

## RECENT PROGRESS OF RESEARCH ON NITRIDE FUEL CYCLE IN JAERI

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### Abstract

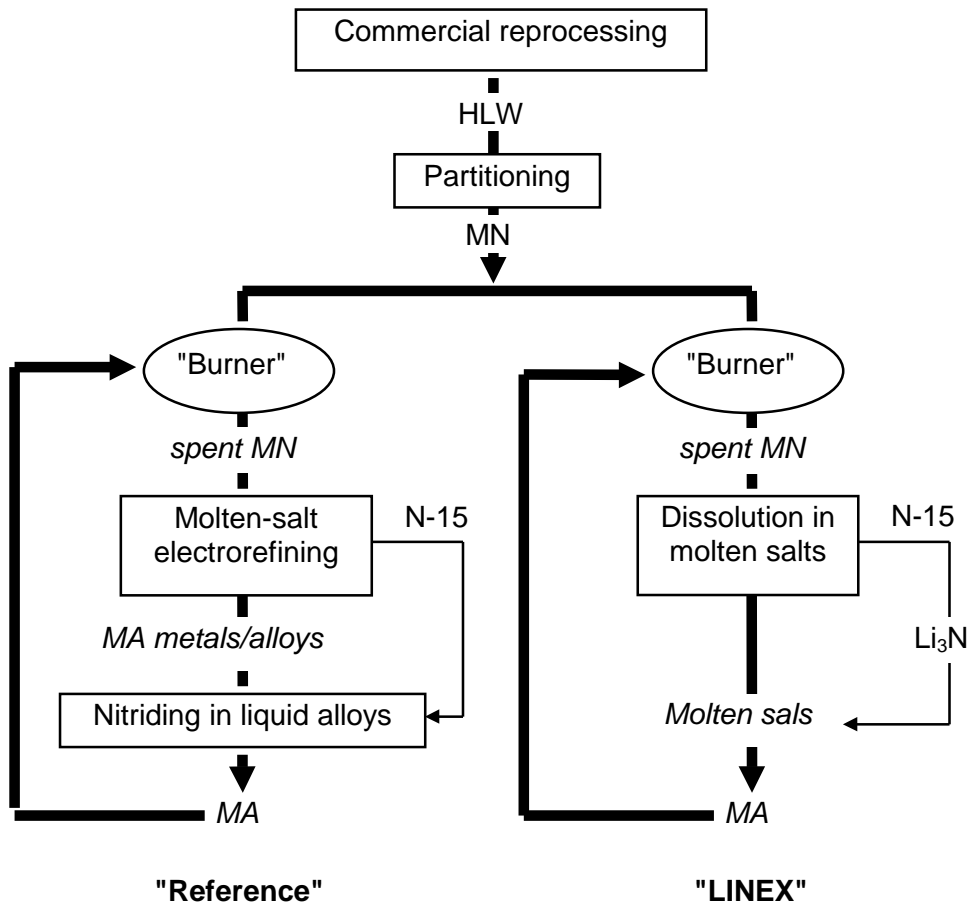
The present status of the research on the nitride fuel cycle for transmutation of minor actinides (MAs) in JAERI is described. The recent research focuses on the pyrochemical process and the database for fuel properties. As for the pyrochemical process, electrochemical studies have been carried out mainly by voltammetry to understand the electrodeposition of actinide elements in the LiCl-KCl system. The recovery of Np and Pu metals was demonstrated by electrolysis of the nitrides at gram-scale experiments. In relation to a new concept "LINEX", the evolution behaviour of N<sub>2</sub> gas was also examined by oxidation of NdN with CdCl<sub>2</sub> and it was confirmed that nitrogen in NdN may be recovered up to 95%. The properties of nitride fuel, such as thermal conductivity and irradiation behavior, have been investigated for the preparation of the database.

**Introduction**

Nitride fuel is a promising candidate for transmutation of MAs because of its excellent thermal and neutronic properties [1,2]. The advantages of nitride fuel have been confirmed through the research on the nitride fuel cycle and the recent interest focuses on the application of pyrochemical process with the LiCl-KCl eutectic melt to the nitride fuel cycle and the preparation of the database on fuel properties such as thermal conductivity and irradiation behaviour.

