研究論文

133. Neptunium-237 in JRR-1 Fuel Solution

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The fuel solution of 20 % enriched uranium was taken out from JRR-1 after 5×10^4 kWh operation for chemical analyses. From this solution, neptunium was separated in combination of solvent extraction and anion exchange techniques, providing that ^{237}Np would be found as the final product of the neutron captures and subsequent beta decay of ^{235}U . According to the alpha-spectrometric study, it was shown that the neptunium fraction contained only ^{237}Np .

INTRODUCTION

Two of the isotopes of neptunium, *viz.* ^{237}Np and ^{239}Np , are formed by neutron irradiation of natural uranium as illustrated in Fig. 1. ^{237}Np is easily obtained by neutron irradiation of natural uranium in the nuclear reactor for few hours and is available for tracer chemical studies of neptunium. ^{237}Np may be formed through two ways:

- (1) from ^{235}U through successive neutron capture *via* ^{236}U , a phenomenon which becomes important in case of enriched nuclear fuels;
- (2) by fast neutron reaction on ^{238}U *via* ^{237}Np .

The long half-lived ^{237}Np makes macro scale studies of neptunium possible. Therefore, in the course of neptunium study, it was desired to prepare the ^{237}Np isotope; and this was the first time to identify ^{237}Np in the JRR-1 fuel solution.

Fig. 1 Formation of ^{237}Np and ^{239}Np

There are several published works on the isolation of ^{237}Np from waste solutions of reactor fuel reprocessing^{(1)~(11)}. However, in some of these works, neptunium in the starting solution was not recovered completely,

Fig. 2 ^{237}Np determination carried out at the ANL

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or the reagent used was thought to be unsuitable. For instance, thenoyltrifluoroacetone was found not so effective when used as separating agent⁽⁹⁾. In the other works separation was carried out in order to prepare gram quantities of this isotope. Besides the above mentioned works, the process of analysis of neptunium which may contaminate plutonium as developed at the Argonne National Laboratory in U.S.A. was reported as Fig. 2. This method involves the use of mono-(2-ethyl hexyl) phosphoric acid as a reagent for the isolation of ^{237}Np .

In this work, the amount of ^{237}Np in a little portion of JRR-1 fuel solution was calculated to be very small, about 20 dpm, and was present together with large amounts of uranium, plutonium and fission products. Therefore the method for neptunium separation was devised conferring with such informations *vis.*, the reductants used in the present work were the same as those shown in Fig. 2. Neptunium in aqueous solution shows usually a complicated chemistry having three oxidation states, and it is difficult to prepare neptunium tracer solution which contains only one oxidation state. This fact makes the complete isolation of neptunium, from uranium, plutonium and fission products difficult⁽⁹⁾. The isolation method used in this work was based on a previous solvent extraction study⁽¹²⁾ in which the TBP (tri-*n*-butyl phosphate) extraction behavior of neptunium in some mineral acids had been investigated, paying particular attention to its oxidation states. Ion exchange studies on neptunium⁽¹³⁾ and plutonium⁽¹⁴⁾ having been already carried out in JAERI were also utilized for the isolation

of ^{237}Np . The present article describes details of the isolation method of ^{237}Np using TBP extraction and anion exchange techniques.

EXPERIMENTAL AND RESULTS

1. Sources of materials

The original solution, a little portion of the fuel solution, was taken out from

Fig. 3 Process for isolation of ^{237}Np

JRR-1 reactor, after attained to the operation time of 2,265 hr with a total power of 5×10^4 kWh. The solution was received after diluting with 1 N nitric acid. The sample was cooled for 3 months so that ^{239}Np and short lived fission products might have decay off before separation process was started. The main constituents of the solution are given in Fig. 3.

Both nitric and hydrochloric acids, of analytical reagent grade, were used as received. The reducing agents, ascorbic acid, hydroxylamine hydrochloride, hydroquinone and potassium iodide, were all C. P. grade. Anion exchange resin, Dowex-1, X-8, 100~200 mesh, was used as the nitrate-form after ordinary conditioning. Tri-*n*-butyl phosphate was purified in the usual way^{(15)~(18)}.

2. Results

The process of isolation of ^{237}Np is schematically shown in Fig. 3. The sample solution was dried up with an infra-red lamp. After being converted to chloride, the obtained residue was dissolved in 1 N hydrochloric acid. Few milligrams of ascorbic acid were then added the hydrochloric acid solution in order to keep neptunium in the reduced state. The resulted solution was evaporated to nearly dryness avoiding any blackening, and the residue was then taken up in 7.5 N nitric acid. The nitric acid solution was passed through a Dowex-1 resin column in nitrate form.

