BASIC PHOTOCHEMICAL STUDY OF PLUTONIUM AND NEPTUNIUM

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ABSTRACT

Photochemical technologies are generally expected that it will contribute to advanced nuclear fuel reprocessing process technologies by means of using selective excitation of objective elements with photon energy and following redox reactions in solution.

In this work,as the beginning of the basic photochemical studies in the field of nuclear fuel reprocessing, feasibility studies. of separation between Pu and Np by using photo-oxidization, reduction reactions have been carried out. The results indicate that there is a possibility of photochemically induced valency adjustment to separate Np from Pu in nitric acid solution.

INTRODUCTION

In the conventional nuclear fuel reprocessing technologies, chemical redox reagents have been used to adjust valencies of U, Pu. For example, U(IV) produced by electrolytic reduction or hydroxylamine(HAN) and sodium nitrite are used to adjust Pu valencies to Pu (Ⅲ) and Pu (IV) respectively. However, these chemical reagents cause secondary waste solution.

The several studies of redox reaction using photochemical technologies for nuclear fuel solution as subustitues for these reagents have been reported. In these reports, there are two kinds of studies which are basic photochemical studies of U, Pu and Np[1,2,3] and its application studies to nuclear fuel reprocessing[4,5,6]. The applicabilities of the photochemical technologies have been confirmed from the these studies. However, photo- redox reactions are generally complicated and such as complex reactions which are consist of direct reactions

$$Pu(III) \xrightarrow{\downarrow h\nu} Pu(IV) \xrightarrow{\downarrow h\nu} Pu(VI)$$

and also indirect reactions,

$$NO_3^- \longrightarrow NO_2^- + O^\cdot$$
$$Pu(VI) + NO_2^- + O' \longrightarrow Pu(IV) + NO_3^-$$

are simultaneously occured by photon energy.

Therefore, basic data concerning a variation of the oxidization-reduction potential by photon-excitation, the rate of reaction and other fundamental theories have to be accumulated to control the valencies of objective elements arbitrarily.

In this work, the several basic tests of light exposure for Pu and Np in nitric acid solution were carried out to evaluate the photochemical behaviors of their valencies. The valencies of Pu and Np in nitric acid solution are ordinarily Pu(Ⅲ) ,Pu(Ⅳ), Pu(Ⅵ) and Np(Ⅳ),Np(Ⅴ), Np(Ⅵ).

The distribution coefficients of their valencies between 30% TBP/dodecane and nitric acid are shown in Fig. 1[7]. As shown in this Fig. ,Pu(Ⅳ) ,and Np(Ⅵ) are easely extracted to TBP. However, Pu (Ⅲ) and Np(Ⅴ) which are not shown in it are scarcely extracted and their distribution coefficients are about 10^{-2} and 10″′ respectively. Therefore, if their valencies can be controlled into the following like conditions ① Pu(Ⅳ)-Np(Ⅴ) or ② Pu(Ⅲ) -Np(Ⅵ), their elements are effectively mutually separated.

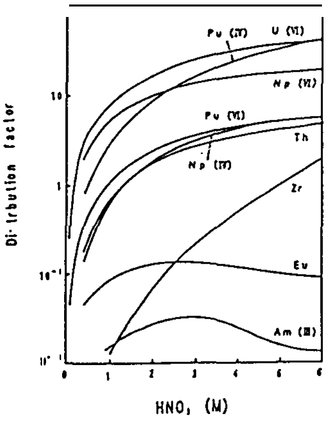

Fig. 1 Plutonium and Neptunium distribution coefficient between 30%TBP/dodecane and nitric acid

EXPERIMENTAL CONDISION

A : Preparation of Test Sample

The concentrations of Pu and Np test nitric acid solutions were adjusted to 1 X10″′ mol and 1 X 10^{-3}mol respectively and they were mixed. The purity of α radioactivity of NP-237 in Np test sample solution was 99.8 %.

Pu test sample solution were prepared by dissolving NBS-949 Pu metal of which abundance ratio of Pu-239 and Pu-241 were about 97 aton % and 0.065 atom % respectively. Therefore, the a -activity contribution of Am-241 compared to the total a -activity of Pu is lower than 1 %.

The valencies of Pu and Np test. mixed solution were completely adjusted to Pu (III) and NP(V) with hydroxylamine(NH_3 OH) and hydrazine(N_2 H,) as shown in Fig. 2 which was the result analyzed by the extraction-chromatographic method.