The pyrochemical process, which has been developed originally by the ANL laboratory [3], may be applicable to the reprocessing of nitride fuel with minor modifications as shown in Figure 1 [4], because actinide nitride is a good electric conductor and the free energy changes for the formation of chlorides from nitrides of actinides and most of FPs are similar to the case of metal fuel. This system may be convenient for recovering <sup>15</sup>N-enriched nitrogen gas, contrary to the Purex method where nitrate solution is used and the recovery of <sup>15</sup>N<sub>2</sub> gas may be difficult. In order to confirm the applicability of the pyrochemical process to the nitride fuel cycle, the electrolysis of nitrides such as UN, NpN and PuN in the LiCl-KCl eutectic melt and the relating electrochemical studies have been carried out in JAERI [5-7]. In addition, a new concept, "LINEX", has been proposed as an alternative option as shown in Figure 1 [8]. In the LINEX process, actinide elements in spent nitride fuel are selectively dissolved as chlorides into the molten salt by electrolysis or oxidation and the actinide nitrides are synthesised from the chlorides by adding Li<sub>3</sub>N, which is formed by the reaction of Li with <sup>15</sup>N<sub>2</sub> gas released at the dissolution step of the spent nitride fuel.

Figure 1 Concepts of nitride/pyroprocess for MA burning



The properties of nitride solid solutions of the UN-NpN-PuN system, such as thermal conductivity and evaporation behavior, have been studied to prepare the database [9-12]. Furthermore, an equipment is being installed in the WASTEF of JAERI to study the fabrication of AmN. With regard to the irradiation behavior, the irradiation tests up to the burnup of about 5.5%FIMA in JMTR have been completed and it has been confirmed that nitride shows excellent performance, i.e., very low fission gas release of about 0.5%/FIMA [9]. Uranium-plutonium mixed nitride fuel is under irradiation in JOYO with a collaboration with JNC up to a target burnup of about 4% FIMA to confirm the performance of nitride fuel in fast neutron circumstances.

This paper describes the present status of the research on nitride fuel cycle in JAERI, especially on the results obtained after the last meeting on P&T [13].

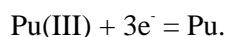
## **Pyrochemical Process of Nitride Fuel**

### *Electrolysis of Actinide Nitrides*

#### *Electrode Reaction of Minor Actinides*

The electrochemical behaviour of Np and Pu on the solid electrodes in the LiCl-KCl eutectic melt was studied by cyclic voltammetry [6] to understand the behavior of actinide elements in the molten salt and the electrodeposition on the electrodes. The chlorides of Np and Pu were prepared as the mixtures with LiCl-KCl by oxidation of NpPt<sub>3</sub> and Pu metal with CdCl<sub>2</sub> in the LiCl-KCl eutectic melt at 773 K, respectively.

The voltammogram of Pu in LiCl-KCl-0.54wt.%PuCl<sub>3</sub> with a Mo working electrode and a Ag/AgCl reference electrode was obtained in the temperature range of 773 – 973 K. The electrodeposition and dissolution of Pu can be expressed by the following equation,

