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State of the Art of Pyroprocessing Technology in Japan

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Abstract

Minor actinide recycling in a fuel cycle is a potential technology to minimize the environmental radioactivity burden in waste disposal in the fast reactor era after 2050. Pyroprocessing technology with metal electrorefining expects that no additional process is required to separate minor actinides and short-cooled fuels can be treated due to no-use of organic solvent that degrades by radiation. Pyroprocessing has been explored for metal fuel cycle and nitride fuel cycle in Japan. Metal fuel fast reactor, which can achieve a high breeding ratio over 1.3, and its fuel cycle is a compact system by integrating pyroprocessing. Oxide fuel can be also treated by converting to metals by reduction. Separation of transuranium elements from high level liquid waste originating from aqueous reprocessing has been challenged. Verification of the process and development of an engineering scale device are the current interests for study. In addition, irradiation study of metal fuel with minor actinides currently much advances from the point of fundamental investigation. Accelerator-driven system (ADS) for transmutation of minor actinides is integrated with pyroprocessing for recycling system. The denitrating at anode and azotizing at cathode together with electrorefining have been fundamentally studied by use of plutonium.

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1. Introduction

The metal fuel cycle with pyroprocessing has the potential to recover most of transuranium elements by electrorefining without additional process, and by applying short-cooled fuels with high radiation and heat. The advantages make pyroprocessing a promising candidate for the next generation fuel cycle with minor actinide recycling [1-3]. High radiation and heat of products through whole process is also advantageous from point of nuclear safeguard [4]. In Japan, pyroprocessing technology has been developed first by the Central Research Institute of Electric Power Industry, CRIEPI and followed by the former Japan Atomic Energy Research Institute, JAERI, and, then by the former Japan Nuclear Cycle Development Institute, JNC, which were merged to the Japan Atomic Energy Agency, JAEA.

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The key device for separation is electrorefining for collecting actinides on solid cathode and into liquid cathode, mainly cadmium. Distillation produces uranium metal and actinide-mixed metal by evaporating salt and cadmium, respectively. The actinides are supplied to a fuel casting furnace, at which fuel composition is adjusted with an addition of zirconium metal.

The electrorefining is a potential device as well in case that actinide nitride target is recycled for an accelerator-driven system (ADS) [5]. The irradiated nitride is loaded in an anode basket where the decomposition of nitride and oxidation of actinide metal into chloride melt occur simultaneously by applying an appropriate potential, and a liquid cadmium cathode is an acceptor of actinides. Actinides recovered are transformed to nitrides by heating the electrodeposits in N₂ stream, and the cadmium is distilled.

The development of metal fuel is another challenge to realize a metal fuel FR cycle, where the characterization and irradiation behavior of metal fuel have to be evaluated as the first step to validate. However, a few has been reported on U-Pu-Zr, mostly by INL [6], and no data are available on the metal fuel with minor actinides. The study of characterization of U-Pu-Zr with minor actinides and lanthanides was initiated in the 1980's with the collaboration with ITU [7], and, then, the program proceeded to the irradiation examination of metal fuels with and without minor actinides [8], and to explore an engineering scale model of fuel casting.

This paper describes the overview of Japanese current activity of pyroprocessing of metal fuel cycle including metal fuel development and of nitride cycle for the accelerator-driven system for minor actinides transmutation.

2. Pyroprocessing

2.1. Pyroprocessing for metal fuel cycle

2.1.1. Integrated system of metal fuel cycle bridged oxide fuel treatment and HLLW treatment

Figure 1 shows LWR and FR fuel cycles integrated with pyroprocessing [1]. Original pyroprocessing proposed is the metal fuel cycle consisting of electrorefining and injection casting for fuel fabrication depicted in the left bottom of this figure. In case the pyroprocessing is applied on spent oxide fuels of LWR, oxides should be electrochemically reduced to metals prior to the electrorefining for actinide separation. In addition, minor actinide separation from HLLW originating from aqueous reprocessing should be incorporated to minimize the environmental impact of the waste. In order to do that, HLLW has to be converted to chlorides for applying reductive extraction to recover minor actinides.