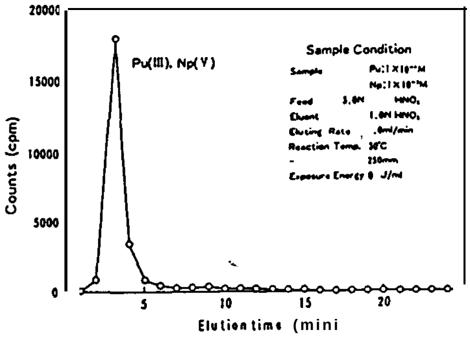

Fig. 2 Valency analysis of mixed solution with Pu and Np by extraction chromatograph

B : Test Instrument

The light exposure instrument system which was used in this work is shown in Fig. 3. This system consists of the Hg lamp light source and the part of a sample cell with a temperature stabilizer and a mixing stirrer to stabilize the temperature of the sample solution and to homogenize it during light exposure.

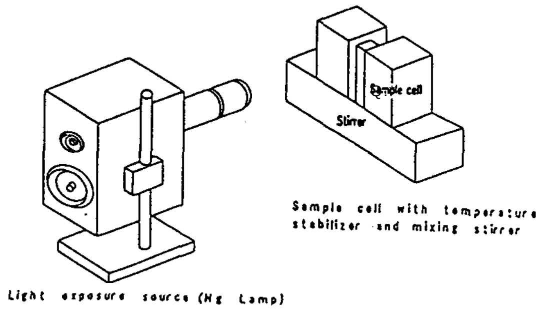

Fig. 3 Outline of instrument of light exposure test

C : Analytical Method

C-1 : Extraction Chromatograph

As a conventional technique of the valency analysis of Pu and Np, calorimetry method has been usually used. However, if concentration of an objective element in a sample solution is less than 10^{-2}mol, the method is not generally applicable.

Therefore, the new method which consisted of the extraction chromatography and the radioactivity analysis of an each valency fraction was used.

First of all, a sample solution is injected into the extraction chromatography column which is filled with Gas- Chrom Q made by Applied Science Corp. and impregnated with TBP. Each valency fraction of Pu and Np is obtained according to specific retention time with the fraction collector.

Then, a -radioactivity of the each fraction is measured by a counting system with ZnS detector. Consequently, the extraction chromatography as shown in Fig.4 is obtained. The horizontal and vertical axis show an elution time and a -radioactivity (CPM) respectively.

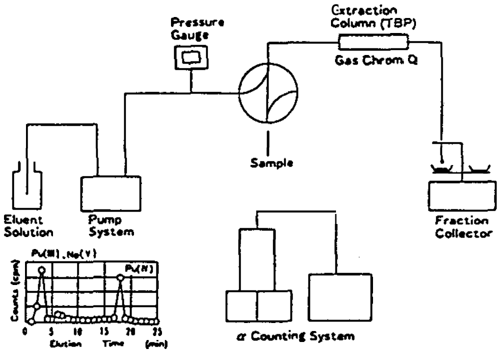

Fig. 4 Schematic diagram of extraction chromatography setup

Fig.5 shows the result of the extraction chromatographic analysis of the Pu, Np mixed solution which contains Pu(III), Pu(IV), Pu(VI) and Np(V). Each valency is eluted in opposite order of an adsorption tendency with TBP.

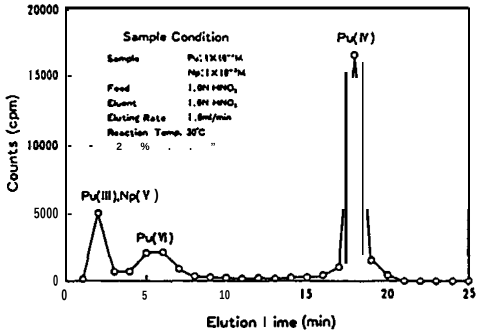

Fig. 5 Valency analysis of mixed solution with Pu and Np by extraction chromatograph

C-2: Pluse Height Analysis

The fraction of Pu(III) and Np(V) mixed solution of which valencies are simultaneously eluted as shown in Fig.5 is analyzed by α spectrometry to distinguish between Pu (III) and Np(V). Fig. 6 shows the result of a spectrometric analysis. As shown in this Fig., Pu and Np are distinguished according to α ray energy from their nuclides and the mixture ratio is quantitatively determined.