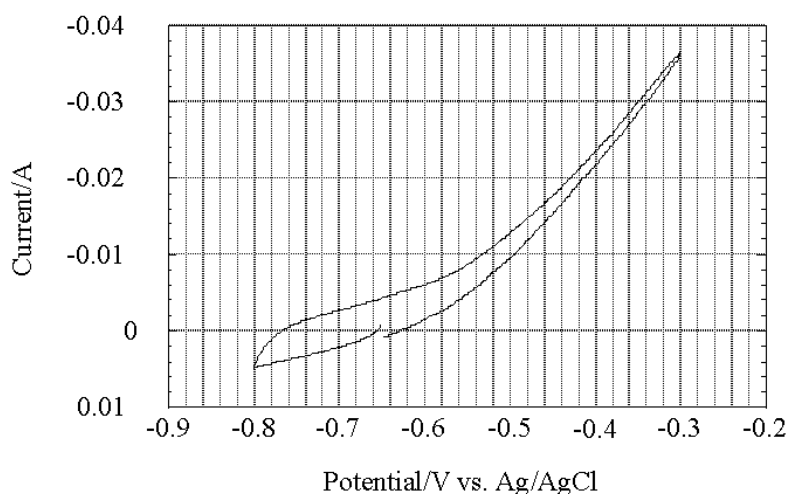


The reaction is considered to be quasi-reversible and diffusion may be a rate-determining step. The observed potentials can be principally explained by the thermodynamic functions, but there were found some discrepancies caused perhaps from the interaction between the actinide metals and the surface of the electrode. The voltammogram of the system of LiCl-KCl-NpCl<sub>3</sub> showed similar behavior to the case of the LiCl-KCl-PuCl<sub>3</sub> system.

#### *Recovery of actinide metals by electrolysis*

The dissolution of NpN and PuN at the anode and the electrodeposition of the respective metals on the solid cathode were examined by electrolysis in gram-scale experiments [7]. The concentrations of actinide chlorides in the LiCl-KCl were about 0.54wt.%. Nitride samples were prepared by carbothermic reduction of the dioxides, NpO<sub>2</sub> and PuO<sub>2</sub>, in a N<sub>2</sub>-H<sub>2</sub> stream [14].

Figure 2. Cyclic voltammogram of NpN in LiCl-KCl



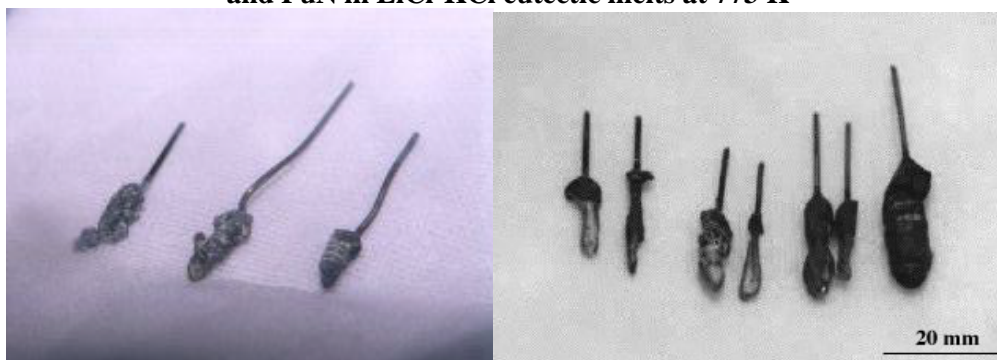
The nitrides of Np and Pu were confirmed from the cyclic voltammograms to dissolve and form the ions such as Np(III) and Pu(III) at the anode. The theoretical potential for the dissolution of PuN was evaluated from the observed one to be  $-0.865$  V vs. a Ag/AgCl reference electrode with 1.00wt.%AgCl, which is close to that estimated from the thermodynamic functions. In case of UN, the formation of UNCl was confirmed theoretically and experimentally [4,5], but no ternary compound like UNCl was observed in cases of NpN and PuN as expected from thermodynamic considerations [4].

For the electrolysis of nitrides, a cage made of tungsten was used as an anode in which several small pieces of nitride blocks were put. A molybdenum wire was used as a cathode. The composition of the salt was the same as above. The electrolysis of nitrides was carried out under the conditions of constant potential ( $-2.00$ V) and constant current (10-20mA) by using a potenti/galvanostat coulometer. The deposits of Np and Pu on the Mo cathodes are shown in Photo 1. In cases of the Pu experiments, it was observed that a part of the deposit was taken off from the cathode. Such tendency was also pointed out from the experiment with LiCl-NaCl-CaCl<sub>2</sub>-BaCl<sub>2</sub> eutectic melt [15]. Therefore, in cases of the NpN experiments, spiral-shaped wires were used to keep the deposits on the cathode. As the concentrations of actinide chlorides in the LiCl-KCl were relatively low, the deposits included a lot of salts. Obviously, the deposits showed a paste-form and were differed from that of U, which forms a dendrite precipitation. After heating the deposits at 1073 K, the parts of metallic form were subjected to X-ray diffraction analysis and confirmed to consist of alpha Np and Pu metals, although the salts still remained.

