

A CONCEPTUAL STUDY OF PYROPROCESSING FOR RECOVERING ACTINIDES FROM SPENT OXIDE FUELS

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In this study, a conceptual pyroprocess flowsheet has been devised by combining several dry-type unit processes; its applicability as an alternative fuel cycle technology was analyzed. A key point in the evaluation of its applicability to the fuel cycle was the recovery yield of fissile materials from spent fuels as well as the proliferation resistance of the process. The recovery yields of uranium and transuranic elements (TRU) were obtained from a material balance for every unit process composing the whole pyroprocess. The material balances for several elemental groups of interest such as uranium, TRU, rare earth, gaseous fission products, and heat generating elements were calculated on the basis of the knowledge base that is available from domestic and foreign experimental results or technical information presented in open literature. The calculated result of the material balance revealed that uranium and TRU could be recovered at 98.0% and 97.0%, respectively, from a typical PWR spent fuel. Furthermore, the anticipated TRU product was found to emit a non-negligible level of γ -ray and a significantly higher level of neutrons compared to that of a typical plutonium product obtained from the PUREX process. The results indicate that the product from this conceptual pyroprocessing should be handled in a shielded cell and that this will contribute favorably to retaining proliferation resistance.

KEYWORDS : Pyroprocessing, Nuclear Fuel Cycle, Non-Proliferation, Separation of Actinides

1. INTRODUCTION

The reprocessing technology PUREX (Plutonium and URanium EXtraction) has long been used as part of the commercial Mixed Oxide (MOX) fuel business. For example, in France and the UK, the PUREX process has been adopted as a commercial reprocessing procedure to supply MOX fuels to domestic and foreign nuclear reactors that are able to use MOX fuel as part of the reactor core. However, this PUREX process brings the risk of exposure to nuclear proliferation because it produces a pure stream of plutonium that can be misused as weapons-related material by terrorists. Therefore, a new technology for the fuel cycle ensuring proliferation resistance is earnestly needed around the world. Under the current circumstances of nuclear energy generation, a new type of fuel recycle technology, with which the PUREX could be replaced, is demanded for a sustainable use of nuclear energy. So, both requirements for the fuel recycle, that is, ensuring proliferation resistance and obtaining a reactor-grade product, must be fulfilled at the same time, in order to establish a satisfactory fuel cycle.

Recently, pyroprocessing is rising as one alternative

technology to prevent nuclear proliferation in a closed fuel cycle. Furthermore, pyroprocessing is known to have some benefits when utilized as a recycling technology. Perceived advantages for typical pyroprocessing include: significantly greater radiation-resistance, smaller amount of final waste, and potential economic superiority. Moreover, since no aqueous moderating solution is involved in the pyroprocess, higher limits of fissile mass can be allowed in terms of criticality, enabling a compact system design. This and other benefits such as compact equipment, reduced amount of wastes and lower cost, are expected to allow pyroprocessing to be used as part of an integral recycling system for advanced burners.

However, pyroprocessing also has some limitations: low throughput in each unit due to a batch process approach; contamination with rare earth elements in the separation of the transuranic elements group (TRU); and safety provisions needed to handle higher dose rates of γ -energy and neutrons than those of a single plutonium product obtained from the PUREX process.

With this background, this study has been conducted to devise a hypothetical pyroprocess and then analyze it in terms of technical viability as well as proliferation

resistance. Hence a conceivable pyroprocess was devised in this work by combining several types of dry processes so that pyroprocessing could be employed to recover the main products, that is, uranium and TRU. Then, the material balances for several major elemental groups in each unit process were calculated from the knowledge base for the elemental group separation that was extracted from experimental results in domestic and foreign laboratories or technical data presented in the open literature.

Consequently, the technical viability of the conceptual pyroprocess was evaluated through recovery yields and purities of the uranium and TRU products. In addition, the proliferation resistance for this process was estimated by predicting the dose rate of γ -activity and the emission of spontaneous fission-neutrons from the TRU product by assuming that this process would be used for treating the spent fuel of a typical pressurized water reactor (PWR) [1].

2. A CONCEPTUAL PYROPROCESS

2.1 Combination of the Dry Unit Processes

Most PWR spent fuel is stored in a water pool before treatment or disposal in order to decrease decay heat as well as to reduce radioactivity. If fuel is to be treated by the PUREX-type reprocessing or pyroprocessing, the mechanical or thermal pre-treatment methods are the same in both cases. First, fuel assemblies are taken out of a spent fuel cask and then dismantled. The fuel rods are extracted and cut to a short length and then decladded before transporting the fuel material to the subsequent process. The fuel cladding is sent to a metal waste treatment process.

In the pyroprocess considered in this study, the fuel material, most of which is composed of uranium dioxide (UO_2), is sent to the next process where it is voloxidized with stoichiometrically sufficient oxygen in air, transforming UO_2 into U_3O_8 in order to make it into a powder-type material with a larger surface area. Besides uranium, some other metal components also become oxidized in this process.

Then the fuel is chemically reduced into a metal form by chemical or electrochemical reduction method. In this work, the latter method was chosen because much experimental data on that method has been accumulated during the past several years in this laboratory. Then uranium is recovered in the electrorefining process by selective deposition onto the surface of the cathode. Since the molten salt still contains U (a small portion out of the entire amount), TRU, and fission products (FP) after the electrorefining process, a reductive extraction process is implemented to recover mainly the TRU into the liquid cadmium phase. However, the TRU is accompanied by the U still remaining in the molten salt as well as by a small amount of rare earths (RE) due to their similar distribution properties to those of TRU in the separation process.

If the TRU is to be utilized as a fuel material in a future-type nuclear reactor (e.g. TRU burner), the long-lived radionuclides composing the TRU elements could be transmuted to short-lived radionuclides by nuclear fission, thus reducing the radiotoxicity of the spent fuel and the economical burden of waste disposal. With these characteristics of the various unit processes, a conceptual pyroprocess was devised in this work as shown in Fig.1.

