

Development of the process flow diagram of the pyrochemical reprocessing of spent nitride fuel for ADS

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Abstract

Solid solutions of actinide mononitrides have been proposed as a candidate fuel of the accelerator-driven system (ADS) for transmutation of minor actinides (MA) because the thermal conductivity and heavy metal density are higher than those of actinide oxides and also they have high melting temperature. In order to apply the pyrochemical reprocessing of spent nitride fuel, the authors have investigated its elemental technologies: the anodic dissolution behaviour of the nitride fuel and the recovery behaviour of actinide elements into the liquid cadmium cathode in the electrorefining process, and the re-nitridation of actinide elements recovered in liquid cadmium cathode. On the other hand, it is necessary to develop the process flow and calculate the material balance of the pyrochemical reprocessing of the spent nitride fuel to evaluate the technological feasibility of the fuel cycle. This study aims at developing the process flow diagram with the material balance sheet of the pyrochemical reprocessing of spent nitride fuel for ADS.

Three process flow diagrams were proposed in this work: i) the currently proposed process with the molten salt electrorefining of spent nitride fuel; ii) the process in which the molten salt electrorefining of the actinide-cadmium alloy is performed following the chemical dissolution of spent nitride fuel into molten chloride and the extraction of the actinides from the molten chloride media with liquid lithium-cadmium alloy; iii) the process combining the chemical dissolution of spent nitride fuel into molten chloride and the multi-stage counter current extraction of actinide elements from the molten chloride media with liquid Li-Cd alloy. Moreover, the material balance was evaluated for the process i) by use of the calculated and experimental data of the nitride fuel for ADS.

Introduction

Nitride fuel cycle for transmutation of long-lived MA has been developed in Japan Atomic Energy Agency (JAEA) under the double-strata nuclear fuel cycle concept [1-7]. The double-strata nuclear fuel cycle consists of commercial reactor fuel cycle without MA recycling (the first stratum cycle) and the dedicated fuel cycle for the transmutation of MA (the second stratum cycle). The minor actinides partitioned from the high-level liquid wastes of the first stratum are fed into the second stratum, where they are transmuted to fission products. The mass flow of the actinides in the second stratum would be about two orders smaller than that in the first stratum. The transmutation system proposed by JAEA is a Pb-Bi-cooled subcritical ADS with ^{15}N -enriched MA nitride fuels containing about 70 mol.% ZrN as inert matrix material [8]. Nitride is suitable for the fuel material for transmutation of MA because of supporting hard neutron spectrum and heat conduction ability. In addition, actinide mononitrides with NaCl-type structure have a mutual solubility leading to the flexibility of accommodating variable composition in the fuel. Pyrochemical process is proposed for the reprocessing of spent nitride fuel, since it has several advantages over wet process such as Purex in treating nitride fuel for transmutation, including recycling feasibility of ^{15}N . In order to apply the pyrochemical reprocessing of spent nitride fuel, the authors have investigated its elemental technologies of the main processes: the anodic dissolution behaviour of the nitride fuel and the recovery behaviour of actinide elements into the liquid cadmium cathode in the electrorefining process [9-17], and the re-nitridation of actinide elements recovered in liquid cadmium cathode [15,18-20]. However, the pyrochemical process should include additional processes such as handling the anode residue of the electrorefining and recycling the used molten salts. Moreover, it is necessary to develop the process flow and calculate the material balance of the pyrochemical reprocessing of the spent nitride fuel to evaluate the technological feasibility of the fuel cycle as reported for pyrochemical process of the metallic fuel [21,22].

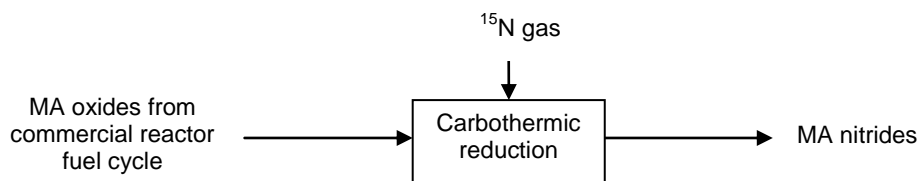
In this study, the process flow diagram with the material balance sheet of the pyrochemical reprocessing of spent nitride fuel for ADS was developed based on the reported experimental data of the pyrochemical reprocessing of spent nitride fuel and spent metallic fuel.

