

Recent Progress in Waste Treatment Technology for Pyroprocessing at KAERI

파이로 공정폐기물 처리기술의 최근 KAERI 연구동향

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(Received June 19, 2019 / Revised July 25, 2019 / Approved September 3, 2019)

This study comprehensively addresses recent progress at KAERI in waste treatment technology to cope with waste produced by pyroprocessing, which is used to effectively manage spent fuel. The goal of pyroprocessing waste treatment is to reduce final waste volume, fabricate durable waste forms suitable for disposal, and ensure safe packaging and storage. KAERI employs grouping of fission products recovered from process streams and immobilizes them in separate waste forms, resulting in product recycling and waste volume minimization. Novel aspects of KAERI approach include high temperature treatment of spent oxide fuel for the fabrication of feed materials for the oxide reduction process, and fission product concentration or separation from LiCl or LiCl-KCl salt streams for salt recycling and higher fission-product loading in the final waste form. Based on laboratory-scale tests, an engineering-scale process test is in progress to obtain information on the performance of scale-up processes at KAERI.

Keywords: Spent PWR Fuel, Pyroprocessing, Filter waste, Salt waste, Metal waste

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사용후핵연료의 효율적 관리를 위하여 한국원자력연구원에서 수행 중인 파이로 공정으로부터 발생하는 폐기물 처리기술에 대한 최근 연구동향을 종합적으로 고찰하였다. 파이로 폐기물 처리기술은 처분 대상 폐기물의 감용 및 포장, 저장과 최종 처분에 적합한 고화체 제조를 목표로 하고 있다. 한국원자력연구원에서 수행 중인 파이로 폐기물 처리 기술개발 접근 방향은 공정 흐름으로부터 발생한 폐기물내 주요 핵종들을 분리하고 회수한 물질 등을 재사용함으로써 폐기물 발생량을 최소화 하며 동시에 분리한 핵종을 별도로 고화처리하는 것이다. 폐기물 처리 주요 기술 특성은 먼저 전해환원용 원료물질 제조를 위하여 전처리 고온 열처리 공정을 사용하며, LiCl 과 LiCl-KCl 염으로부터 핵종을 분리하고 회수염의 재사용 및 핵종 함유량을 증대시킨 최종 고화체 제조 기술을 개발하는 것이다. 따라서 실험실 규모 실험 결과를 토대로 최근에는 공정 용량 증대를 위한 자료 확보를 목적으로 공학규모 시험을 수행 중에 있다.

중심단어: 경수로 사용후핵연료, 파이로프로세싱, 필터폐기물, 염폐기물, 금속폐기물

1. Introduction

Pyroprocessing, which is believed to be a non-proliferation technology based on group recovery from spent fuels, is one of the most widely used technologies for spent fuel management. The Korea Atomic Energy Research Institute (KAERI) has been developing pyroprocessing technology since 1997 and several technologies have been developed in this area to reduce the volume, radioactivity and heat load of pressurized water reactor (PWR) spent fuels [1,2]. Pyroprocessing development for the treatment of spent oxide fuel at KAERI consists of five unit processes from the head-end to the waste treatment system. This approach aims to minimize the amount of transuranic elements (TRU) in waste streams as well as to effectively recover uranium and TRU for reuse. An additional objective of this approach is to minimize the high-level waste volumes for final disposal, thus minimize the footprint of the geological repository.

KAERI's pyroprocessing unit includes six waste streams that can be categorized into three groups : 1) filter wastes trapping gaseous radionuclides, 2) metal wastes, and 3) salt wastes. In particular, two types of salt waste are generated. The first type includes LiCl salt waste with group I and II nuclides, such as cesium and strontium, generated by the oxide reduction process, and the second type is LiCl-KCl eutectic salt that contain rare earth elements (REEs)

and trace amounts of transuranic elements from electrorefining and electrowinning processes. The remaining wastes are classified into metal waste and filter waste. The KAERI approach for waste treatment in pyroprocessing emphasizes product recycling and minimization of waste form volume by grouping fission products (FPs) recovered from process streams for immobilization in separate waste forms [3]. This involves the head-end thermal treatment of the spent PWR fuel to collect volatile and semi-volatile fission products [4], melt cladding hull mixing with noble metal wastes or recovering Zr from cladding hulls [5], and salt waste treatment by separating fission products from LiCl or LiCl-KCl salt streams and then immobilizing them as durable final waste forms [6,7]. This approach for salt waste treatment allows for salt recycling and higher fission products loading in the final waste form.

This review summarizes recent progress and developments in these wastes treatment technologies in pyroprocessing.