### *LINEX Concept*

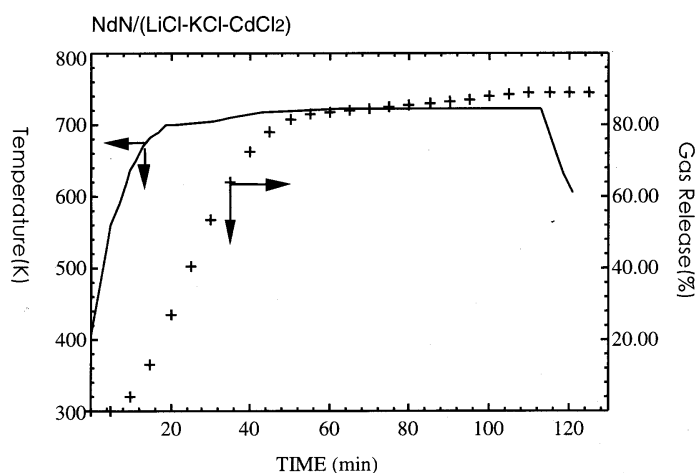
A new concept, "LINEX", has been proposed as an alternative option to the ANL method [4,8] as shown in Figure 1. As for nitride fuel, the recycle of <sup>15</sup>N-enriched nitrogen is a subject to be solved to compensate the cost of <sup>15</sup>N enrichment. In the process, <sup>15</sup>N<sub>2</sub> is recycled by use of Li<sub>3</sub>N, i.e., <sup>15</sup>N<sub>2</sub> gas released from spent fuel is combined with Li to form Li<sub>3</sub><sup>15</sup>N and Li<sub>3</sub><sup>15</sup>N reacts with actinide chlorides in the molten salt to form the nitride. In this case, it is important to understand the evolution behavior of nitrogen in the salt. As a preliminary test, the evolution of nitrogen gas during the oxidation of NdN by CdCl<sub>2</sub> in the LiCl-KCl eutectic melt was examined [8].

Photo 1. Deposits of Np(right) and Pu(left) on cathodes by electrolysis of NpN and PuN in LiCl-KCl eutectic melts at 773 K



A typical result is shown in Figure 3, which shows that 90% of nitrogen in NdN was evolved from the salt. Considering the oxygen impurity in the NdN sample used in the experiments, it was evaluated that 95% of nitrogen could be recovered in this case. This result suggests that  $^{15}\text{N}$ -enriched nitrogen gas may be recovered with high efficiency in the pyrochemical process of nitride fuel. In case of no recycle of  $^{15}\text{N}_2$  gas(100% loss), the price of  $^{15}\text{N}$  may be required to be lowered to around \$10/g- $^{15}\text{N}_2$ (99.9% enrichment). However, if 90% of  $^{15}\text{N}_2$  can be recycled, the required price of  $^{15}\text{N}_2$  enrichment may be around \$100/g, which may be commercially achieved on the basis of the present technology.

Figure 3. N<sub>2</sub> evolution during oxidation of NdN\* by CdCl<sub>2</sub> in LiCl-KCl eutectic melt. Molar ratio, NdN/(LiCl-KCl) = 0.021, \* 7.90 wt% N, 1.45wt% O, 0.063 wt% C.