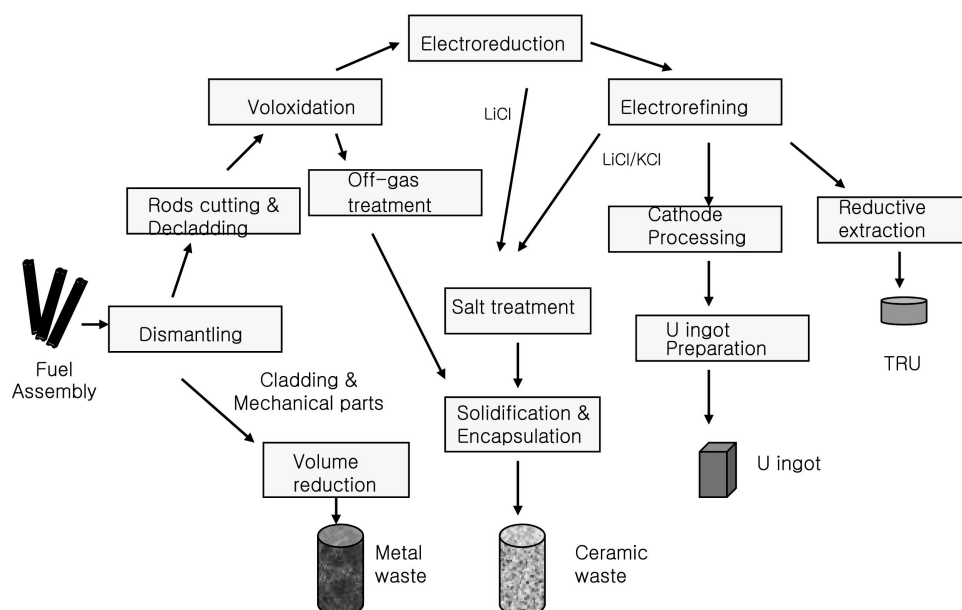


Fig.1. Processing Steps of Pyroprocess for Treating Typical PWR Spent Fuel

Table 1. Major Specifications of the Spent PWR Fuel Considered in this Work

Uranium enrichment	3.5 wt%
Burnup	35,000 MWD/MTU
Cooling time	5 yr
<u>Contents of elementary groups in 20 kg fuel material</u>	
-U	19.074 kg
-TRU(Np, Pu, Am, Cm)	0.201 kg
-NM(Ru, Rh, Pd, Ag)	0.085 kg
-RE(La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy)	0.210 kg
-Cs	0.054 kg
-Sr	0.018 kg
-FP(gas : Br, Kr, I, Xe)	0.126 kg
-Others	0.232 kg

Table 1 shows the specific conditions of a typical PWR spent fuel considered in this work.

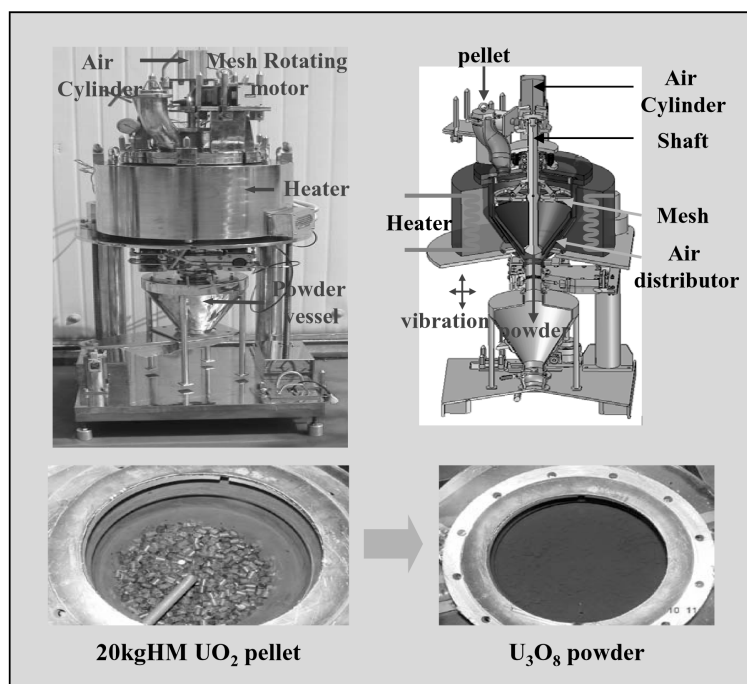
2.2 Mechanical Pre-Treatment

In a laboratory scale treatment of spent fuel for the fabrication of DUPIC (Direct Use of PWR Spent Fuel in CANDU) fuel in this laboratory, the fuel rods are cut to a short length and then slit in an axial direction. Fuel pellets are then collected from the cladding [16]. The fuel

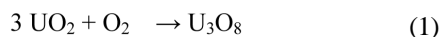
pellets are transported to the subsequent voloxidation process, whereas the fuel cladding is transported to the metal waste treatment cell. Since this process shows no hazard of operation, it can also be introduced in the pre-treatment of pyroprocessing.

2.3 Voloxidation

Uranium dioxide (UO_2) can be oxidized to U_3O_8 by air in a voloxidation reactor (Fig.2) according to the

**Fig.2.** Experimental Voloxidizer and its Product

reaction below and then transformed into powder form, making its surface area much larger and thus providing a higher rate of electroreduction.