2. Overview of Waste Treatment in Pyroprocessing

2.1 Waste stream characteristics in pyroprocessing

Six primary radioactive waste streams are generated

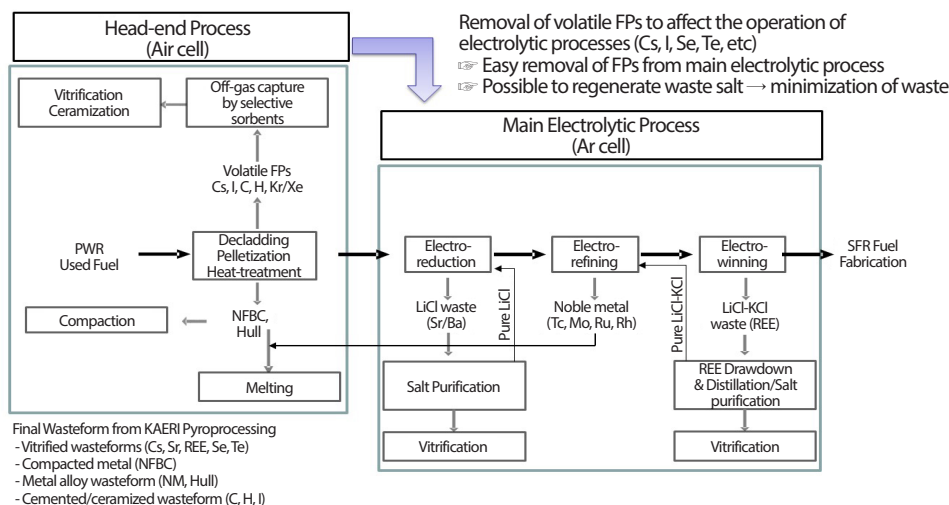


Fig. 1. Processing diagram representing pyroprocessing of spent PWR fuel with waste streams.

Table 1. Summary of waste group generated from KAERI’s pyroprocessing

Category	Waste	Main Characteristics	Treatment Approach
Gaseous waste	Spent filters	Cs-trapped filter Iodine-trapped filter Tc-trapped filter (minor) Fission gases trapped sorbents	Selective trapping
Metal waste	NFBC Cladding hull Noble metal	NFBC : Activation (Nb-94, etc.) Hull : FPs, TRU penetration Noble metal : Anode sludge in ER	Compaction/melting Zr recovery (option)
Salt waste	LiCl LiCl-KCl	LiCl : Sr, Ba, Cs (minor) LiCl-KCl : REE, TRU (minor)	FPs separation & Recycling purified salt

* NFBS : Non-Fuel Bearing Component (Assembly hardware), REE : Rare-Earth Element

during the pyroprocessing of spent PWR fuel : 1) contaminated fuel assembly hardware, 2) cladding hull, 3) filter media from head-end treatment, 4) LiCl salt waste from oxide reduction, 5) metallic waste from electrorefining, and 6) eutectic LiCl-KCl salt waste from electrowinning (or drawdown). A schematic of the KAERI pyroprocessing flowsheet is shown in Fig. 1. Table 1 presents a brief description of each waste stream.

Table 2 summaries the estimation of radioactivity level of each waste group in Table 1. This estimation is based on

the KAERI’s flowsheet for internal use, which has some assumptions regarding separation factors (~99.98%) due to a lack of experimental results using spent fuel. Although radioactivity level is qualitative prediction instead of quantitative estimation, it is expected that there is no high-level radioactive wastes defined in the Nuclear Safety Law in the process of pyroprocessing of spent PWR fuel. However, based on the evaluation of waste characteristics, REEs waste with alpha bearing isotopes and some fission products as well as salt wastes with iodine would be needed to be

Table 2. Summary of radioactivity level on each waste group

Category	Waste type	Main radionuclides	FPs loading (%)	Radioactivity level
Gaseous waste	Cs-trapped filter	Cs, Rb	5	Medium-level
	Iodine-trapped filter	I, Br	3	Medium-level*
	Tc-trapped filter	Tc, Mo	8	Medium-level*
	C/H filters	¹⁴ C, ³ H	1	Medium-level
	Noble gas trapped	Kr, Xe	-	Low-level
Metal waste	NFBC	Ni, Nb	-	Low-level
	Cladding hull	U, Zr	7	Medium-level
	Noble metals	NMs, U		Medium-level
Salt waste	Sr waste	Sr, Eu	9	Medium-level
	REE waste	REE, TRU	42	Medium-level*

* Needed to be disposed in the deep geological repository

disposed in the deep geological repository. Therefore, important radionuclides in connection with safe disposal are long-lived fission products (Iodine, Tc) with high mobility in repository environment as well as an effective long-term storage of high heat-emitting medium-level wastes which contains with Cs, Sr and Ba. It is expected that a smaller repository for final waste forms with high integrity is more important than simple waste-stream treatment.

2.2 Approach for waste treatment technology development in pyroprocessing

Table 3 shows a progress of technologies development for effective waste treatment in each waste group. Technology improvement focused to resolve some technical issues based on the objectives of waste minimization and simple process. Following sections describe the technical approach for three kinds of wastes in detail.

2.2.1 Off-gas treatment and waste forms fabrication of gas-trapped sorbents

Various radioisotopes present in spent oxide fuels are released as gases or particulates during mechanical

de-cladding, low- and high-temperature processing, electrolytic processing and solidification and these must be captured by filters. Based on the KAERI pyroprocessing flowsheet in Fig. 1, volatiles (⁸⁵Kr, Xe, ¹⁴C and ³H, etc.) and semi-volatiles (^{134,137}Cs, ⁹⁹Tc, ¹²⁹I, etc.) are vaporized during head-end high temperature processing and are captured by a series of filter media. Using high-temperature treatment to fabricate feed materials that are supplied to the oxide reduction process has several advantage as following. A greater fraction of the fuel can be separated from the cladding and the particle sizes of spent fuel material are easily controllable for improving the efficiencies of subsequent processes. Another advantage is that both volatile and semi-volatile fission products including Cs, Tc, Ru, and I can be removed from the fuel material prior to subsequent operations, which will benefit the overall process by reducing the adverse effects of volatile and semi-volatile fission products. Therefore, if considering high-temperature treatment as a head-end option, an off-gas treatment system is essential for the selective trapping of volatile fission products such as I, Tc, and Cs. In the off-gas capturing system developed at KAERI, a fly ash (FA) filter is used to capture Cs, a silver ion-exchanged zeolite