As Table 1 shows, ^{237}Np can not be separately identified from ^{234}U , but from ^{235}U , ^{236}U , ^{238}U and ^{239}Pu . Accordingly, the resin column must be sufficiently washed with 7.5 N nitric acid to remove off uranium completely. Therefore, excessive 7.5 N nitric acid of 80 ml were passed through the column at this stage.

The gamma activity measured at the outside of the ion exchange column decreased by washing from 150 mr/hr to 0.15 mr/hr. The combined solution of the effluent and washings was set aside to recover enriched uranium.

The Dowex-1 resin column holding all of neptunium and plutonium was washed

Table 1 Alpha energy of nuclides liable to be present in JRR-1 fuel solution (MeV)

^{234}U	4.763, 4.707
^{235}U	4.40, 4.58
^{236}U	4.499
^{238}U	4.18
^{237}Np	4.77
^{239}Pu	5.150

with 0.3 N nitric acid. All neptunium was contained in the initial 50 ml of eluant together with a part of ^{239}Pu , which was separated from neptunium in the following step with solvent extraction technique. Besides that, plutonium remaining in the resin column was eluted with 20 ml of 0.3 N nitric acid which contained 5 % hydroxylamine.

The behavior of neptunium and plutonium in TBP extraction will be surveyed in order to know the conditions in which neptunium is purified effectively from plutonium. The

K_d values for Np(IV) and Pu(IV) or Np(VI) and Pu(VI) in TBP extraction are to be found in some published papers^{(19)~(22)}, and these oxidation states are thought to be unsuitable for separating these two elements by solvent extraction. The K_d values for ^{239}Pu , reduced to trivalent state with 0.1 M hydroquinone and 0.1 M ammonium iodide, in the system 100 % TBP vs. hydrochloric acid were determined⁽¹⁹⁾, and the results

Fig. 4 The K_d values for Pu and Np in the system of 100 % TBP-HCl

obtained are plotted in Fig. 4 together with the acid dependence curves for Np (IV), (V) and (VI) obtained in the previous work⁽¹²⁾. From the magnitude of their K_d values, Np (IV) and Pu(III), the two species obtained by the above mentioned reducing agents, can be separated from each other at 12 N hydrochloric acid. Hence, the purification of ^{237}Np was carried out according to these informations.

The 0.3 N HNO_3 eluant from Dowex-1 resin column containing ^{237}Np and a part of ^{239}Pu was brought to dryness. The residue was dissolved in concentrated perchloric acid and was dried up in order to make neptunium in quinquivalent state and iron in trivalent state. After drying up, iron (III) was immediately removed from the 4 N hydrochloric

acid solution of the residue⁽¹⁵⁾ with 50 % TBP-toluene; a part of plutonium was also extracted into the organic phase. The resulted aqueous phase was washed with benzene and then allowed to dry up. The residue obtained was dissolved in 12 N hydrochloric acid containing the reducing agents, and neptunium was extracted with the pre-equilibrated 100 % TBP, and then scrubbed 7 times with the same aqueous solution in order to remove plutonium.

Out of the 2 ml organic and the 6.5 ml aqueous solutions resulted, 0.1 ml portions were plated on platinum plates. The plates obtained gave counts of 130 and 915 cpm of alpha particles respectively with 2 pi gas flow counter, and were sent to St. Paul University,

Fig. 5 α -spectrogram of the last aqueous and organic phase

Tokyo, in order to assign the particular nuclide by alpha spectrometry. The alpha spectrum of the two phases are shown in Fig. 5. The value of 4.77 MeV was calculated as the alpha energy for the peak measured. Since alpha energy of ^{237}Np is found to be 4.77 ± 0.05 MeV, the alpha emitter in the organic solution obtained was ^{237}Np . Fig. 5 also shows that no ^{239}Pu was detected in the spectrogram for the isolated ^{237}Np . The purity of ^{237}Np was high. In the aqueous phase, a very small amount of ^{237}Np was shown to exist in ^{239}Pu ; in other words the separation of neptunium from plutonium was fairly good. Finally the amount of ^{237}Np found in this work was calculated as 10^2 cpm/mg U. The gamma and beta activities found in the prepared ^{237}Np sample was small.

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JRR-1 燃料中のネプツニウム-237

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総合調査の目的で一部分取り出された JRR-1 の燃料中には、長寿命の α 放射体である同位体の存在が予想される。共存する多量のウラン、 ^{239}Pu および核分裂生成物からネプツニウムを分離精製し、 ^{237}Np の存在を確認した。

陰イオン交換および溶媒抽出について、すでに得られているデータを基礎とし、プルトニウムについてのデータを一部補足して分離精製法を計画した。

得られたネプツニウムのフラクションについて、 α スペクトロメトリを行なった結果、 α エネルギーは ^{237}Np に一致した。得られた量は 10^2 cpm/mgU であり、 β , γ 放射体の量は少なかった。