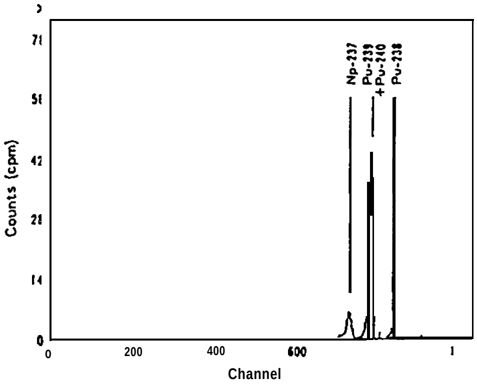

Fig. 6 Pluse height analiysis of α-ray from Pu and Np

RESULTS AND DISCUSSION

Fig. 7 shows the step flow of the light exposure tests for Pu and Np in this work. First, the initial valencies condition of Pu, Np mixed sample was adjusted to Pu (III), Np (V) and their concentrations were 1×10^{-4}mol, 1×10^{-3}mol respectively .

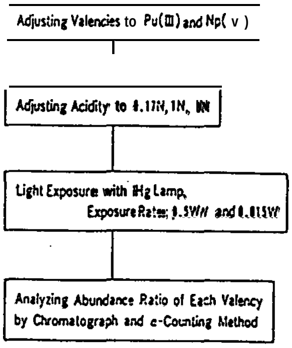

Fig. 7 Step flow of light exposure tests

At the second step, the acidities of several aliquots of the initial sample were adjusted to about 0.2N,1N and 3N.

Next, the light exposure tests were carried out with the exposure rates of 0.5W and 0.015W using the Hg lamp.

At the final step, the radioactive analyses of the each fraction from the extraction chromatography colurn were carried out. As shown in this fig. ,the parameters of these tests are the acidity of the sample solution and the rate of light exposure.

Fig. 8 shows the results of the light exposure tests under the conditions of which the parameters are 3N nitric acid and 0.5W exposure rate.

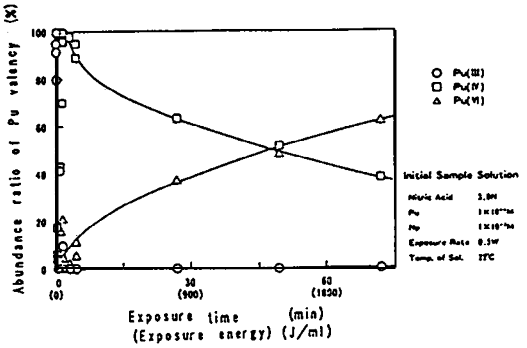

Fig. 8 Redox reaction of Pu by light exposure

The horizontal and the vertical axis in this Fig. show the exposure time (energy) and the abundance ratio (%) of the each valency in the element respectively.

This result indicates that 0.5W of the light exposure rate was too strong so that Pu (III) momentarily decreased untill about zero percent level and Pu (IV) oppositely momentarily increased. After several minutes, Pu (IV) gradually decreased and on the contrary, Pu (Vi) gradually increased. In other words, it shows that Pu (III) was momentarily oxidized to Pu (IV) and seemingly, Pu (IV) was gradually oxidized to Pu (VI) under such as the conditions due to the equilibrium of the oxidization-reduction reaction.

Fig. 9,10,11 show the results of the light exposure tests under the conditions of the light exposure rates ; 0.015W and of the acidities ; 0.17N,1N,3N. These Fig. show that Pu(III) was more slowly oxidized to Pu (IV) than at the case of Fig. 8 and the rates of these oxidization became faster according to the increase in acidity.