Combined with aqueous reprocessing of spent fuels used in LWR and pyropartitioning of minor actinides in HLLW coming from the reprocessing, the extremely high recovery yield, mostly five nine, for uranium and plutonium, and more than 99.5% for minor actinide could be achieved. This means that the radiotoxicity of HLW is equivalent to the natural uranium of 7.5ton after 500 years at the disposal.

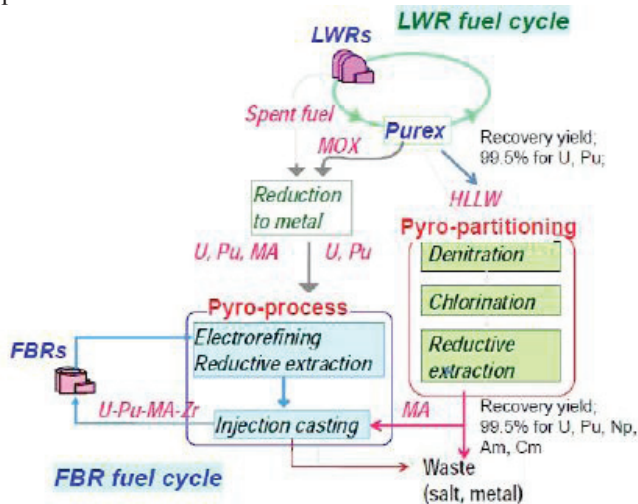


Fig.1. Integrated system of fast reactor cycle bridged LWR fuel cycle and TRU recovery from HLLW.

2.1.2. Electro refining

Two kinds of approaches on electrorefining are executed to investigate a process chemistry by use of plutonium and genuine materials and to explore an engineering model of electrorefiner. Figure 2 shows an experimental installation set up in ITU [9]. This installation has been used to verify electrorefining by use of unirradiated U-Pu-Zr-MA (-RE), in which deposition of uranium on a solid cathode and collection into liquid cadmium cathode have been successfully achieved. The cross section of metal alloy half way to the completion is depicted in this figure.



Fig.2. Inert atmosphere caisson in hot cell with pyroprocessing equipment set up in ITU. The figure also indicates cross section of anodic dissolution alloy.

Another setup of electrorefining apparatus with inner diameter of 40mm accommodating a liquid cadmium cathode of diameter of 25mm was prepared to collect plutonium and americium in JAEA, as shown in figure 3 [10]. Microstructure and EPMA analysis of cadmium cathode after electrolysis suggest the formation of intermetallic compound such as $(U,Pu)Cd_6$ and $(U,Pu)Cd_{11}$ [11]. Americium concentration in liquid cadmium increases with plutonium concentration. An engineering model of electrorefiner was setup in a uranium laboratory of Toshiba. Figure 4 shows a glove box equipped with an electrorefiner [9,12]. Inner wall with diameter of 380mm acting as cathode (see bottom of the right in fig.4) to collect uranium accommodates two pairs of anode basket (see above of the right), loaded with pieces of a simulated metal fuel of U-Zr with stainless cladding, which was fabricated by injection casting.

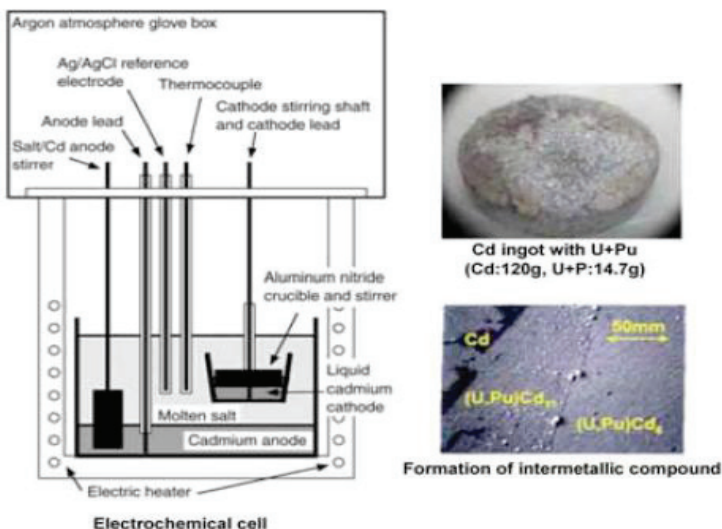


Fig.3. Equipment of electrorefining. Cadmium cathode contained U and Pu and microstructure of actinide-Cd intermetallic compounds are indicated.