Table 3. Summary of waste group generated from KAERI's pyroprocessing

Group	Waste	Main FPs	Development Progress of Treatment Technology	
			Technologies progress (1) → (2)	Technical issues
Gaseous waste	Spent filters	Cs, Tc, I	(1) Selective trapping	Limitation in chemical stability during immobilization : slightly desorption of Iodine
			(2) Combination of trapping and easy solidification	In progress : Need an experimental results
Metal waste	NFBC Hull & Noble metal	U, Zr Tc, Mo	(1) Zr recovery by chlorination or electrorefining	Use corrosive chlorine gas & need multi-step unit process
			(2) Melting	Simple and reuse of other wastes : In progress
Salt waste	LiCl	Cs, Sr, Ba	(FPs separation) (1) Ion-exchange by zeolite (2) Layer melt crystallization	Low ion-exchange capacity Feasible, but need scale-up demonstration
			(Immobilization) SAP*/M-SAP/U-SAP	Effective separation in multi-component system (High Cs content in salt)
	LiCl-KCl	REE*	(FPs separation) (1) Selective precipitation (2) Combination of precipitation and distillation	Feasible, but scale-up demo. In progress : Effective in multi-component system
			(Immobilization) (1) ZIT/A-ZIT/LIPS/RCP* (2) LABS*	Need to improve physical integrity of waste form In progress : effective for high waste loading & high density
Salt purification process	-	(1) Two-step process : Melt crystallization → Reactive distillation (2) One-step process : Reactive crystallization /distillation	Feasible, but need multi-step process In progress : Effective in multi-component system	

* REE : Rare-Earth Elements (Lanthanide elements), SAP : $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$

* ZIT : $\text{ZnO-TiO}_2\text{-SiO}_2\text{-CaO-B}_2\text{O}_3\text{-P}_2\text{O}_5$, LIPS : $\text{PbO-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$, RCP : $\text{CaO-P}_2\text{O}_5\text{-REPO}_4$

* LABS : Lanthanide-borosilicate ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-REO}_x$)

(AgX) is used for I capture, and a calcia filter is used for Tc capture. Recently, alternative filter media has been developing for off-gas capturing [4,8], including a kaolinite-based filter to capture gaseous cesium to overcome some of the limitation FA filters and a bismuth-based adsorbent for the removal of ^{129}I in the off-gas stream for improving capture capacity [9]. Furthermore, solidification methods for disposing these used filters are under development at KAERI [10].

2.2.2 Waste salt treatment and immobilization of residual waste

The novel step in KAERI's salt waste treatment process is the dechlorination of salt waste stream, performed either prior to or during waste form fabrication for substantial reduction in waste volume [11]. The major challenge to immobilize salt wastes lies in avoiding disruption to the physical and chemical integrity of the host phase with the fission products due to chlorine. Chloride-based wastes generated

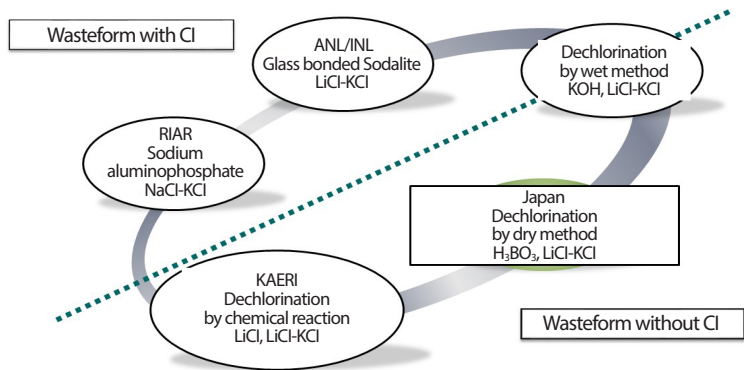


Fig. 2. General approach for immobilization of salt waste for final disposal.

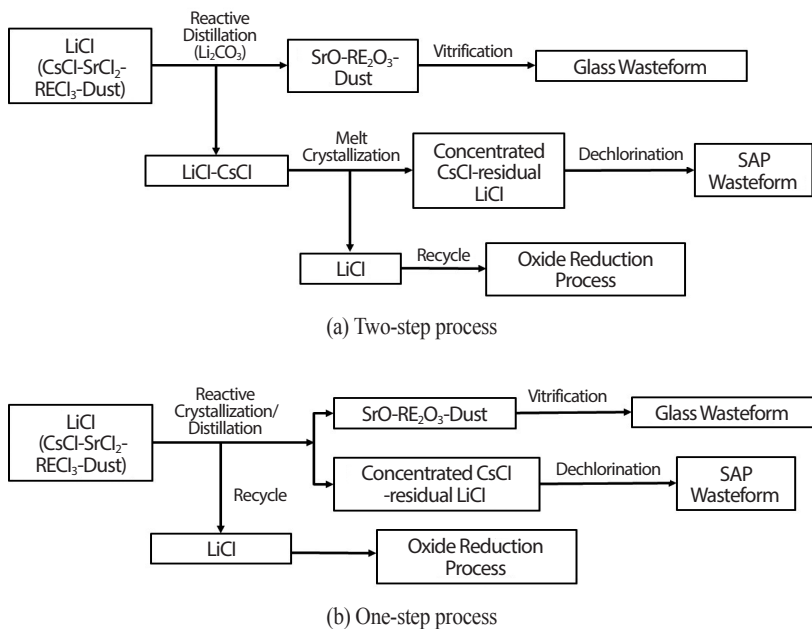


Fig. 3. Scheme of improved process for LiCl salt waste treatment.

during pyroprocessing are comprised of highly ionic compounds; these compounds are volatile above the melting temperature of the electrolyte salt. Salt waste from pyroprocessing is considered as challenging due to its incompatibility with conventional solidification processes, such as vitrification or ceramization. There are two approaches to immobilize these wastes. The first uses a Cl-containing matrix and the other employs a non-Cl-containing matrix via dechlorination, as shown in Fig.2. KAERI adopted the

dechlorination reaction with synthetic composites and applied it to the conversion of metal chlorides under oxidative conditions; this resulted in a release of chlorine gas, which was captured using metal oxides, such as Li_2O that can be converted into metal chlorides (LiCl) for recycling in electrolyte [11,12].

