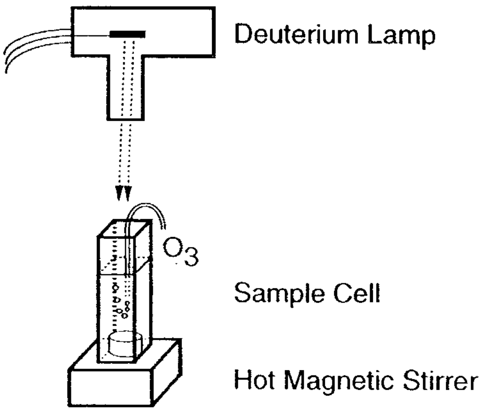


FIG. 1 Schematic view of experimental system.

of roughly 2.0×10^{-3}. The solubility of ozone in distilled water is 2.9×10^{-4} M at room temperature. In nitric acid the solubility decreases with increasing acid concentration up to 16%, but it does not require an acid concentration above 0.01 N (11).

Analytical Method

The recognized oxidation states of Am in an ordinary aqueous solution are tri-, penta-, and hexavalent. They can usually be identified by means

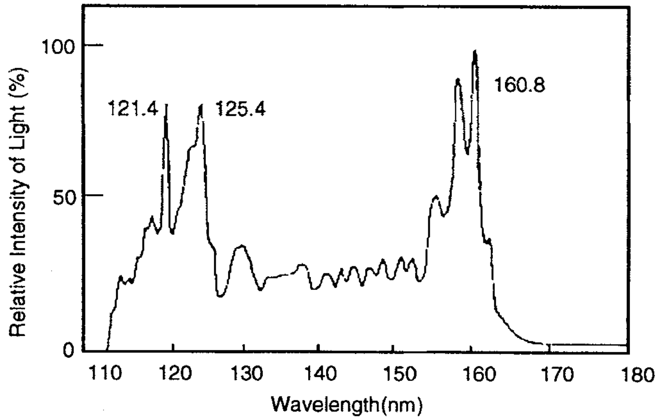


FIG. 2 Relative spectra of the energy distribution curve from a deuterium lamp.

of spectrophotometry (12). This method, however, is not sensitive enough in this work because of the low extinction coefficients of both Am^{5+} and Am^{6+} ions. For this study we selected the LaF_3 coprecipitation method. The coprecipitation technique involving LaF_3 is based on the fact that the Am^{3+} ion is carried while the Am^{6+} ion is not carried by LaF_3 (13, 14). LaF_3 carries portions of the Am^{5+} in proportion to the amount of the lanthanum ion added under any given conditions. The fraction of Am in the supernatant was determined by measuring the gamma-ray radioactivities of the solution with a Ge detector. The fraction of each valence state was calculated by using data obtained by Hara et al. (15).

Experimental Procedures

The initial concentration of Am was 2.0×10^{-9} M in all tests. The concentration of HNO_3 was adjusted to be 0.02, 0.05, 0.1, and 0.2 N just before the irradiation tests. The temperatures of the solutions were maintained at 25°C (room temperature) to 75°C by using the hot stirrer.

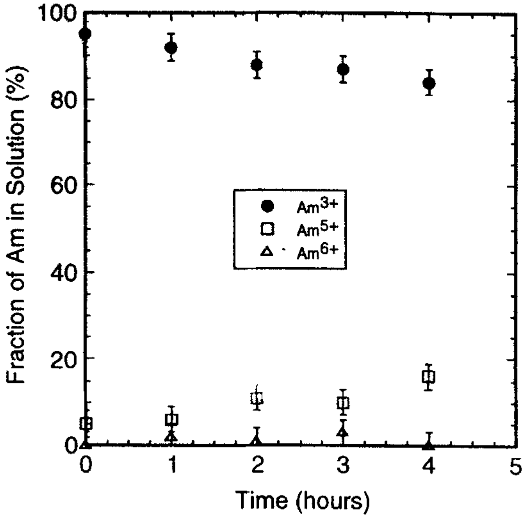
Light irradiation was performed for 1 to 4 hours using the full wavelength and power of the deuterium lamp. Using the LaF_3 coprecipitation method, fractions of Am valence states were calculated.

The parameters of the test procedures were acidity, irradiation time, and the temperature of the solutions. For comparison, experiments were also carried out for cases where ozone alone and where light alone was introduced.

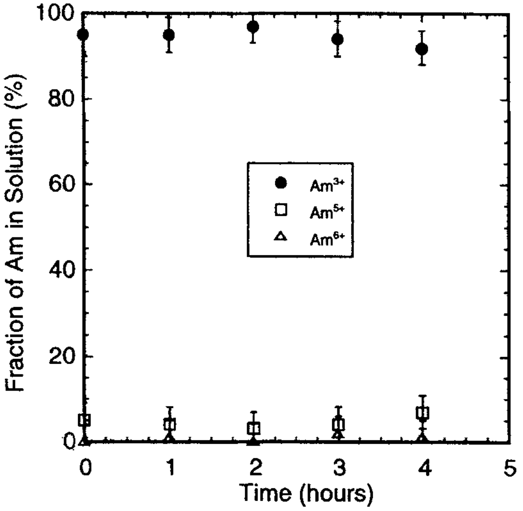
RESULTS AND DISCUSSIONS

Figure 3(a)–(c) show the time dependency of the fraction of Am valence states when light, ozone, and both were introduced. The concentration of HNO_3 was 0.1 N and the solution temperature was 65°C.