This pulverization takes place by decreasing the density of 11.0 g/cm^3 (UO_2) to 8.3 g/cm^3 (U_3O_8), thereby increasing its volume. Meanwhile, most of the gaseous fission products (Tritium, Krypton, Xenon and Iodine etc.) and a part of the metal elements (Cesium, Ruthenium and Technetium etc.) that are subject to a transformation to volatile oxides, are sent to the off-gas treatment system. In this case, the flow rate of air should be controlled below a certain level in order to prevent small powders from being accompanied by the off-gas flow and also to adjust the air pressure of the cell. The dominant factor for gaseous evolution in this case is known to be the system temperature. The experimental results, obtained in this laboratory as well as at the INL

(Idaho National Laboratory), USA [2,14,15], are summarized in Table 2. As a result, the gas evolution yields are higher as the system temperature increases in the range of 500–1500 °C. This result also reveals that almost all of the above elements evolve as gas forms at 1500 °C. However, a sintering of these powders, which is unfavorable for pulverization, was found at above 1000 °C, thus requiring optimization of the system's temperature.

2.4 Electroreduction of Fuel Powders

It is necessary to chemically reduce the fuel material into a metallic form in order to treat it in a subsequent electrorefining process. An experimental electroreduction cell was prepared as shown in Fig.3-4. A molten salt $\text{LiCl-Li}_2\text{O}$ was employed as the electrolyte at 650 °C and a platinum rod was used as the anode. As the cathode, an oxide powder container was connected with a platinum rod; the wall of the container was composed of a magnesia membrane so that ions could pass through the membrane during the reaction. The mechanism of this

Table 2. Elimination Yields of the Fission Products in the Voloxidation Process

Temperature	Elimination yields (wt%)										
	H	Kr	Xe	C	I	Cs	Tc	Ru	Rh	Te	Mo
500 °C	~99	~15	~5	~20	~5	21	53	81	39	2	-
700 °C		~95	~90	~95	~60	21	53	81	39	2	-
950 °C		~100	~100	~100	~90	37	98	94	78	32	12
1200 °C					~100	~90	~100	~100	~80	~90	~80
1500 °C						~100	~100	~100	~90	~100	~90

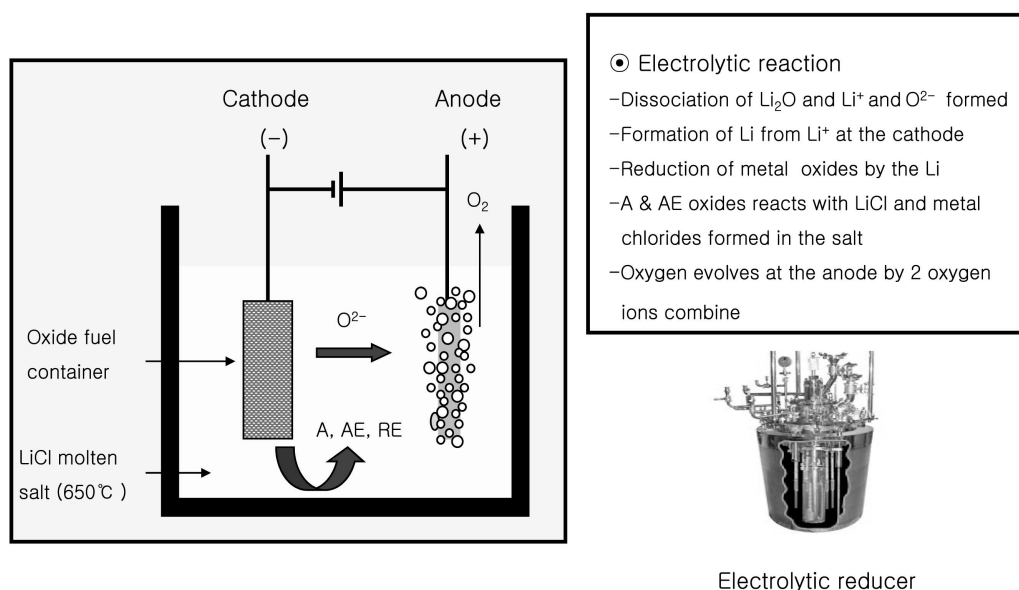


Fig.3. Principle of the Electrolytic Reduction of Spent Oxide Fuels

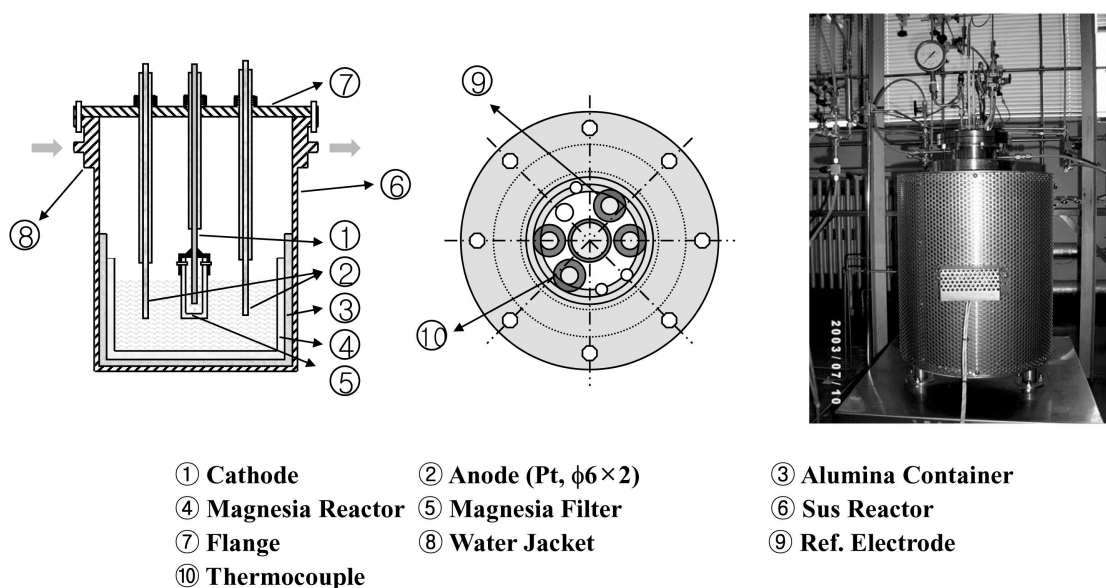
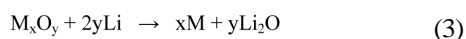