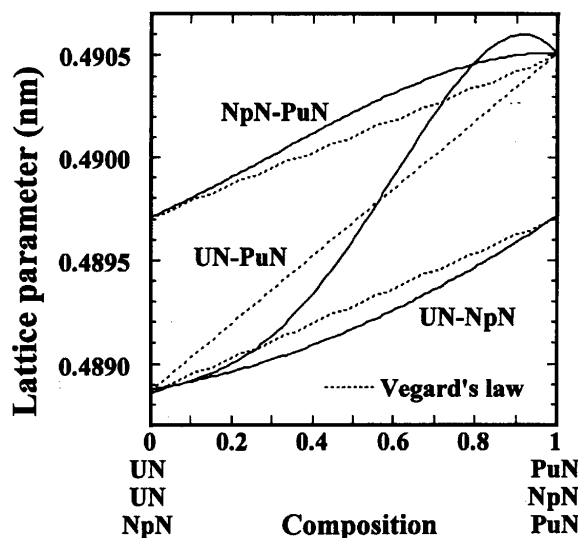
## Database of fuel properties

### Formation of Nitride Solid Solutions

The formation of the solid solution of actinide mononitrides can be pointed out as an advantage of nitride from the viewpoint of fuel stability under irradiation, contrary to oxide and metal fuels in which the solubilities of MAs are very limited. The binary solid solutions in the UN-NpN-PuN system were, therefore, prepared and the phases formed were checked by X-ray diffraction analysis. The procedure of sample preparation was described in earlier papers [9,14]. From the X-ray diffraction analysis no compound was observed except the NaCl-type cubic-structured mononitride and faint dioxides.

As shown in Figure 4, the lattice parameters of the solid solutions change continuously with the compositions, but deviate from the Vegard's law. It may be understood that the lattice parameters of the solid solutions deviate positively in the PuN-rich region, while negatively in the UN-rich region in a case of the UN-PuN solid solutions. Similar behavior can be seen in cases of the UN-NpN and NpN-PuN solid solutions as shown in the figure. The results indicate that the actinide mononitrides may form solid solutions in the whole composition range, but they are not ideal from thermodynamic aspects [11].

Figure 4 Lattice parameters of UN-NpN-PuN solid solutions

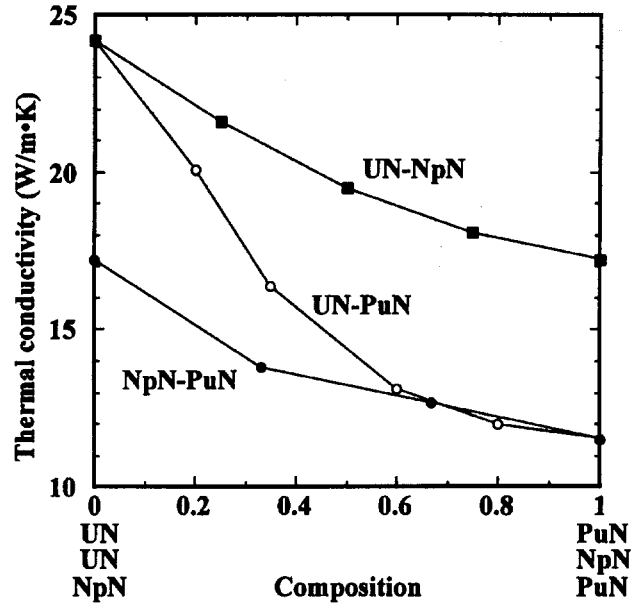


#### *Thermal conductivity and evaporation behavior*

The thermal conductivities of the binary solid solutions of the UN-NpN-PuN system were evaluated from the data on thermal diffusivity determined by a laser flash method, the specific heat capacity and the density [9,11,12]. The specific heat capacities were estimated from literature or by an additive method in case no literature datum was available. The theoretical density was calculated from the lattice parameters described above. The porosity correction to 100% theoretical density was made by use of the Maxwell-Eucken equation. The thermal conductivity of the solid solutions of the UN-NpN-PuN system was found to increase gradually with temperature like the respective mononitrides. Figure 5 shows the thermal conductivities of the binary solid solutions at 1273K. It can be seen that the thermal conductivities change continuously with the compositions, but the values for the solid solutions are lower than those evaluated by a simple additive law. Recently the PuN-ZrN solid solutions were prepared and the determination of the thermal conductivity is under way. A preliminary result indicates that the solid solutions show similar values to those of the respective mononitrides, PuN and ZrN.