Development of the process flow diagrams

Figure 1 shows process flow diagram of the nitridation of MA partitioned from HLLW of the commercial reactor fuel cycle. In this study, MA are supposed to be fed into the second stratum cycle as oxides. MA oxides are converted to nitrides by the carbothermic reduction and used as fuel for ADS after mixing with the nitride products from the pyrochemical reprocessing of the spent nitride fuel from ADS. In the carbothermic reduction process, the mixtures of MA oxides and C were heated at the temperature from 1 573 to 1 773 K in $^{15}\text{N}_2$ gas stream [23].

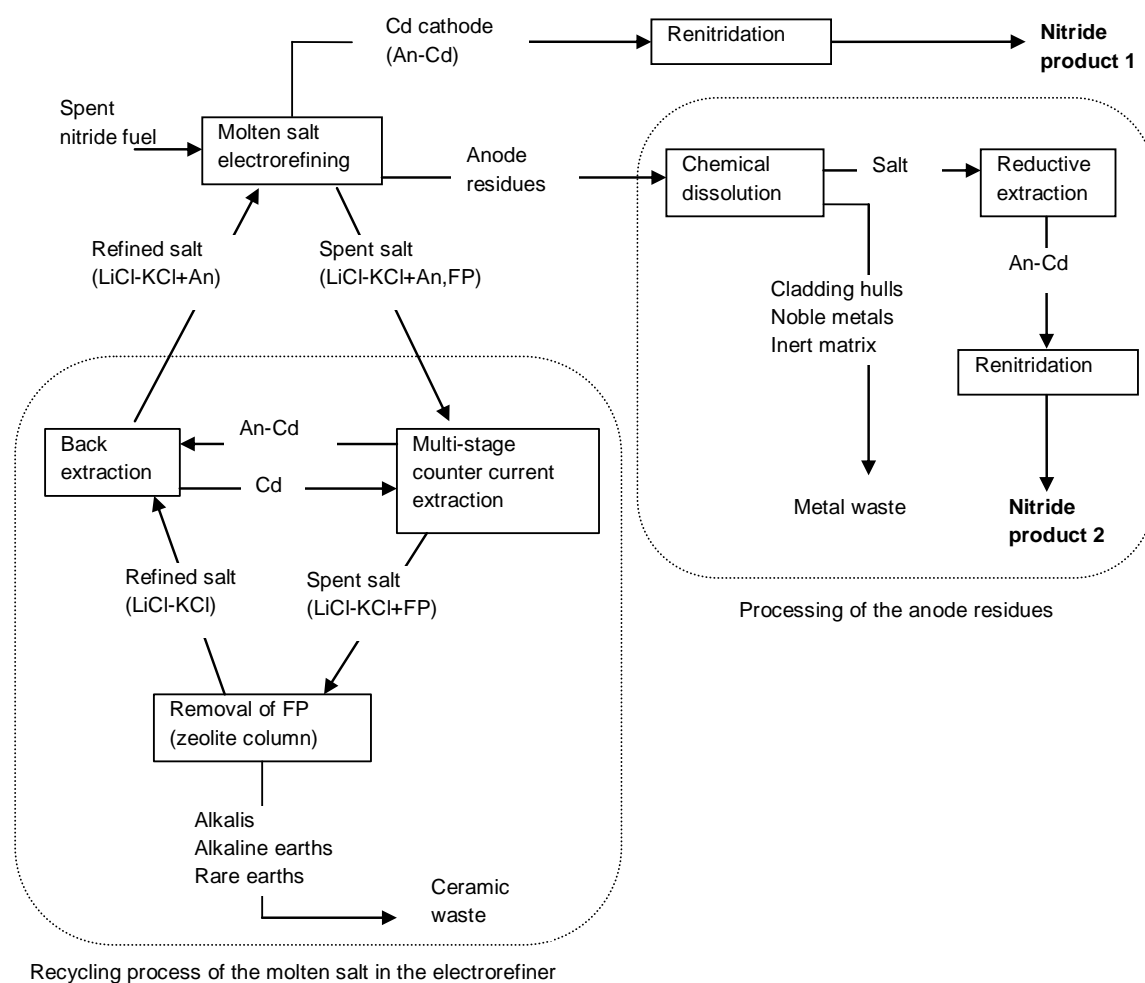
The following three process flow diagrams of pyrochemical reprocessing of spent nitride fuel were proposed in this work:

- i) the currently-proposed process with the molten salt electrorefining of spent nitride fuel [4];
- ii) the process in which the molten salt electrorefining of the actinide-cadmium alloy is performed following the chemical dissolution of spent nitride fuel into molten chloride and the extraction of the actinides from the molten chloride media with liquid Li-Cd alloy;
- iii) the process combining the chemical dissolution of spent nitride fuel into molten chloride and the multi-stage counter current extraction of actinide elements from the molten chloride media with liquid Li-Cd alloy.

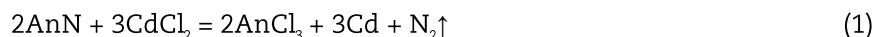
Figure 1: A process flow diagram of the nitridation of MA from the commercial reactor fuel cycle

Currently-proposed process with the molten salt electrorefining of spent nitride fuel

Figure 2 shows the process flow diagram of the currently-proposed process with the molten salt electrorefining of spent nitride fuel [4]. In the electrorefining process of spent nitride fuel in the LiCl-KCl eutectic melt, actinide nitrides are dissolved as chlorides at an anode. At the same time, actinide metals are recovered at the liquid Cd cathode, whereas alkali metal elements (AL), alkaline-earth elements (ALE) and RE remain in the molten salt as chlorides. Actinide elements recovered in the liquid Cd cathode are converted to nitrides again by the nitridation-distillation combined method [15,18-20]. In this method, nitridation of actinides and the distillation of Cd occurred simultaneously by heating the actinide-Cd alloys in N_2 gas stream.

Figure 2: A process flow diagram of the currently-proposed process with the molten salt electrorefining of spent nitride fuel

In the present study, the processing of the anode residues and the recycling process of the molten salt in the electrorefiner are considered. In the processing of the anode residues, the remaining actinide nitrides (AnN) in the anode residues are dissolved into molten LiCl-KCl eutectic salt as chlorides by chemical reaction with the oxidising agents such as CdCl_2 or ZrCl_4 . The chemical dissolution by using CdCl_2 is expressed as Eq. (1) [24]. Cladding hulls, inert matrix materials and noble metal FP such as platinum group metals and Mo should not be dissolved and processed into a metal waste form.



The actinide elements dissolved into molten salt are extracted into liquid Cd by the chemical reaction expressed by Eq. (2) with liquid Li-Cd alloy and converted to nitrides again.



As for the recycling processes of the salt, the salt treatment process using zeolite column system proposed in the pyrochemical reprocessing of the metallic fuel can be adopted [25,26]. A part of the molten salt in the electrorefiner is transferred to the multi-stage counter current extraction of actinide elements from the molten chloride media with liquid Li-Cd alloy. In the extraction process, most of actinides in the salt are extracted into the liquid Cd. The actinides recovered in Cd are chemically dissolved into molten salt as chlorides again by using CdCl_2 . For the removal of the FP from the salt, the salt containing FP is contacted with zeolite columns and the FP in the salt are occluded into the zeolite. The salt-occluded zeolite is converted to sodalite and processed into a ceramic waste form. On the other hand, the refined salt is returned to the electrorefiner.

The major disadvantages of this process are: i) the decrease of the anodic dissolution rate of actinide nitride by addition of the inert matrix materials [16]; ii) two kind of the nitride products with different composition are obtained: the product from electrorefining process and that from the processing of the anode residues; iii) it is necessary to treat large amount of Pu and MA including the inventory of them in the electrorefiner.