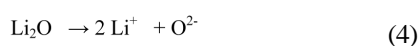
Fig.4. Experimental Apparatus for Electrolytic Reduction of Spent Oxide Fuels

electroreduction can be expressed as follows:

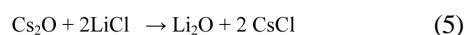
<Cathode reaction>



Oxides of actinides and noble metals are reduced to metallic form (M) as shown in equation (3). Meanwhile, the produced Li_2O is dissociated as



Since Li^+ moves to the cathode whereas O^{2-} moves to the anode, reactions (2)~(4) take place repeatedly, thus continuing the reduction of the oxides. Since the alkaline and alkaline earth elements such as Cs, Sr, and Ba etc. are highly reactive with Li and K chlorides in the molten salt, they are easily dissolved in the molten salt by transformation into chlorides as follows:



< Anode reaction >



In this process, most of the alkaline and alkaline earth metals are converted to metal chlorides, dissolved in the molten salt and finally eliminated as wastes when the salt

is regenerated. As for RE elements, however, their reduction rate depends on the concentration of Li_2O in the molten salt. It is known that their transformation rate becomes higher as the concentration of Li_2O decreases. Although it was estimated that the RE elements are not reduced to metal form when the concentration of Li_2O in the molten salt was 3 wt%, which was used in this laboratory in order to reduce uranium oxide, a small portion of RE elements is predicted to be reduced. An example of INL's experimental results [18] reveals the reduction yields: 36~43% for Nd; 40~49% for Ce; 38~47% for Pr; 27~33% for Sm; and 34~40% for Y. The reduction yields of actinides are as follows: 98~99% for U; 93~96% for Pu; 97~98% for Np-237; and 77~84% for Am.

When the electrolytic reduction is completed, the salt is separated from the cathode basket containing metals and unreduced metal oxides by means of salt evaporation at 900~950 °C. Once the salt is eliminated by evaporation, the cathode basket is further heated to 1150~1200 °C to recover the molten metallic product, because the unreduced RE oxides are contained in the dross that is floating above the molten metal.

This dross is then mechanically separated from the molten metal and sent to the waste treatment process. Since some actinides accompany this dross, it would be advantageous to recover the actinides and recycle them into the main stream, namely by an electrorefining process, while preventing the actinides from being released into the waste and then into the environment. This would require the development of another unit process for recycling the actinides from the dross. Finally, most of the uranium, TRU, noble metals, and a part of the RE,

which are converted to metallic forms, are separated from the salt by filtration.

This intermediate product is then supplied to the electrorefining process as feed. Moreover, this procedure should be conducted in an inert atmosphere because the Li and metallic products are subject to oxidation with oxygen or moisture in the atmosphere. According to the experimental results obtained in this laboratory, over 99

% of the uranium was reduced to a metal form under the following conditions: 650 °C, 3wt% Li₂O in LiCl and an electric potential of <3.4 V vs. Ag/AgCl [3].

2.5 Electrorefining

This process is employed to selectively recover uranium from the metallic mixture supplied from the electroreduction process (Fig.5). The feed is placed in the

Table 3. Free Energy of Formation of the Various Metal Chlorides at 500°C

Unit : kcal/mol of Cl

High stability		Electrotransportable		Low stability	
	$-\Delta_f G_f^\circ$		$-\Delta_f G_f^\circ$		$-\Delta_f G_f^\circ$
BaCl ₂	87.9	CeCl ₃	68.6	CdCl ₂	32.3
CsCl	87.8	NdCl ₃	67.9	FeCl ₂	29.2
KCl	86.7	YCl ₃	65.1	NbCl ₅	26.7
SrCl ₂	84.7	*AmCl ₃	64.0	MoCl ₂	16.8
LiCl	82.5	*CmCl ₃	64.0	TcCl ₄	11.0
NaCl	81.2	PuCl ₃	62.4	RhCl ₃	10.0
CaCl ₂	80.7	NpCl ₃	58.1	PdCl ₂	9.0
LaCl ₃	70.2	UCl ₃	55.2	RuCl ₄	6.0
PrCl ₃	69.0	ZrCl ₄	46.6		