The evaporation behavior of actinide mononitrides and their solid solutions has been investigated by Knudsen-effusion high temperature mass-spectrometry [10,16]. UN and NpN were confirmed to form liquid precipitations at evaluated temperatures and the pressures of the actinide metal vapours are close to those of the respective pure metals, while PuN evaporates congruently [16].

Figure 5 Thermal conductivity of UN-NpN-PuN solid solutions



The binary solid solutions of the respective nitrides show relatively complicated evaporation behavior [10,11]. With regard to the solid solutions of UN and PuN, (U,Pu)N, the pressures of U(g) and Pu(g) depend on the composition of the solid solutions. It indicates that (U,Pu)N evaporates congruently and no liquid phase may form at least in the experimental conditions. In the system of NpN-PuN, the partial pressures of Np(g) over the solid solutions are close to that over pure metal, Np(l), and slightly depend on the PuN concentration. It suggests that a selective precipitation of a liquid phase containing Np may be occurred at evaluated temperatures. On the other hand, the pressure of Pu(g) depends on the PuN concentration in the solid solutions at higher temperatures. It may indicate that the liquid phase does not contain significant concentration of Pu. At lower temperatures, the formation of a liquid phase with Pu was suggested, because of the relatively high Pu vapour pressure.

### *Irradiation behaviour*

The irradiation tests of uranium-plutonium mixed nitride fuel in JMTR show the advantages especially in the lowering of fission gas release by adoption of the cold fuel concept as described earlier [9,13]. It was confirmed from the puncturing tests that FP gas release of mixed nitride fuel irradiated up to 5.3-5.5%FIMA is 1.7-2.8% and the observed ratios of Xe/Kr agreed with calculated ones, 16. While most of FP gas was retained within fuel pellets, the increase in diameter of fuel pins was rather small; 0.4% at the maximum. The swelling rates evaluated from the porosity measurements were 0.6-0.8%/FIMA. These results suggest that the observed swelling may be caused mainly from the accumulation of solid FPs. No chemical interaction was observed at the interface with cladding tubes and pellets.

Two (U,Pu)N fuel pins are under irradiation in JOYO with a collaboration with JNC(previously PNC) up to a target burnup of about 4%FIMA. According to the operation program of the JOYO, the irradiation will end in the middle of 1999 followed by post-irradiation examinations in the facilities of JNC and JAERI.

## Concluding remarks

The recent progress of the research on nitride fuel cycle, which is the reference system for transmutation of MAs in JAERI, is described. The electrochemical studies in the LiCl-KCl eutectic melt have been carried out in order to establish the database for the design and evaluation of the pyrochemical reprocessing system of nitride fuels. The electrolysis of UN, NpN and PuN was examined at 773 K. The dissolution of actinides at the anode occurred around the theoretically evaluated potential and the respective actinide metal was found to deposit on the solid cathode. The other pyrochemical process, "LINEX", has been proposed for the reprocessing of nitride fuel. In the process, actinide elements in spent nitride fuel are dissolved in molten salt as chlorides and directly converted to the nitrides in the salt by the reaction with  $\text{Li}_3\text{N}$ . The evolution behavior of  $\text{N}_2$  gas, which must be recycled in the nitride fuel system because of the utilisation of enriched N-15, was studied by use of lanthanide nitrides. The fundamental behavior of actinide elements in the molten salts, such as the distribution between the salt and molten metal and the electrodeposition, was also determined by electrochemical experiments.

The database of the properties of nitride fuel is also being prepared. The properties of actinide mononitrides such as thermal conductivity and evaporation behaviour have been determined. The quasi-binary system of NpN and the other actinide mononitride forms the solid solution, but is not considered to be thermodynamically ideal because of the deviation of the lattice parameters from the Vegard's law. The thermal conductivity of the solid solutions of actinide mononitrides was derived from the data on thermal diffusivity determined by a laser flash method. The evaporation behavior of the nitrides has been determined by high temperature mass spectrometry. From the irradiation tests of (U,Pu)N fuel in JMTR, the fuel shows excellent performance; the fission gas release was found to be very low, around a few percent, and there was no significant chemical interaction between fuel and cladding, at least up to the burnup of 5.5%FIMA.



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