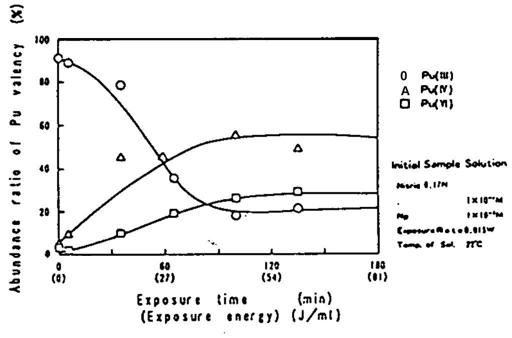

Fig. 9 Redox reaction of Pu by light exposure

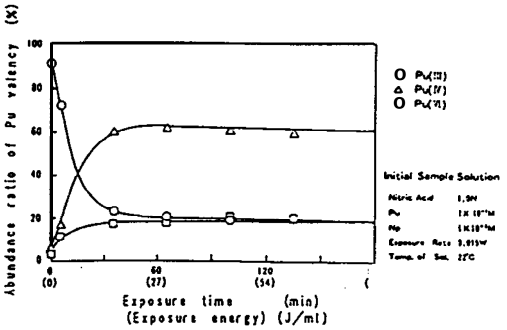

Fig. 10 Redox reaction of Pu by light exposure

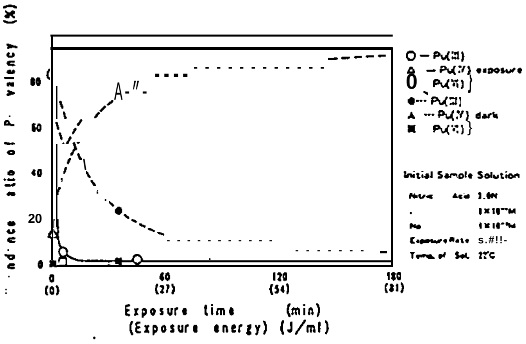

Fig. 11 Redox reaction of Pu by light exposure

Particularly, the results of Fig, 11 were characteristic in the redox reaction because Pu (III) uas momentally completely oxidized to Pu (IV). Furthermore, there was little Pu (III) and Pu (VI) issued from the oxidization of Pu(IV) and the equilibrium state reached within about 10 minutes after the beginning of light exposure.

The result of the dark test without light exposure was also shown in Fig. 11. This result shows that Pu(III) was very slowly oxidized to Pu(IV) and it took about two hours untill the equilibrium state.

Fig. 12 shows the result of the extraction chromatographic analysis of the sample at the equilibrium state when the exposure energy was 56 J/ml in Fig. 11. From this result, it was also found that the valencies of Pu were controlled to Pu (IV) and there was little Pu(III) and Pu(VI).

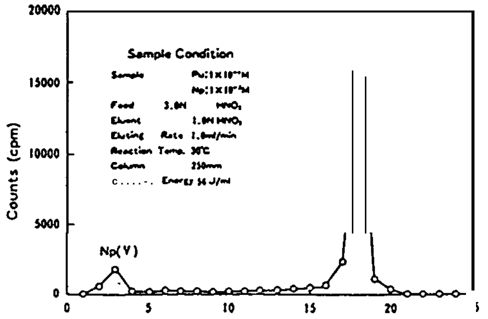

Fig. 12 Valency analysis of mixed solution with Pu and Np by extraction chromatography

Then, this Fig. shows that Np(V) in the initial sample was not oxidized and also was not reduced by light exposure under these conditions.

Such as controlled valencies condition, Pu (IV) and Np(V), is most suitable for the separation between Pu and Np.

These photochemical behaviors were caused by the direct excitation with photon energy for an objective ion, redox reactions with the photolytic products such as HNO_2, NO_x from HNO_3 and other excited species.

The supposed theories for these results should be discussed in several aspects of the standard electrode potentials for all of coexisting element species, excitation level by photon energy and wave length characteristic of exposure light, etc on the basis of the data obtained from furthermore detail photochemical tests.

CONCLUSION AND R&D PLAN IN THE NEXT STEP

From this work, following conclusions were obtained

● Results of Photochemical Behaviors of Pu and Np

① Pu・Pu(III) is oxidized to Pu(IV) and until Pu(VI) by light exposure.

- As to the oxidization of Pu(III)→Pu(IV), the more the acidity of nitric acid solution increase, the more the reaction is easily proceed in the range of 0.1N→3N HNO_3.
- On the other hand, in the case of the reaction of Pu(IV)→Pu(VI), the more the acidity decrease, the more the generation rate of Pu(VI) increase in the range of 0.1N→3N HNO_3.

② Np・Np(V) is not oxidized to Np(VI) and also is not reduced to Np(IV) by light exposure in HNO_3 of 0.1N→3N.

◆ Conclusion

- It is defined that there is a possibility of removal of Np from Pu, Np mixed solution which is adjusted to Np(V) and Pu(III) by using photochemical reactions with the adequate rate of light exposure and the adequate acidity of HNO_3.

From above the discussions and conclusions, following R&D of the next step are planed.

◆ R&D Plan in The Next Step

- The continued photochemical studies for the removal technologies of several percent of Np contained in Pu production solution simulating the reprocessing process.
- The studies of photochemical behaviors of U, Pu and Np in a mixed nitric acid solution.
- The studies of selective separation technologies of objective elements (U, Pu, TRU and FP) by using photochemical techniques with a selective wave length of laser.
- The development of the quantitative analysis method of trace amounts of an objective element by the laser-induced thermal lensing spectroscopy.

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