Two chloride-based waste streams are generated during pyroprocessing; these include a LiCl stream from the reduction of spent oxide fuel and a LiCl-KCl stream from

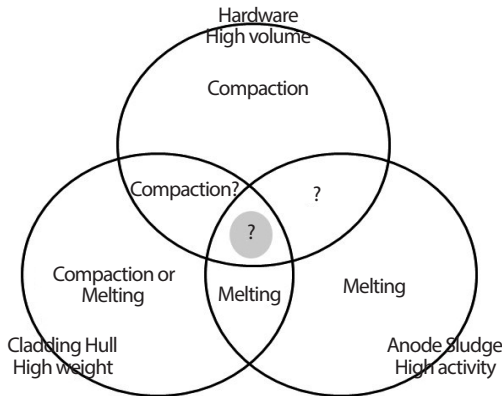


Fig. 4. Basic concept for metal waste treatment in KAERI's pyroprocessing.

the treatment of metallic fuel. Generally, during the treatment of spent oxide fuel, group I and II fission products (Rb, Cs, Sr and Ba), I, Se, and Te accumulate in LiCl salt during the oxide reduction step. Meanwhile, lanthanide fission products and trace amounts of actinides are included in the LiCl-KCl salt during the electrorefining step. During the treatment of metallic fuel, all these fission products accumulate in LiCl-KCl eutectic salt. The traditional approach to treat these waste streams is direct immobilization for disposal in a waste form suitable for chloride-bearing waste, such as glass-bonded sodalite or a tellurite glass. Alternatively, separation of fission products concentrated into a reduced electrolyte volume allows for recycling of the remaining salt. A general approach to minimize waste salt volume is the selective separation of FPs from bulk salt waste and recycling the purified salt back to the main process [6, 13-15]. Conventional separation technologies, such as ion-exchange and selective reaction precipitation have been investigated to concentrate FPs and allow physical or chemical separation from the salt stream. The goal of these processes is to concentrate FPs for waste form volume minimization and salt recycling. The salt treatment processes developed at KAERI include melt crystallization for the LiCl salt stream and selective precipitation for the LiCl-KCl salt stream. Other separation processes, such as selective distillation for Sr(Ba) and Ln chlorides

(or oxide) separation from salts based on differences in the vapor pressures of metal compounds, are being developed. Recently, for simplifying the salt waste treatment process, development of an integrated multi-component FPs separation technology from LiCl waste salt is in progress, in this technology, the two-step process (melt crystallization and reactive distillation) is simplified to a one-step process (reactive distillation/distillation) as shown in Fig. 3. The one-step process is highly beneficial as it reduces load on the melt-crystallization process by removing corrosive materials and waste nuclides that react with the precipitation agent; simultaneously, unreacted nuclides such as Cs can be purified by crystallization.

Waste salts containing fission products that result from separation treatments are processed into final waste forms. Extensive research at KAERI has resulted in the development of two alternative waste forms referred to as SAP (SiO_2 , Al_2O_3 , and P_2O_5) and ZIT (ZnO , TiO_2) [16-18]. Different SAP (SAP, M-SAP and U-SAP) waste forms were developed to immobilize FPs from waste salts and ZIT (ZIT and A-ZIT) and LABS (lanthanide-borosilicate) waste forms were developed to immobilize lanthanide fission products in oxide, oxychloride or phosphate forms; such immobilization is based on a monazite host phase with a high waste loading (50wt%), high density, and a low leach rate from the waste form.

2.2.3 Metal waste treatment

Metal wastes from KAERI pyroprocessing are mainly composed of cladding hulls and non-fuel bearing component (NFBC) hardware in the head-end process and noble metal components in the anode basket of electrorefining. Fig. 4 represents the KAERI concept for developing a metal waste treatment technology by combining cladding hull with noble metals or hardware components by melting.

NFBC hardware from the spent fuel assembly is removed prior to pyroprocessing and is maintained as a separate waste stream. This includes top/bottom nozzle assemblies, outer guide tube assemblies, and top/mid/bottom grids

composed of Type 304 stainless steel, Inconel-718, Zirlo, or Zircaloy-4. Although hardware waste is categorized as NFBC, its radioactivity is regarded to exceed the intermediate-/low-level waste disposition regulations due to the presence of ^{59}Ni and ^{94}Nb generated by neutron activation. Generally, hardware waste is treated by mechanical compaction or melting for volume reduction. Traces of actinides such as some fission products (Cs) and minor amounts of U and TRU penetrate the inner layers of zircaloy cladding hulls [19]. Zircaloy-4 and Zirlo cladding consist of about 98% Zr. Two major streams for metal waste treatment for storage or disposal are compaction and melting. The melting process has a higher volume reduction factor compared to the compaction method; however, because it is a high temperature process, it involves high energy and cost requirements.

Noble metals including Tc, Zr, Mo, Rh, and Pd, are retained in the anode basket of the electrorefiner. After residual salt is removed from the basket by distillation, these metals can be recovered from the anode basket, which can then be reused. To immobilize noble metal fission products, noble metals can be processed directly to form an epsilon-phase alloy waste form [20] or alloyed with added steel to produce a metallic waste form similar to that used for the treatment of EBR-II used fuel cladding [21].