Fig.4. An Engineering model for electrorefining.

2.1.3. Reductive extraction

Reductive extraction in a LiCl-KCl/Cd or Bi system by use of lithium reductant is another potential means to recover actinide by separating other fission product species. Figure 5 indicates experimental achievement of actinide separation from simulated HLLW by multistage reductive extraction together with electrorefining [13]. Uranium, which is a large portion among actinides in HLLW, was electrochemically deposited on the solid at the first stage, and the deposition included a small amount of transuranic elements. The following reductive extraction succeeded to recover more than 99.5% of neptunium and plutonium, and 99.4% of americium from the salt to the liquid cadmium or bismuth by separating fission products in a salt existing 10 times more than transuranium elements [14]. The experimental equipment together with uranium deposited on the cathode by electrorefining is given in Fig. 5.

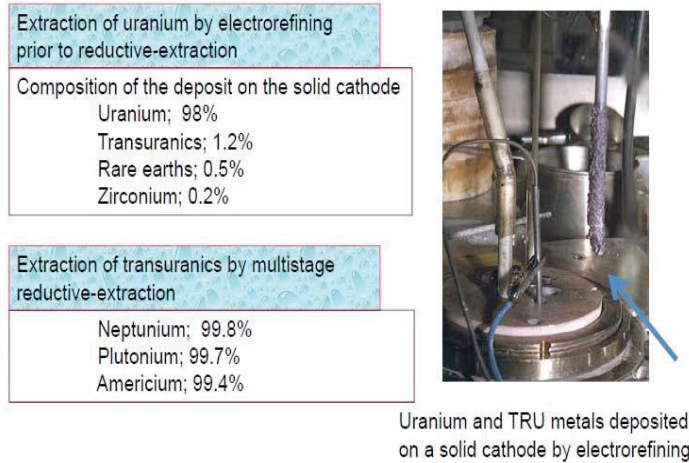


Fig.5. TRU separation by reductive extraction from simulated HLW

After the achievement of high decontamination in a simulated system, the reductive extraction through oxide conversion and chloride conversion of HLLW was carried out to confirm the decontamination factor and distribution coefficients of actinides by use of genuine material. Small scale experimental equipment was installed in a hot cell, and 520g of HLLW was prepared by reprocessing commercially used MOX fuel [15]. The experimental equipment is shown in figure 6 [9, 15]. In addition to the knowledge of thermodynamic properties of actinides and lanthanides, this experimental result verifies the technical feasibility of transuranic separation from HLLW by pyroprocessing. On the other hand, a three-stage of counter current reductive-extractor for engineering model development has installed, by which technological feasibility has to be explored from point of operability and material flow.

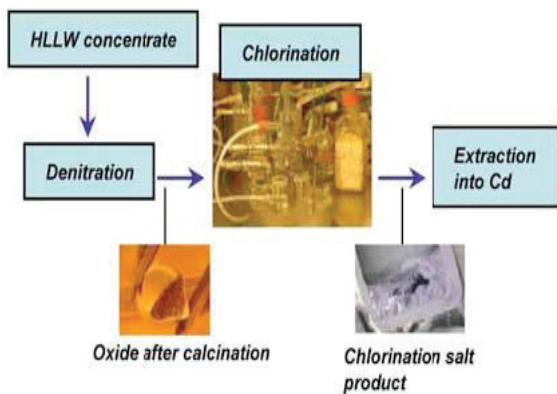


Fig.6. TRU separation from genuine HLLW through oxide and chloride conversion.