* estimated value

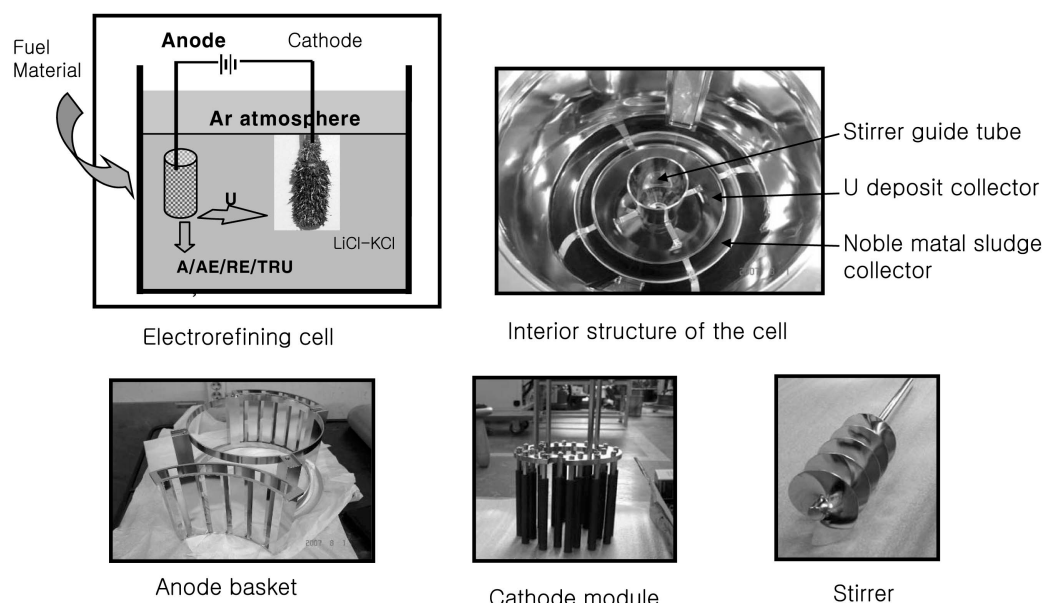


Fig.5. Major Parts of an Experimental Electrorefiner

anode basket in the electrolysis cell. LiCl-KCl (eutectic salt with a molar ratio of 58.5% LiCl and 41.5% KCl) molten salt is adopted as the electrolyte. Though the melting point of this salt is 361 °C, a working temperature above that (400~500 °C) is generally employed as an operation condition. The chlorides of the metallic elements constituting the spent fuel were classified into three groups according to their magnitude of free energy as shown in Table 3 [4]. Since the chlorides of alkaline and alkaline earth are very stable in the salt system, they tend to remain in the salt phase throughout the processing steps. However, the rare earths, U, and TRU, in metallic form are chlorinated at the anode and then U is selectively deposited onto the cathode by properly controlling the cell voltage. Since noble metal chlorides have a much lower free energy for formation as shown in Table 3, they tend to retain metallic form at the anode.

In general, electrochemical reactions can be described by the Nernst equation [5] as follows:

$$E = E_M^0 + \frac{RT}{nF} \ln(X_{MCl_3}) - E_{AgCl} \quad (7)$$

where E : cell voltage (V)

E_M^0 : standard electrode potential based on Cl_2/Cl (V)

E_{AgCl} : electrode potential for Ag/AgCl (V)

R : gas constant (J/K)

T : temperature (K)

F : Faraday constant (A.sec)

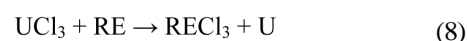
n : number of electrons involved in reduction and oxidation (REDOX)

X_{MCl_3} : concentration of MCl_3 in the salt (M)

The cell voltage was calculated using equation (7) with a variation of the metal chloride concentration in the salt for various actinides and rare earths under the following condition: $X_{AgCl} = 0.0039$ M and 450 °C. Then we obtained a plot of the cell voltage vs. logarithmic concentration of a metal chloride as shown in Fig.6. According to this estimation, when the electrode potential is maintained at -1.4V, the U is recovered by deposition to the cathode from the salt. However, if the electrode potential is elevated to a higher value, then Np will start to deposit onto the cathode. As a result, the deposition takes place in the order of $U > Np > Pu > Gd > La$ in this case. Therefore, when the electrode potential increases above -1.8V, rare earth elements such as Gd also deposit together with Am because the dotted line-2, which is indicating the value of allowed voltage, meets the Gd line as shown in Fig.6. Since the dotted line-2 intersects Gd line at the point of $X_{GdCl_3} = 10^{-2}$ M, for example, this means that Gd also deposits until X_{GdCl_3} in the salt decreases to 10^{-2} M. Likewise, when the electrode potential is elevated, other rare earth elements will also deposit together with actinides. On the contrary, however, as the dotted line-1 does not meet any lines of other elements except U at the cell voltage -1.4V in the

range of 10^{-4} M $< X_{UCl_3} < 10^{-1}$ M, a pure U product can be recovered by maintaining this electrode potential.

In this study, the deposition of U was observed in experiments where 9 wt% of UCl_3 and 1 wt% of RE (La, Nd and Ce) chlorides were contained in the salt under the conditions of 100 mA/cm² and 500 °C. As a result, the RE contents in the U deposit were found to be less than 10 ppm, which might be attributed to the fact that the allowed potential is less than the reduction potential of RE. Otherwise, a re-oxidation might have taken place as follows:



However, a considerable amount of salt is included in the deposit (20~40 wt% of the entire deposit), so cathode processing is a following essential step.

In this process, the anode sludge contains most of the remaining noble metals because they are so difficult to oxidize in the molten salt. As these noble metals are expensive materials with industrial values, it would be advantageous to develop a recovery system in the future.

2.6 Reductive Extraction

After the recovery of U is accomplished by electrodeposition, the molten salt still contains a small amount of U because the operation is cut in the middle of the deposition in order to prevent the U product from being contaminated by impurities such as TRU or RE. Therefore, the mixture of actinides U, Np, Pu, Am, and Cm remaining in the molten salt should be recovered by introducing another separation method in order to prevent the TRU from being lost into the waste stream. In this study, a reductive extraction method was

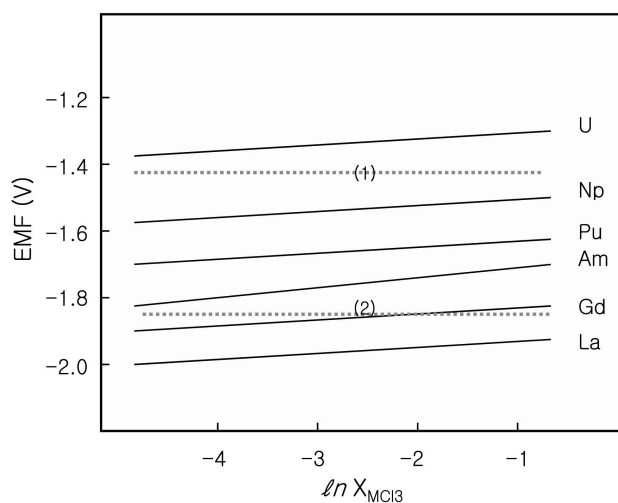


Fig.6. EMF vs. $\ln X_{MCl_3}$ in the LiCl-KCl Eutectic Salt at 450°C ($X_{AgCl} = 0.0039$ M)

considered as a suitable way to fulfill the purpose of this process because it can be applied to the purification of certain metal elements mixed with other metallic impurities.