3. Development of Wastes Treatment Technologies at KAERI

3.1 Gaseous wastes treatment and immobilization of spent filters

3.1.1 Off-gas treatment technology in head-end process of pyroprocessing

The removal of volatile and semi-volatile fission products during high-temperature treatment in head-end step can reduce operational burden on subsequent electrochemical treatment steps. KAERI has developed an off-gas trapping system to capture gaseous fission products released

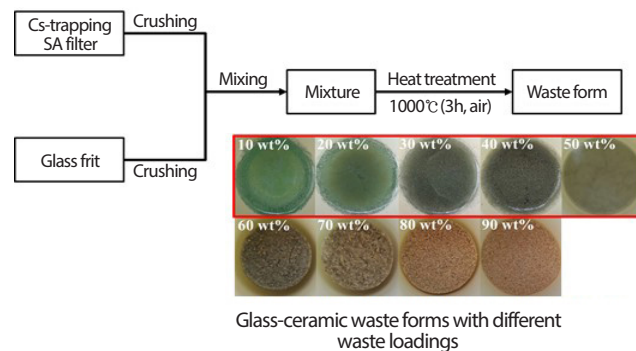
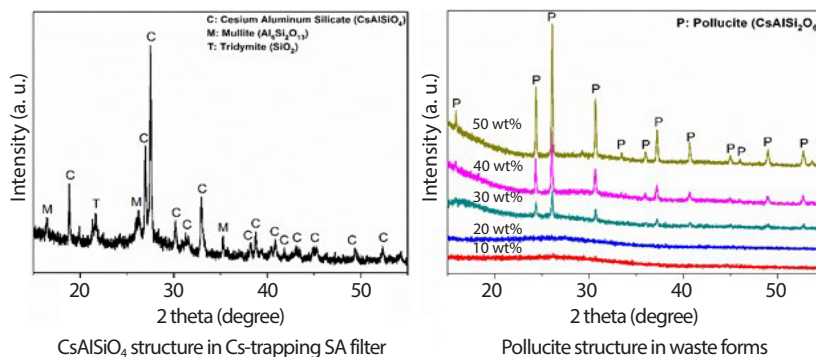


Fig. 5. Procedure of glass-ceramic waste form fabrication for Cs-trapped ceramic filter.

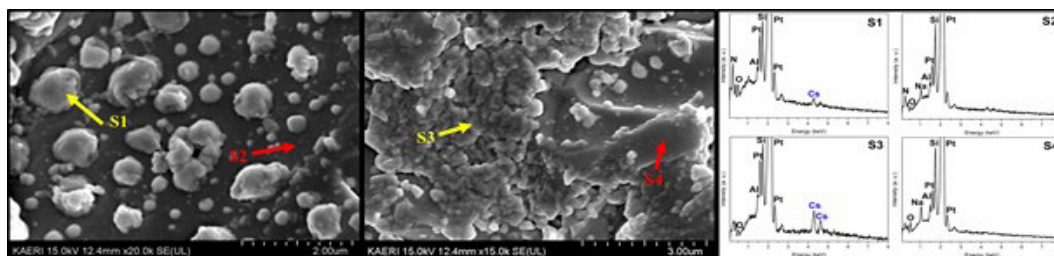
from the decladding and head-end, high-temperature off-gas processes [22].

A fly-ash (FA) disk-type filter has been developed and it showed good performance for the capture of gaseous Cs in hot-cell experiments [4, 10]. Additionally, five types of granule filters, including a ball, tube, and sponge structure-type filters have been tested [23]. Semi-volatile Cs compounds (e.g., Cs_2O and CsI) are chemically reacted with aluminosilicate materials to form hydrochemically stable cesium compounds ($\text{CsAlSi}_2\text{O}_6$, CsAlSiO_4 , and $\text{CsAlSi}_5\text{O}_{12}$), mainly the pollucite type ($\text{CsAlSi}_2\text{O}_6$) in the fly-ash filter [11]. Fly-ash filters fabricated with raw materials from power plants contain some impurities such as Fe_2O_3 , CaO , K_2O and MgO . These impurities make it difficult to maintain uniform quality of the filter media. Therefore, a new filter using kaolinite as the raw material was developed for capturing Cs [24, 25]. This kaolinite-based silica-alumina (SA) filter consists of only silicon and aluminum oxides, and feasibility tests showed that Cs compounds chemically reacted to form a thermally stable form of CsAlSiO_4 at $900\sim 1,000^\circ\text{C}$.

Conventionally, radioactive iodine (^{129}I) in off-gas stream is removed using silver-exchanged zeolites (AgX and AgZ) [26, 27]. Although these materials show high removal efficiency for ^{129}I , zeolite-based sorbents cannot exclude the physical sorption of iodine [28]. Such physically adsorbed iodine can be easily dissolved in groundwater, or can be released during the immobilization of spent filters



(a) XRD pattern for pollucite structure



(b) Microstructural morphology

Fig. 6. XRD pattern and microstructure for glass-ceramic waste forms of Cs-trapped filter.

at elevated temperatures. In this regard, KAERI has been studying the development of new sorbents for ^{129}I removal. Bismuth is being employed to induce the chemisorption of iodine [29]. Preliminary studies at KAERI showed that the adsorption capacity of iodine on synthesized samples is approximately 2 times higher than that on commercial AgX, and this iodine was retained by forming BiI_3 or BiOI compounds that are thermally stable up to 300°C , which suggests that physical sorption of iodine can be successfully avoided [11]. Additional optimization studies are in progress at KAERI to increase the capture efficiency of iodine.