Figure 3(a) shows that photons alone can cause the oxidation of Am^{3+}. In this figure the amount of Am^{3+} decreases with irradiation time while the amount of Am^{5+} increases. Since the oxidation of Am^{3+} yields only Am^{6+} in acid solution (7), it is conceivable that Am, which was oxidized from the trivalent to the hexavalent form, was autoreduced to the pentavalent form due to the instability of Am^{6+}. Autoreduction of Am^{6+} to Am^{5+} in HNO_3 solution occurs with respect to total Am concentration. The rate of autoreduction from Am^{6+} to Am^{5+} in HNO_3 solution is kinetically first order to Am concentration, and depends on the acidity of the solution (7). Unless the rate of photooxidation from Am^{3+} to Am^{6+} exceeds that of autoreduction from Am^{6+} to Am^{5+}, the fraction of Am^{6+} in HNO_3 solution cannot increase by irradiation. Since the purpose of this work is

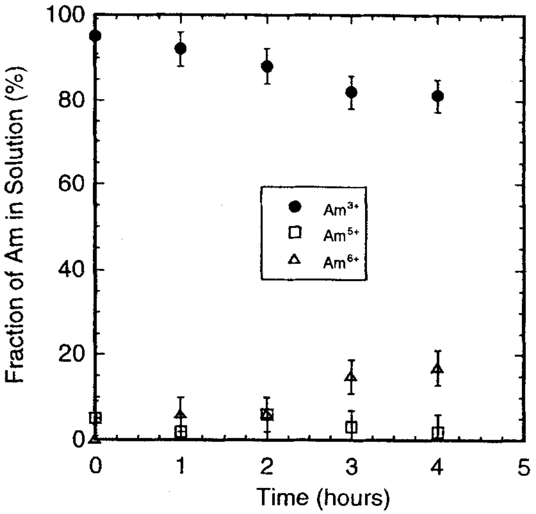


(a) Light



(b) Ozone

FIG. 3a–c Time dependence of valence states of Am.



(c) Light and Ozone

FIG. 3 Continued

to use the higher valence state of Am in separation processes, it is necessary to keep Am in its hexavalent form so that it can be extracted with TBP solution.

Figure 3(b) shows that ozone alone does not cause the oxidation of Am^{3+} to higher valence states in 0.1 N HNO_3 solution.

Figure 3(c) shows that the combination of photolysis and ozone is effective for oxidation. This can be explained by the fact that ozone, which does not oxidize Am^{3+} to Am^{6+} in acid media, readily oxidizes Am^{5+} to Am^{6+} in HNO_3 solution (7). While Am is oxidized to its hexavalent form by light irradiation, ozone plays a role in maintaining Am in its hexavalent form by oxidizing Am which was autoreduced to its pentavalent form. Ozone also has a role in decomposing any nitrous acid formed in HNO_3 solution by radiolysis and photolysis (11). Nitrous acid reduces Am to lower valence states, and eventually to stable Am^{3+}. Decomposition of nitrous acid is thus desirable to make oxidation effective.

Dependence of Oxidation Rate on Temperature and Acidity

The dependence of the oxidation rate of Am on solution temperature and on HNO_3 concentration was examined. Figures 4 and 5 show the time

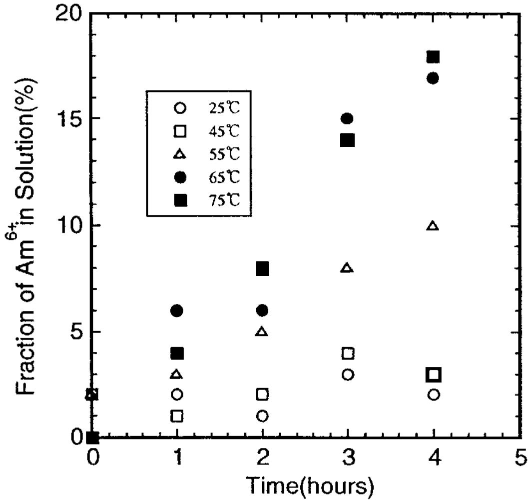


FIG. 4 Time dependence of Am^{6+} fraction at various temperatures.

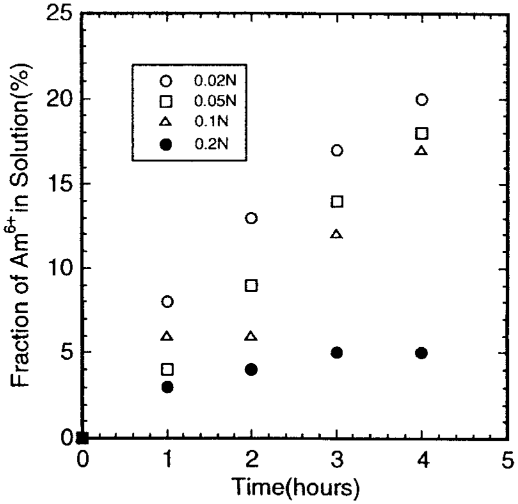


FIG. 5 Time dependence of Am^{6+} fraction at various acidities.

dependency of the Am^{6+} fraction when experiments were carried out at various temperatures and acidities.