For example, a metallic chloride dissolved in the salt phase can be reduced by lithium dissolved in the liquid metal phase with the following reaction:



where M denotes the m -valence metal element and the overhead bar denotes the species in a metal phase during the two-phase chemical reaction. Since the metallic chloride (MCl_m), metal (M), lithium chloride ($LiCl$), and lithium (Li) are distributed between the salt phase and the metal phase in this system, their distribution coefficients, D_M and D_{Li} , are defined as

$$D_M = \frac{C_M}{C_{MCl_m}} \quad (10)$$

$$D_{Li} = \frac{C_{Li}}{C_{LiCl}} \quad (11)$$

where C_M is the concentration of metal component M .

When a multistage extraction system is applied, the separation of actinides from rare earths can be further enhanced with an increase in the number of stages. Therefore the separation factor will be dependent on the number of stages, the flow ratio between the salt and metal phases, and the concentration of Li working as a chemical reducing agent. In this case, almost all of the

TRU can be extracted into the liquid metal (Cd or Bi) phase while rejecting the RE in the salt phase due to the comparatively lower distribution coefficients of the RE elements in the system. However, some elements of RE such as Pr , Ce , Nd , Gd , and La tend to be accompanied by a small portion of TRU because TRU and RE do not reveal enough of a difference in their reduction potential [6,17].

In this case, the accompanied RE contributes to proliferation resistance because the TRU product retains a higher level of γ -activity due to the RE impurities compared to that of a pure plutonium product obtained from the PUREX process. In addition, it has a significantly higher level of neutron emission because of the curium contained in the TRU product. Meanwhile, another requirement for this product should be satisfied if it is to be used as a fuel material, i.e. it should satisfy the condition of reactor-grade quality in a future reactor, e.g. a TRU burner. Since the long-lived radionuclides in the fuel will be transmuted into short-lived radionuclides while generating electricity, it will reduce the radiotoxicity of the spent fuel. In conclusion, the TRU product should be satisfactory for both contradictory purposes, that is, proliferation resistance and quality as a fuel material.

2.7 Cathode Processor

There are two kinds of deposits to recover in this process. One of them is the uranium deposit from the electrorefining process that contains molten salt up to 20~40%. Therefore, this entrained salt is removed by vacuum evaporation to consolidate the dendritic deposits. According to the experimental results from this laboratory [7], the salt began evaporating at 700°C at a vacuum

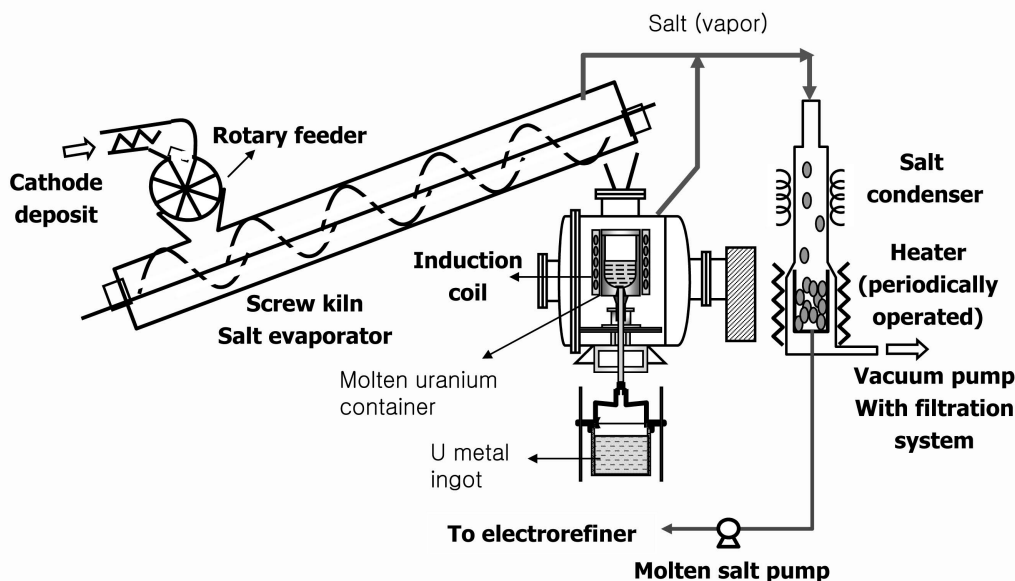


Fig.7. Equipment for Manufacturing Uranium Ingot

condition of 0.2–0.5 torr and revealed a linear increase rate up to 900°C. It is still uncertain that some portion of uranium might be evaporated under the vacuum conditions in this procedure. If so, proper conditions have to be determined by considering a combination of the vacuum state, temperature, and evaporation time in order to find the optimum conditions.

2.8 Manufacturing of a Uranium Ingot

Finally, uranium is cast in ingot form after removing the salt by evaporation. The uranium is smelted in an induction-heating furnace by elevating the temperature up to 1300°C and then the smelted liquid is poured into a graphite crucible (Fig. 7). Though the melting point of uranium is only 1134°C, an operating temperature of 1300°C, was determined for stability of the process. However, a problem with the crucible material has not yet been solved. A new technology for coating a graphite crucible with various coating agents such as alumina, zirconia, Ni-zirconia, or yttria is under development in order to prevent the uranium from reacting with the carbon in the graphite when it is smelting.