3.1.2 Waste form fabrication of gas-trapped sorbents

Immobilization methods to fabricate waste forms for disposing used filters are under investigation at KAERI. This section summarizes immobilization technologies for two kinds of Cs-trapped filters (fly-ash and kaolinite-based silica-alumina filters) developed by the addition of glass

frits and for an iodine-captured filter using Bi_2O_3 as an additive for low-temperature sintering glasses.

It has been identified that pollucite is a feasible final waste form for the long-term disposal of ^{137}Cs -containing waste [30]. Specific structure of pollucite provides strong bonding to Cs ions by virtue of excellent hydrochemical and thermal properties. Therefore, KAERI has developed a simple immobilization process to fabricate glass-ceramic waste forms for Cs-trapped filters [31]. Fig. 5 illustrates the procedure of such waste form fabrication with a Cs-trapped SA filter and glass frit addition. Two types of Cs-trapped filters, FA and SA filters, and two types of glass frit (SiO_2 : 60~75%, B_2O_3 : 0~23%, Al_2O_3 : 2~9%, CaO : 4~11%, Na_2O : 11~15%) were used in the temperature range of $950\sim 1,150^\circ\text{C}$. The results of structural characterization of the fabricated waste forms showed that the major phase of Cs was pollucite with a crystal size of $1\sim 20\ \mu\text{m}$, as shown in Fig. 6. This result implies that the pollucite structure was

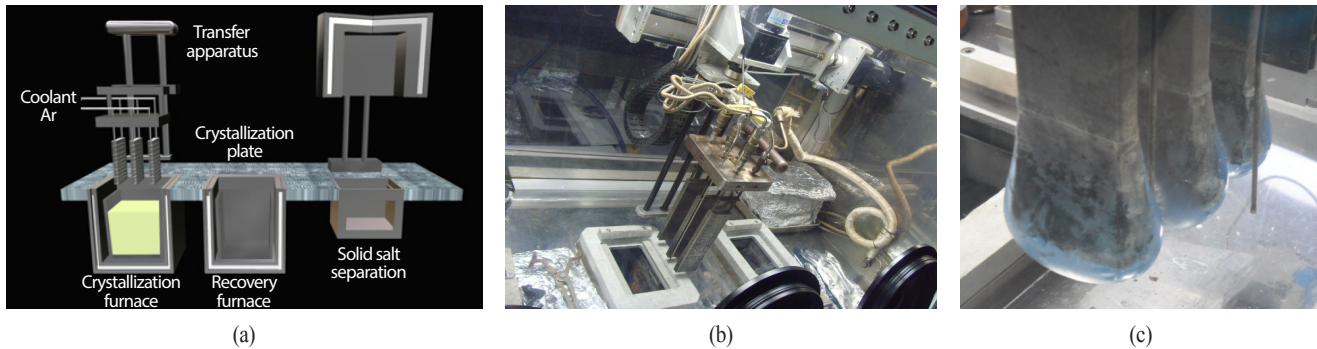


Fig. 7. (a) Scheme of melt-crystallization system, (b) lab-scale apparatus for the melt-crystallization, and (c) purified LiCl salt.

maintained in Cs-FA/SA filters during thermal processing and that glass-ceramic waste forms were fabricated. The PCT leach test revealed that the chemical resistance of these glass-ceramic waste forms showed a leach rate of $10^{-2} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (PCT test) and $7\cdot 10^{-5} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (MCC-1 test).

The key issue in immobilizing an iodine-trapped filter lies in minimizing iodine loss during high-temperature treatment. Therefore, low-temperature melting methods at 650°C were studied to synthesize glass waste form using binders with a composition of Bi_2O_3 (40-50%)- SiO_2 (20-25%)- B_2O_3 (30-40%) and a loading of 30wt% of spent iodine filters [11]. Recent studies have focused on developing a low-temperature sintering process for fabricating silver phosphate glass waste forms. Silver iodide (AgI)-incorporated silver phosphate glasses were prepared to immobilize ^{129}I -trapped AgX filters [32]. A melt-quenching method was employed to synthesize these glasses at 450°C to prevent the evolution of iodine during heat treatment. As a consequence, silver iodide could be incorporated into $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$ glasses up to 50 mol% without significant crystallization and an iodine leach rate of about $2\times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (PCT-A test) was obtained. However, an improvements are is required to reduce iodine loss during the immobilization process.

3.2 Separation technology of radionuclides in waste salts

In the pyrochemical process, two kinds of waste salts

are generated. To reduce the volume of waste salt, fission products in waste salt should be separated and concentrated in a small volume. Furthermore, it is also beneficial to recycle purified salt in the electrochemical process for economic and environmental needs.

Target fission products in the waste salt purification process are mainly group I / II nuclides, such as Cs/Sr and rare-earth nuclides. To separate fission products from molten chloride salts, several methods, such as melt-crystallization, precipitation, and distillation, have been studied. KAERI's R&D is focusing on developing a separation process by combining above methods, mainly based on the melt-crystallization. Therefore, this section describes progress in separation studies from the lab-scale to engineering scale test.