2.1.4. Melt transport rig

Melts of salt and cadmium have to be transported by a remotely controlled device in an industrial implementation. The equipment to transport molten salt and liquid cadmium was designed and installed in which an electrorefiner with throughput of 30kg-HM/d is located, as given in figure 7 [16]. The operation is done in a glove box with a size of 7m x 3m x 5mH, with circulating argon gas. The salt and cadmium are conveyed remotely in stainless steel piping with inner diameter of 1/2inch to a distillation furnace and they return to the electrorefiner by gravity. The salt and cadmium transport rigs are equipped with a centrifugal pump in each. This system can operate at temperatures up to 550°C. The transportation rig succeeds to convey stably cadmium with lifting height of 1.7m [17].

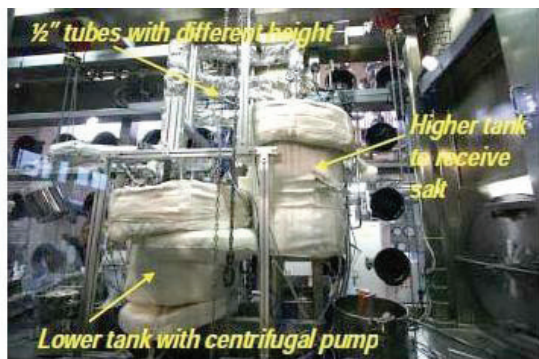


Fig.7.melt transport rig with a centrifugal pump equipped in the inert atmosphere glove box

Spent MOX fuels with high burnup should be the most acceptable target to treat by pyroprocessing because no additional process is required to separate minor actinides and no organic solvent is treated in the process. In order to supply spent MOX fuels to electrorefining step, the oxides should be reduced chemically or electrochemically. Past expertise of chemical reduction used lithium achieved to reduce a simulated spent MOX with minor actinides, Np and Am, to metals by controlling Li_2O concentration in LiCl [18]. Currently, the electrochemical reduction has been exploring instead of lithium reduction which causes to produce some amount of secondary waste. The technological feasibility was verified by the fact that slices of MOX, and UO_2 mixed with some of fission products were reduced to metals electrochemically by applying a certain potential [19]. Currently, a series process demonstration through pretreatment to electrorefining as shown in figure 8 has been studied with 100g scale.

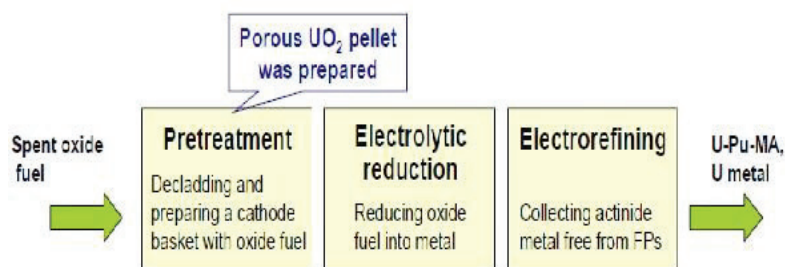


Fig.8.Pyroprocessing flow for spent oxide fuels

3. Metal fuel irradiation program

3.1. Metal fuel irradiation at Phenix reactor

Only 600 metal pins with composition of U-Pu-Zr have been irradiated, though thousands of U-Zr pins were irradiated in EBR-II and FFTF [11]. No data is available for alloys with minor actinides and/or lanthanides. Based on the properties described above, three alloys for each of U-Pu-Zr as for reference, U-Pu-Zr-2wt%MA-2wt%RE, U-Pu-Zr-5wt%MA-5wt%RE and U-Pu-Zr-5wt%MA were prepared by arc-casting except U-Pu-Zr-5wt%MA-5wt%RE by powder metallurgy in ITU in 1994. After nearly 10 years standby, total nine pins were loaded in the Phenix FR reactor in the end of 2003 and irradiated at normal power from the beginning of 2004. Figure 9 shows the pin configuration [8]. The three lower burnup pins were discharged in mid-2004 by achieving 2.4at%, 3 middle burnup pins with 7.0at% in mid-2006 and another 3 pins with high burnup over 10at% in mid-2008. The non-destructive analysis on stack length, pin diameter, gamma spectrometry and neutronography indicated that no visual deformation and defect was observed in the lower burnup pins [8]. The pins were transported to ITU, and will be examined by pin puncture for gas release, and metallography, elemental distribution and MA concentration by ICP-MS.