2.9 Off-Gas Treatment

Gaseous fission products and volatile metal compounds are evolved as an off-gas in the process, especially during the voloxidation procedure. They must be captured at any rate and fixed in a consolidated form so that they cannot be released into the environment after disposal. Studies are being conducted at present in several countries [8]. Examples of such studies:

- Cs adsorption at 650°C in a filter made of fly ash.
- Industrially valuable isotopes such as Kr and Xe recovered by cryogenic distillation method.
- Tc transformed to the volatile form of Tc_2O_7 (boiling point: 311°C) in an oxidizing atmosphere.
- Ru oxidized to RuO_4 (boiling point: 25.4°C), which can be captured in a yttria filter.
- Iodine adsorbed on zeolite, whose metal group is displaced by silver and thus most of the iodine can be fixed onto the zeolite in the form of AgI at 150°C.
- Tritium converted to tritium water using a catalyzer of CuO or SDBC (Styrene Divinyl Benzene Copolymer) and then adsorbed onto a molecular sieve.

2.10 Salt Regeneration

If the electroreduction and electrowinning processes are improved to a continuous or a semi-continuous-type process, a part of the electrolytes, LiCl and LiCl-KCl, can be continuously taken out of the process, cleaned up by a certain method and then recycled to the process again. Therefore it is considered in this study that a certain portion of the molten salt is continuously taken out, passed through a fission product adsorbent column (e.g. zeolite column), and then recycled to the main process again.

2.11 Radwaste Treatment[9,10]

There are several kinds of radwaste generated in pyroprocessing, e.g. structural parts of a fuel assembly, fuel cladding, electrolyte salts, off-gas, and secondary wastes. The electrolyte salts, types of high level waste, should be solidified and encapsulated before disposal. In the Argon National Laboratory, USA, researchers studied vitrification of these molten salts by occluding them into a pore of zeolite and adding glass frits and finally consolidating the mixture at a high temperature (850-900 °C) and high pressure (14,500-25,000 psi). They also found that the ceramic waste revealed better properties in terms of leaching than those of a conventional borosilicate glass of high level waste. Meanwhile, at the Research Institute of Atomic Reactor in Russia, researchers precipitated the phosphates of the fission products in the molten salt and then vitrified them by adding glass frits. However, this process's suitability for final disposal has not yet been examined.

3. MATERIAL BALANCE FOR PYROPROCESSING

In order to calculate the material balance for the pyroprocess described in this work, the fuel material was classified into several elemental groups, that is, uranium, TRU, RE and heat-generating elements (Cs and Sr). These are the major elemental groups of interest from a technical point of view. The mass flow of each group in each unit process on the flowsheet was then calculated by means of the calculation bases given in 3.1. The treatment capacity of the pyroprocess was based on 20 kg of fuel material (the weight of the cladding excluded) per batch.

3.1 Calculation Bases for the Material Balance

The following bases were used to calculate the material balance for each unit process. Some of this data has been collected from experimental results in this laboratory or from reference data presented in literature; other data were assumed on the basis of experimental experiences.

- Fuel rods cutting and decladding.
 - 0.5 wt% of each group remains in the hull.
- Voloxidation
 - 50 wt% of the gaseous FP drawn out to the off-gas.
 - 20 wt% of the Cs drawn out to the off-gas.
 - 50 wt% of the noble metals drawn out to the off-gas.
- Electroreduction
 - 99.5 wt% of the actinide is reduced to a metallic form while 0.5 wt% is contained in the dross.
 - 10 wt% of the RE is reduced to metallic form and 90 wt% of the RE, which consists of oxides, is contained in the dross.
 - All the Cs and Sr remain in the salt.

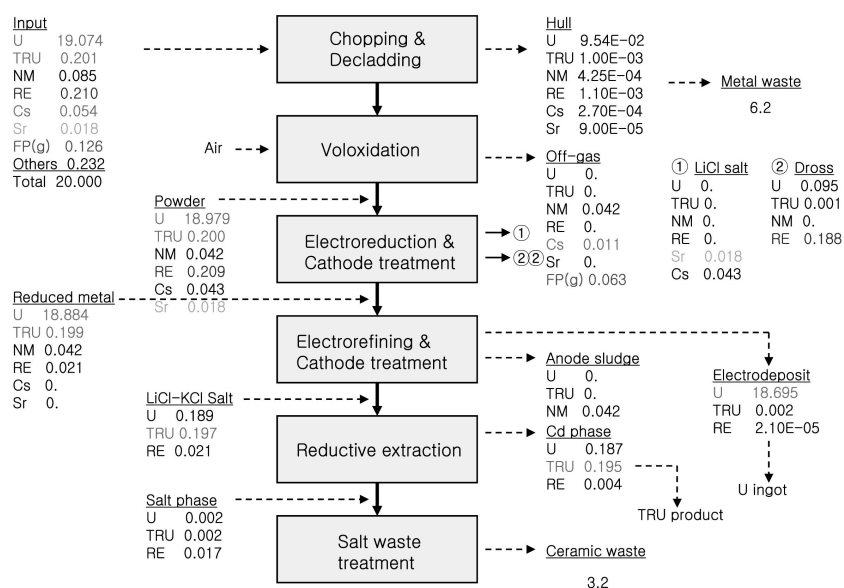


Fig.8. Predicted Material Balance for the Major Elemental Groups in the Pyroprocess (unit : kg/batch)