3.2.1 Lab-scale melt-crystallization studies

A scheme depicting the melt-crystallization system is shown in Fig. 7. The procedure for lab-scale melt-crystallization process is as follows. 3 kg of LiCl containing surrogate fission products of CsCl , SrCl_2 , and BaCl_2 are melted at 700°C in a furnace. Purified LiCl crystals are recovered on crystallization plates as a solid-state LiCl crystals by cooling the plates to below their melting point using an Ar coolant gas flowing inside crystallization plates [33-35]. Meanwhile, fission products are concentrated in the residual salt. At the optimized temperature and Ar coolant gas flow, LiCl waste salt containing $\sim 10\text{wt}\%$ surrogate fission

products was successfully purified with a nuclide separation efficiency of over 90%.

3.2.2 Engineering-scale melt-crystallization studies

Based on the lab-scale study, an engineering-scale melt-crystallization system capable of 20 kg/batch treatment was designed and installed at PRIDE (PyroProcess Integrated inactive DEMonstration facility); it operates in an argon atmosphere [6]. The system consists of a crystallization furnace, melting furnace, crystallizer with 6 crystallization plates, and an automated crystallizer moving device. The crystallizer and reaction vessels are made of Inconel-625 to withstand high operation temperature (700°C) and corrosion environment. All the operations are designed taking into consideration remote operations by reflecting design characteristics of the melt-crystallizer and the melt-crystallization process where the Ar coolant gas is injected through the zigzag flow path within the plates. Thermocouples for monitoring the melt-crystallization process are installed through ports at several measurement points. Due to the scale up, there were several issues with respect to temperature gradients in the reaction vessel, which resulted in the formation of over-grown crystals and low separation efficiency. Therefore, a melt-crystallization monitoring system was developed and verified using engineering-scale equipment. The previous monitoring system, based on lab-scale monitoring systems, was controlled by monitoring temperatures at two characteristic points. However, the enhanced monitoring system evaluates temperature gradients at one more point, and each crystallization plate is separately controlled by monitoring its temperature profile. Using the enhanced monitoring system that prevents over-grown LiCl crystals, uniformly distributed LiCl crystals could be obtained on the plates. High nuclide separation efficiencies of over 90% were obtained in the engineering-scale study. The engineering-scale melt-crystallization monitoring system can be applied to even larger system containing many crystallization plates and processing different molten salt systems.

3.3 Immobilization Technology of Residual Salt Wastes

Salt waste is problematic waste of pyroprocessing due to its incompatibility with conventional solidification processes, such as vitrification or ceramization. Currently, there are two known approaches for immobilizing these wastes. One approach is to use Cl-containing matrices while the other approach uses non Cl-containing matrices via dechlorination. During these processes, especially in the case of the dechlorination method, large amounts of chloride compounds, such as HCl and Cl₂, are produced by heating. KAERI investigated the chemical conversion of metal chlorides into manageable products at a high temperature using a sol-gel process based on an aqueous solution system (Na₂SiO₃-H₃PO₄-Al(NO₃)₃-H₂O). Furthermore, the chemical durability and physical properties of their waste forms were analyzed. The products were successfully solidified as a monolithic waste form at high temperatures without vaporizing radionuclides or other elements in the waste and showed reasonable properties. This approach indicated that phosphate-related products are compatible with borosilicate glass at some mixing ratios. However, the reaction system, which is present in an aqueous state, has intrinsic problems due to its highly acidic condition, even though limitations related to host matrices and processing temperature for the immobilization of metal chloride wastes are avoided.

3.3.1 Immobilization of residual salt waste in oxide reduction process [7,8,9,16]

Based on the Si-O-Si-O-Al-O-P-O-P sequentially bonded matrix, our research group studied the chemical conversion of metal chloride waste into manageable products at high temperatures using an inorganic composite (SAP) composed of SiO₂, Al₂O₃, and P₂O₅. Metal chlorides in LiCl waste were effectively dechlorinated to produce metal aluminosilicates, aluminophosphates, and orthophosphates as thermally stable compounds. Using borosilicate glass as a chemical binder, they could be consolidated as a

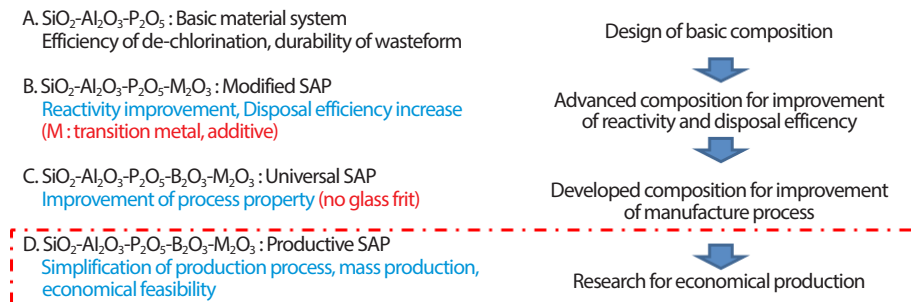


Fig. 8. Development history of U-SAP waste forms and current research purpose.

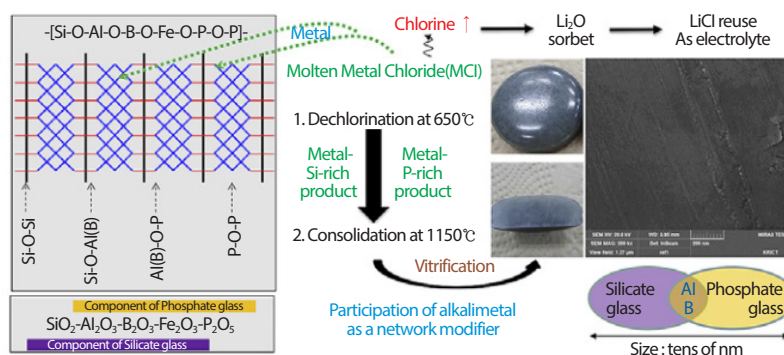


Fig. 9. Overall description of U-SAP process and definition of U-SAP waste form.

monolithic form with good chemical durability. Additionally, transition metal components were added to the SAP matrix to increase the reactivity of the de-chlorination process. The improved matrix was named M-SAP. However, the addition of a chemical binder affects the microstructure and chemical durability of the waste form. Large amounts of silicate glass as a binder results in a more durable waste form, but conversely, with a low waste loading. To avoid such problems, a U-SAP matrix was developed. A chemical binder was no longer needed and the overall process was simplified. Currently, our study is focused on developing an economical method to produce U-SAP matrices and waste forms. Detailed studies are being conducted to investigate the structure of the U-SAP waste form. The development history of the U-SAP waste form and current research directions are illustrated in Fig. 8.