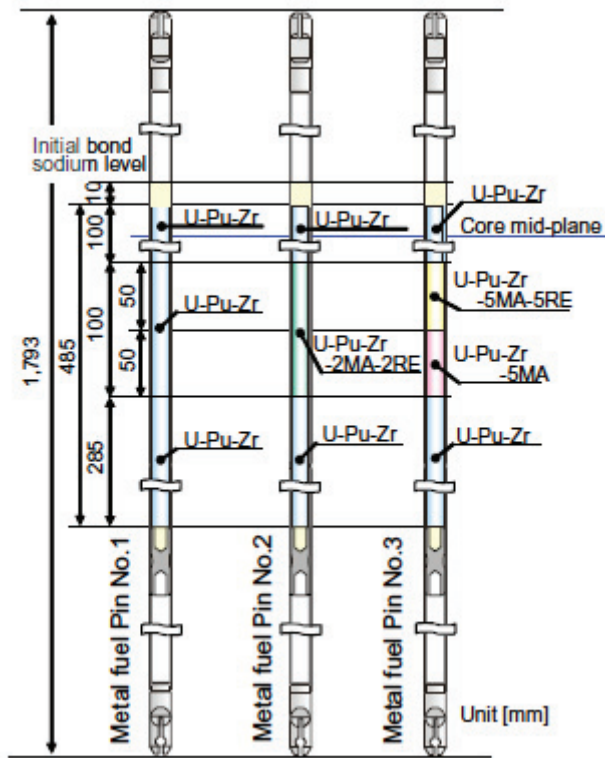


Fig.9. Schematic views of irradiation pins.

3.2. Metal fuel irradiation at JOYO reactor

Segments of metal fuel are now under preparation to irradiate in JOYO fast reactor. UO_2 - PuO_2 pellets were supplied to produce U-Pu metal by electrochemical reduction, and some U-Pu metal were collected into cadmium cathode by electrorefining. Injection casting apparatus with single casting device was set up to prepare U-Pu-Zr rod. Six pins contained a casted segment of U-10% Pu-10% Zr with length of ca. 200mm were produced, and are now standby for irradiation.

4. Pyroprocessing of nitride fuel cycle

Nitride fuel cycle for transmutation of long-lived MA has been developed in JAEA under the double-strata fuel cycle concept [20]. One of the advantages of the concept is that hazardous MA is confined in the small transmutation fuel cycle without disturbing performance and economy of the electricity generation fuel cycle. The dedicated fuel for such a transmutation system as ADS has a fairly different composition from that of LWR or FBR; MA are included as a principal component in the fuel and diluent materials are added in place of U. In the ADS designed by JAEA, a mononitride solid solution of MA and Pu is proposed as a fuel in sub-critical core and ZrN is considered as the first candidate for diluent materials.

Spent nitride fuel for ADS is treated by pyroprocessing for recycling MA and Pu. In addition to general advantages of pyroprocessing mentioned before, recycling of N-15 highly enriched nitrogen used in nitride fuel will be feasible by applying pyroprocessing to nitride fuel cycle. Spent nitride fuel is anodically dissolved, and MA and Pu are recovered in the liquid Cd cathode by molten salt electrorefining. In nitride fuel cycle, MA and Pu in liquid Cd cathode electrodeposits are to be converted nitride again.



Fig.10.Appearance of TRU-HITEC and electrorefiner for Am and Cm bearing nitrides.