Table 4. Flow of each Elemental Group in the Pyroprocess

Elemental group	Input (kg/batch)	Output(kg/batch)	Ratio vs. input (wt%)	Impurity(wt%)
Uranium	19.074	U ingot 18.695	98.0	
		TRU product 0.187	1.0	TRU 0.002
		Electroreduction dross 0.095	0.5	RE 2.10E-05
		Metal waste 0.095	0.5	
TRU	0.201	TRU product 0.195	97.0	
		U ingot 0.002	1.0	
		Recovery from salt 0.002	1.0	U 48.4
		Electroreduction dross 0.001	0.5	RE 1.04
		Metal waste 0.001	0.5	
		Drawdown waste 0.	0.	
RE	0.210	Electroreduction dross 0.188	89.5	
		Uranium ingot 2.10E-05	0.01	
		Salt waste 0.017	8.10	
		TRU product 0.004	1.91	
		Metal waste 0.001	0.48	
FP(g)	0.126	Voloxidation off-gas 0.063	50.0	
		Other off-gases 0.063	50.0	
Heat generating				
Cs	0.054	Voloxidation off-gas 0.011	20.3	
		LiCl salt waste 0.043	79.5	
		Metal waste 2.70E-04	0.5	
Sr	0.018	LiCl salt waste 0.018	99.5	
		Metal waste 9.00E-05	0.5	

- All the noble metals remain in metallic form.
- Electrorefining
 - 99 wt% of the uranium is deposited on the cathode and 1 wt% remains in the salt.
 - 1 wt% of TRU and 0.1 wt% of RE are accompanied by the uranium deposit.
 - All the noble metals are contained in the anode sludge.
- Reductive extraction
 - 99 wt% of the actinides remaining in the salt are extracted into the liquid metal phase.
 - 20 wt% of the RE remaining in the salt is extracted into the liquid metal phase.

3.2 Recovery Yields and Purities of the Actinide Products

According to the above bases, material balances for the elemental groups in each unit process were calculated (Fig.8). As a result, the flow of each group was estimated on the flowsheet that was created combining the essential unit processes. It is important to estimate how the elemental groups are separated in each unit process, i.e. which route they follow in the process and how many impurities the products contain in the system, because these results can be criteria from which to judge whether the process is feasible or not.

As shown in Table 4, for example, 19.074 kg of U is injected into the system for a one-batch operation. Then, throughout the process, 98.0 wt% of the uranium is predicted to be recovered into the U ingot. As for the remainder of uranium, it is estimated that 1.0 wt% is routed into the TRU product, 0.5 wt% into the electroreduction dross, and then finally 0.5 wt% lost into the metal waste. For the TRU, likewise, 0.201 kg is input into the system and then 97.0 wt% is recovered as TRU product, with 1.0 wt% routed into the U ingot, 0.5 wt% into the electroreduction dross, and finally 0.5 wt% lost into the metal waste. It is fortunate that most of the TRU is recovered as a product, whereas most of the RE is eliminated in the electroreduction dross; otherwise, a considerable amount of RE might be accompanied by the

TRU product. Another point of viability of this process is that Cs and Sr remain in the molten salt of the electroreduction process, while being separated from U and TRU. In conclusion, this process seems to be favorable for recovering actinides while removing other elemental groups such as alkalines, alkaline earth, RE, noble metals and gaseous fission products as radioactive wastes.

4. EXAMINATION FROM THE ASPECT OF PROLIFERATION RESISTANCE

As shown in Table 4, the TRU product contains a similar content of U as of TRU and a considerable amount of RE as impurity. The one-meter-distance γ -ray dose of the RE elements was calculated using the specific γ -ray dose constants [11] with a variation of the RE content and cooling time of the spent fuel as listed in Table 5.

The reactor-grade plutonium obtained from the PUREX process has a negligible dose rate [12] compared with the TRU product considered in this study, which has a much higher γ -activity, revealing a sort of self-protection. Besides the γ -activity, the neutron dose rate is also much higher in the case of pyroprocessing. According to the neutron dose rates of pure plutonium and the total TRU for spent PWR fuel, the latter is 40 times higher than that of pure plutonium [1]. Koch [13] also reported that the neutron dose of the TRU product from pyroprocessing is 140 times higher than that of pure plutonium from a conventional LWR spent fuel (40000 MWD, 1 year cooling). Consequently, the TRU product obtained from pyroprocessing should be treated in a shielded cell, which would make it difficult to convert the TRU into suitable weapons-grade material. Another key point for the TRU product is that it must be suitable as a fuel material in a future reactor; for example, in a TRU burner that could be used for a dual purpose, that is, electricity generation as well as transmutation of long-lived TRU nuclides. If both of the contradictory conditions between proliferation resistance and satisfactory fuel quality can be satisfied at the same time, this fuel cycle technology will be realized.

Table 5. γ -ray Dose-Equivalent Rate at 1 m with Cooling Time and RE Quantities of TRU Product (20 kg PWR Spent Fuel Treated)

RE contained in the TRU product	Cooling time of spent fuel			
	1 yr	3 yr	5 yr	10 yr
10 %	0.52	0.18	0.11	0.07
5.0 %	0.26	0.09	0.055	0.035
*1.04 %	0.05	0.02	0.01	0.007

* For the material balance in this study

5. CONCLUSIONS

PWR spent fuels still contain fissile materials such as uranium and TRU even after discharge from a nuclear reactor. These fissile materials, if separated from the fission products in spent fuels, can be recycled as a fuel material. However, the PUREX recycling technology can be misused as a weapon-related technology by a malicious party. Moreover, high-level waste from the PUREX process is a great burden in terms of environmental safety even after disposal underground. With this background, for nuclear power generation

around the world, development of an alternative technology for fuel recycling in conjunction with a long-lived nuclides burner is earnestly needed to replace conventional nuclear-generation strategies. A conceptual pyroprocess was devised in this work and its characteristics were analyzed in terms of its fissile material recovery yields and proliferation resistance. As a result, it was found that the pyroprocessing procedure could be employed as an alternative recycling technology while protecting it from the possibility of nuclear proliferation.

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