The process with the chemical dissolution of spent nitride fuel and molten salt electrorefining of the actinide-cadmium alloy

Figure 3 shows the process flow diagram of the process with the chemical dissolution of spent nitride fuel and molten salt electrorefining of the actinide-cadmium alloy. In this process, the molten salt electrorefining of the actinide-cadmium alloy is performed following the chemical dissolution of spent nitride fuel into molten chloride expressed by Eq. (1) and the extraction of the actinides from the molten chloride media with liquid Li-Cd alloy expressed by Eq. (2). The major advantage of this process is the improvement in processing rate. The chemical reaction is expected to be suitable for dissolution of the spent nitride fuel because it forms to powdery shape by mechanical shear of the fuel pins. In addition, the anodic dissolution potential of actinide metal is more negative than that of nitride [14]. However, it is necessary to confirm the possibility including the processing rate and the recovery rate of the actinides of the chemical dissolution process of spent nitride fuel by experiment.

The process combining the chemical dissolution of spent nitride fuel and the multi-stage counter current extraction

Figure 4 shows the process flow diagram of the process combining the chemical dissolution of spent nitride fuel into molten chloride and the multi-stage counter current extraction of actinide elements from the molten chloride media with liquid lithium-cadmium alloy. The major advantages of this process are: i) the improvement in processing rate; ii) the homogenisation of the composition of the nitride products; iii) the reduction of the amount of actinide elements treated in the reprocessing process because the inventory of them in the electrorefiner is not required. However, it is necessary to confirm the possibility of the chemical dissolution process of spent nitride fuel by experiment as well as in the case of the process shown in Figure 3.

Figure 3: A process flow diagram of the process with the chemical dissolution of spent nitride fuel and molten salt electrorefining of the actinide-cadmium alloy

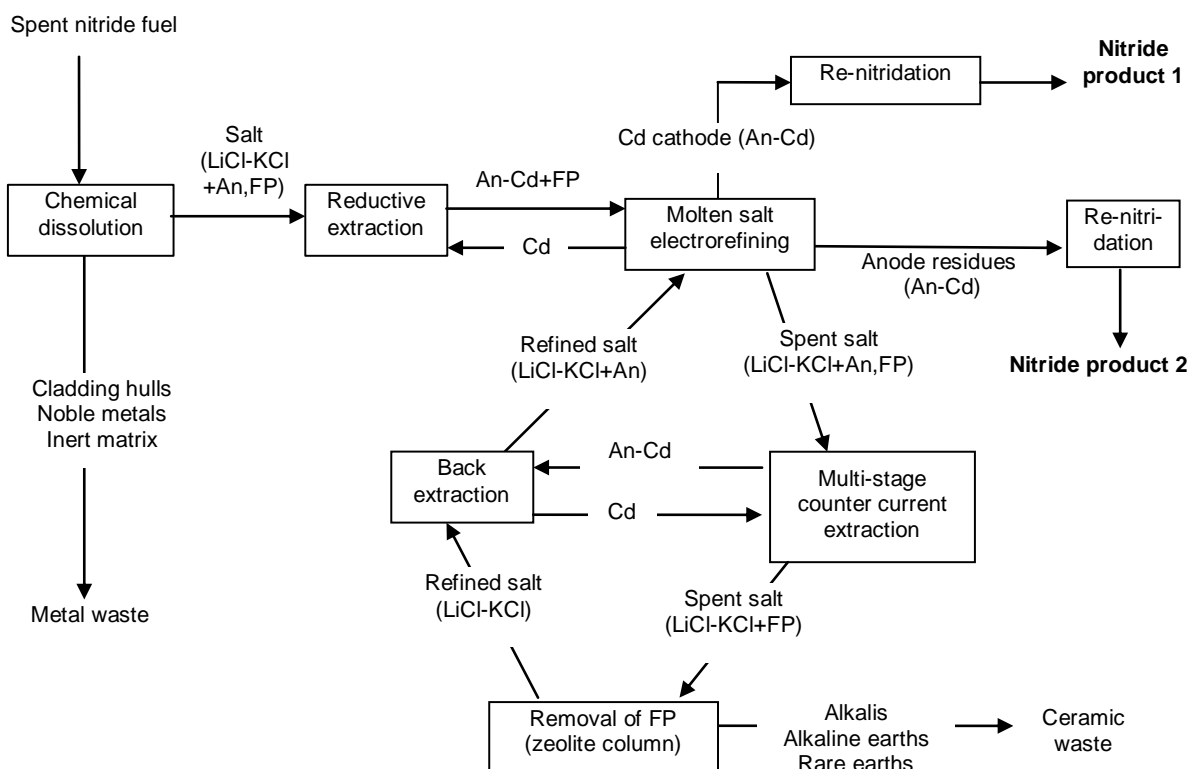
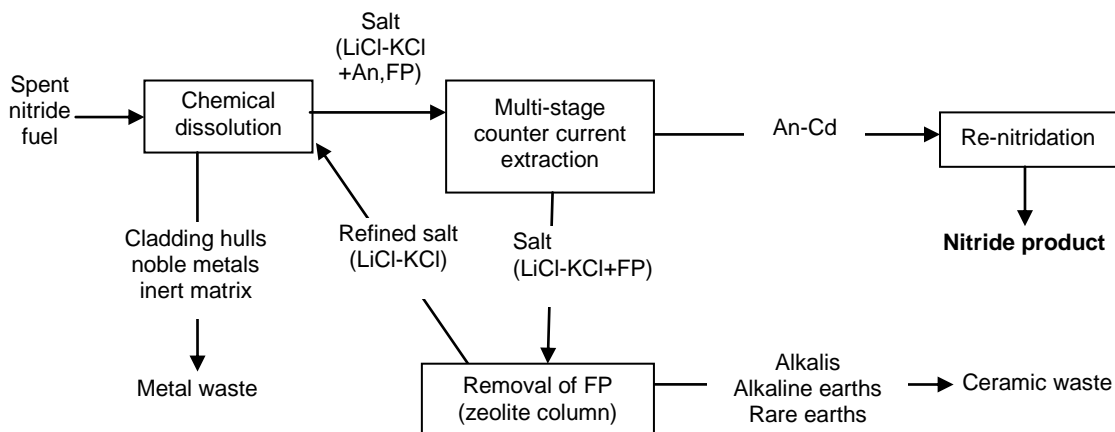