Pyroprocessing of nitride fuel cycle has been investigated by the experimental study with MA and Pu, which includes electrorefining [21] and re-nitridation [22] processes. Figure10 shows an appearance of the electrorefiner for Am and Cm bearing nitrides equipped in the module for TRU High Temperature Chemistry (TRU-HITC) of JAEA [23]. Furthermore, the process flowdiagram with the material balance sheet of nitride fuel cycle has been developed.

Behaviours of solid fission products during the electrorefining were investigated by use of burnup-simulated uranium based nitrides, in which UN+Mo, UN+Pd and UN+Nd samples were prepared and subjected to electrorefining in LiCl-KCl-UCl₃ molten salt [24]. The rest potentials of the burnup-simulated nitrides were similar to that of pure UN. After the anodic potential-controlled electrorefining at 773K, most of U was recovered in the liquid Cd cathode in all samples. On the other hand, Nd was dissolved at the anode but accumulated in the salt phase as NdCl₃, while Mo and Pd were not dissolved and remained at the anode. These results were summarized in Table 1. Furthermore, behaviours of possible diluent materials added to nitride fuel for ADS, ZrN or TiN, were also investigated with uranium and plutonium based nitrides [25].

Table 1. Results of electrorefining of bumup-simulated UN samples

	UN+Mo		UN+Pd		(UNd)N		
	U	Mo	U	Pd	U	Nd	
Metal in initial sample (mg)	154	4.8	185	9.44	152	12.8	
Metal in the salt (wt%)	Initial	0.54	ND	0.54	ND	0.54	0.0097
	Final	0.54	ND	0.54	ND	0.53	0.0218
Passed charg(coulomb)	189		232		209		
Current Efficiency	90 ^a	-	90 ^a	-	82 ^a	0.36 ^a	
Metal recovered in the LCC (mg)	140	ND	172	ND	141	13 ^b	
Recovery yield (%)	91	ND	93	ND	93	2.9	

^a (weight of metal recovered in the LCC) / (Weight of recovered metal calculated from passed charge)

^b (Increase of weight of metal in the salt) / (Weight of recovered metal calculated from passed charge)

LCC: Liquid cadmium cathode

ND: Not detected (below detection limits)

5. Summary

Pyroprocessing study of metal fuel cycle has been initiated in the 1980's in Japan led by CRIEPI in cooperation with former JAERI and JNC. CRIEPI has been devoting metal fuel cycle integrated spent oxide fuel and recovery of transuranium elements form HLLW originating from aqueous reprocessing. JAEA focuses on the basic study of electrorefining for nitride target with MA recycling. Spent nitride target is decomposed to metal in an anode and cathode product is azotized in liquid cadmium during or after electrorefining. Each process chemistry including the application to oxide fuel or residue are intensively investigated. Current activities focus on the verification of the process flowsheet by use of genuine materials such as irradiated alloys and MOX, and exploration of engineering models of

electrorefiner, electrochemical reduction cell, distillation cell, counter current extractor, waste salt treatment column and fuel fabrication casting device for commercial application. The remote transferring system of melt is another essential device to treat at high temperature in a high radiation field.

The irradiation and post irradiation examination programs of metal fuel of U-Pu-Zr and fuel with minor actinides are now progressing by using JOYO and Phenix fast reactor, respectively.

With regard to pyroprocessing of nitride fuel for transmutation of MA, the experiments on the electrode behavior of burnup-simulated nitride and nitride fuel with possible diluent materials have been started. The materials balance and separation characteristics of each element have to be investigated as well as the kinetics of each process, from which the feasibility of nitride fuel cycle is to be demonstrated.

The domestic/international collaboration continues to establish the chemical flowsheet of the pyroprocessing, to develop an engineering installation and to evaluate the metal fuel behavior under irradiation. International programs of GENERATION-IV and ACSEPT are proposing a pyroprocessing for next generation fuel cycle options. Both multilateral and bilateral cooperation should play an effective role to realize the technology. Japan intends to keep and extend such cooperation to develop a world standard fuel cycle technology.

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