It is shown in Fig. 4 that oxidation is more effective when the solution temperature is higher. This is because even though the solubility of ozone into HNO_3 solution become lower with increasing temperature, ozone does oxidize Am^{5+} to Am^{6+} better in HNO_3 solution (8). The oxidation rate does not increase when the temperature exceeds 65°C. At this temperature, all Am^{6+} reduced to Am^{5+} is instantly reoxidized to Am^{6+} by ozone.

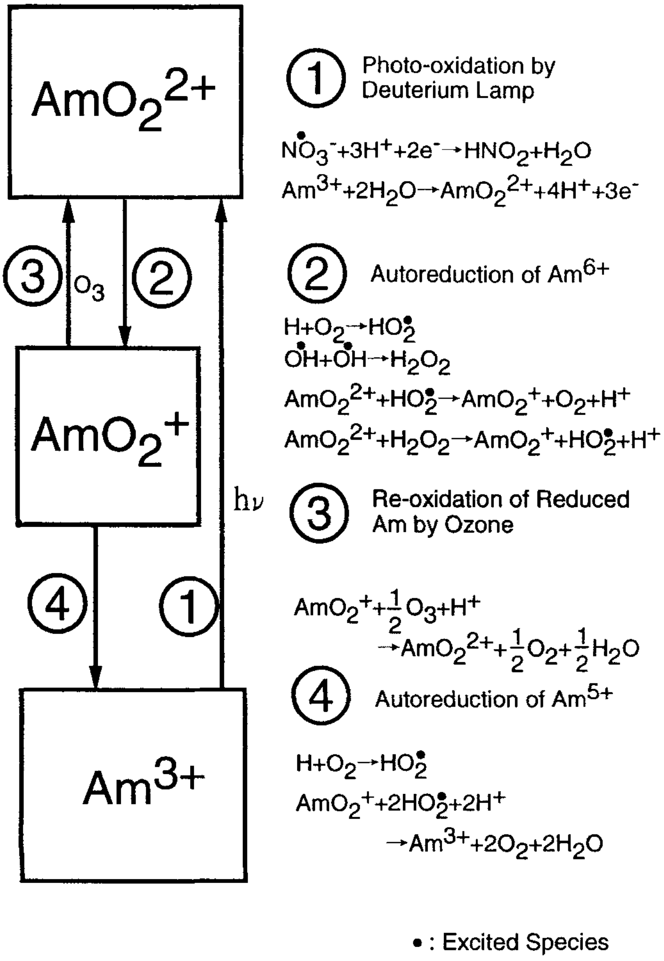


FIG. 6 Chain of redox reactions in sample solution.

It is shown in Fig. 5 that lower acidity is desirable for oxidation. According to Friedman, the reasons for this are: 1) Am is more easily oxidized when the higher valence states are more stable; 2) the quantum efficiencies for Pu and Np, which are elements similar to Am, are in a reverse ratio to the acidity; and 3) Am^{3+} is oxidized by gamma radiation in low-acid solution (5).

Mechanism of Redox Reactions of Am

The following reactions appear to be of particular importance to comprehend Am redox behaviors in the sample solution: 1) photoexcited oxidation of Am^{3+} to Am^{6+}; 2) autoreduction of Am^{6+} and Am^{5+}; and 3) oxidation of Am^{5+} to Am^{6+} by ozone. Since nitrous acid in HNO_3 solution is decomposed rapidly by ozone (11), its effects on redox reactions can be neglected. Figure 6 shows the chain of redox reactions evaluated in the sample solution used in the present work.

According to Wada et al. (3), when light is emitted to Pu^{3+}, the photoexcited nitric acid ion $*NO_3^-$ oxidizes Pu to its higher valence states. It can be assumed that Am, which is similar to Pu, is also oxidized by $*NO_3^-$ when light is emitted. Am^{6+} produced by photolysis will be autoreduced by radicals and ions formed by alpha-radiolysis. Blown ozone, however, reoxidizes Am^{5+} to Am^{6+}. A part of Am^{5+} will not be reoxidized but will be autoreduced to Am^{3+}. Ozone also plays a role by decomposing NO_2, and reduction of Am by NO_2 ions can be prevented.

CONCLUSIONS

The photochemical oxidation of Am^{3+} in HNO_3 solution was demonstrated by using a deuterium lamp (30 W) which emits light in the vacant UV region. Because of the autoreduction of Am^{6+}, it is difficult to maintain Am in its hexavalent form when only a deuterium lamp is used. We were able to carry out the oxidation effectively by using the combination of a deuterium lamp, ozone, and heat because ozone reoxidizes autoreduced Am^{5+} to Am^{6+} in HNO_3 solution when heated.

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