Figure 4: A process flow diagram of the process combining the chemical dissolution of spent nitride fuel and the multi-stage counter current extraction



Material balance calculation

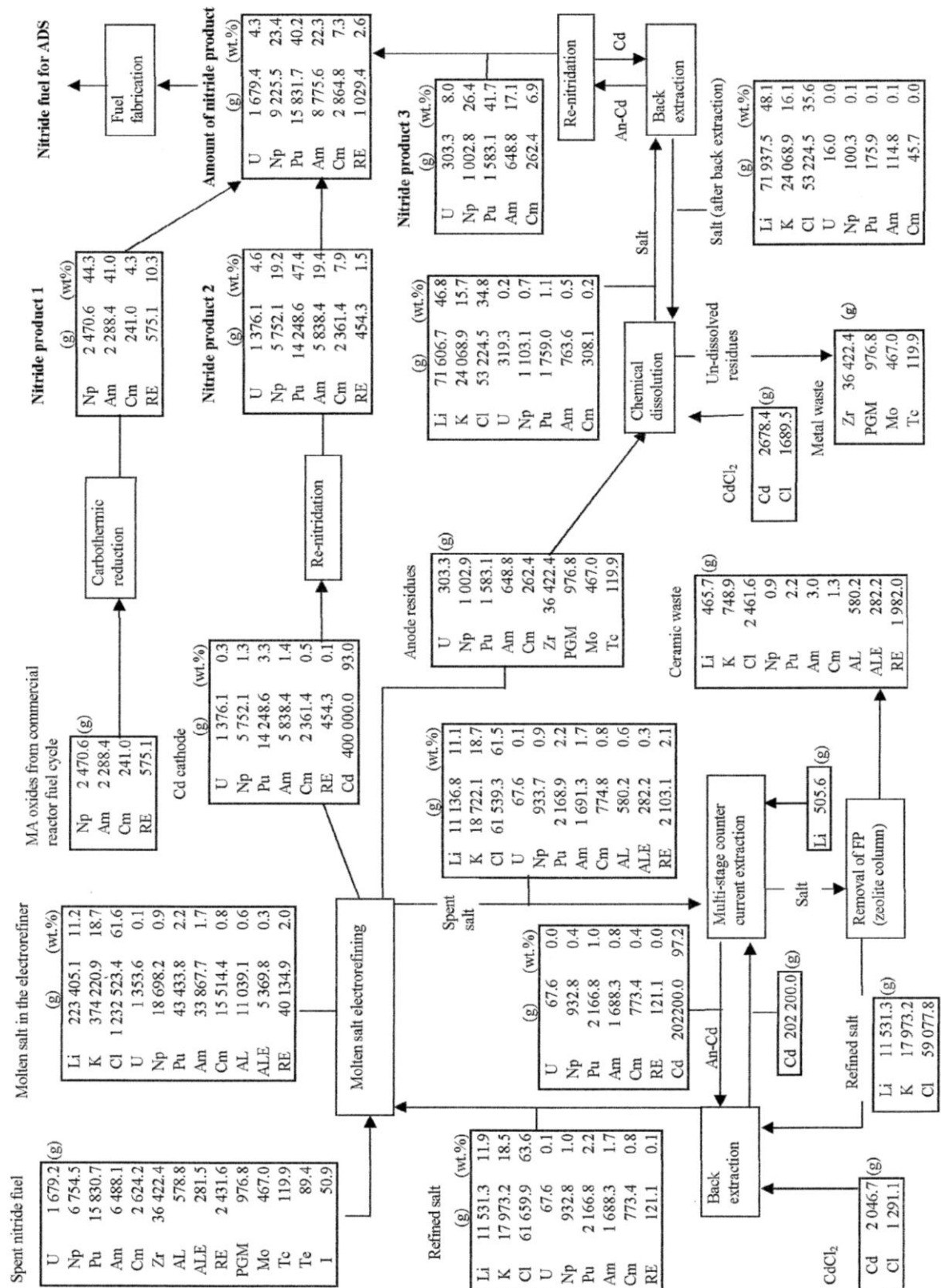
The material balance of the currently-proposed process shown in Figure 2 was evaluated by use of the calculated and experimental data of the nitride fuel for ADS and metallic fuel for fast reactor [25-28]. The calculation conditions are as follows: about 5 000 g of MA is fed into the transmutation cycle from the commercial reactor fuel cycle per day, spent nitride fuel from ADS containing about 33 400 g of actinide elements is processed per day, the number of ADS is 4, the

number of days of operation is 200 per year, 5% of the molten salt in the electrorefiner is transferred to the salt recycling process per day, 10% of the actinide elements remains as an anode residue after the electrorefining process, and, all of the attached salt and Cd are assumed to be returned into the process after distillation without loss. The detailed information about the ADS and the nitride fuel is described in the previous report [8]. The criteria of the reprocessing of spent nitride fuel were set by the core design calculation of ADS aimed to transmute over 99% of MA: the criterion of the recovery yield of the amount of Pu and MA is over 99.95% and that of the concentration of RE in the nitride products is less than 3.0 wt.%.

Figure 5 shows the material balance sheet of the currently-proposed process [4]; the throughputs per day after one year operation are shown in the schematic. As the result of the material balance calculation, the recovery yield of the amount of Pu and MA was about 99.97% and the concentration of RE in the nitride products was about 2.6 wt.%. It was thus elucidated that this process can satisfy the criteria required by the core design of ADS in principle.

Summary

Three process flow diagrams of the pyrochemical reprocessing of spent nitride fuel for ADS were proposed in this work: i) the currently-proposed process with the molten salt electrorefining of spent nitride fuel; ii) the process in which the molten salt electrorefining of the actinide-cadmium alloy is performed following the chemical dissolution of spent nitride fuel into molten chloride and the extraction of the actinides from the molten chloride media with liquid lithium-cadmium alloy; iii) the process combining the chemical dissolution of spent nitride fuel into molten chloride and the multi-stage counter current extraction of actinide elements from the molten chloride media with liquid Li-Cd alloy. Moreover, the material balance was evaluated for the process i) by use of the calculated and experimental data of the nitride fuel for ADS. As the result of the material balance calculation, it was elucidated that this process can satisfy the criteria required by the core design of ADS in principle.



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