Fig. 10. SEM image of U-SAP waste form.

The U-SAP waste form is dense and solid without defects and is a promising option for immobilizing waste salts generated from pyroprocessing. Fig. 9 shows an overall

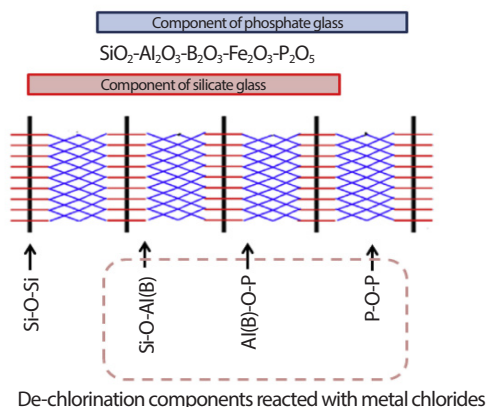


Fig. 11. Conceptual description on the function of component in U-SAP.

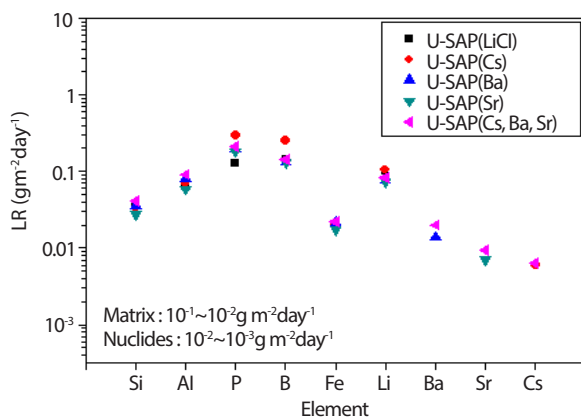
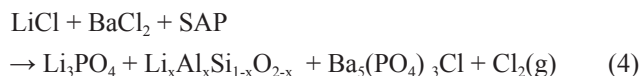
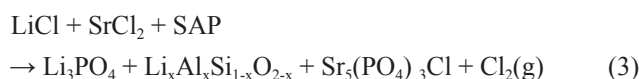
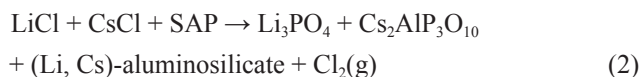


Fig. 12. Leach rates (LR) of the U-SAP wasteforms by the PCT-A method.

description of the U-SAP process. Within this waste form, nanosized droplets are uniformly distributed and encapsulated in a glassy silicate matrix (Fig. 10). The droplets are composed of a mixture of crystalline Li_3PO_4 and amorphous phosphorous-based phases. The glassy silicate matrix is composed of Si-O-Si and Si-O-Al(B) components with low contents of Li. The Si-rich and P-rich phases are connected by Si-O-Al(B) and Al(B)-O-P upon the addition of Al and B elements. A conceptual description of the U-SAP matrix is shown in Fig. 11. After de-chlorination, the products of reaction between CsCl, SrCl_2 , and BaCl_2 and U-SAP materials are deemed to be metal-aluminophosphates

($\text{Cs}_2\text{AlP}_3\text{O}_{10}$) or apatite [e.g., $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ and $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$]. Chemical reactions occurring between the salt and SAP matrix during the de-chlorination process are shown in Eqs. (1) - (4).



The chemical durability of U-SAP consolidated forms was evaluated by product consistency test (PCT-A) testing. Fig. 12 shows the results of PCT-A leaching test. The normalized leaching rates of matrix components such as Si, Al, P, B, Fe and Li were about $1 \times 10^{-2}\text{ g}\cdot\text{cm}^2\cdot\text{day}^{-1}$, while those of surrogate nuclides, such as Cs, Sr and Ba, were about $1 \times 10^{-3}\text{ g}\cdot\text{cm}^2\cdot\text{day}^{-1}$, respectively. U-SAP consolidated forms exhibited very low leaching rates of the nuclides when compared to environmental assessment (EA) glass ($0.97\text{ g}\cdot\text{cm}^2\cdot\text{day}^{-1}$). The leaching rate of the low-activity reference material (LRM) glass for Na reported by ANL was $0.07\text{ g}\cdot\text{cm}^2\cdot\text{day}^{-1}$. In terms of leach resistance, the U-SAP waste form is comparable to other waste forms.

3.3.2 Immobilization of lanthanide waste in electrochemical recovery process

Due to LiCl-KCl purification processes, such as a selective reaction or distillation, lanthanide (Ln) precipitates (chloride, oxides, phosphates or some mixed compounds) are expected to be present in the waste salt along with a small quantity of actinides. Considering the chemical form of lanthanides as precipitates, a properly chosen host matrix or waste form is required. Lanthanide oxides, oxychlorides

Table 4. Development history of ZIT waste forms at KAERI

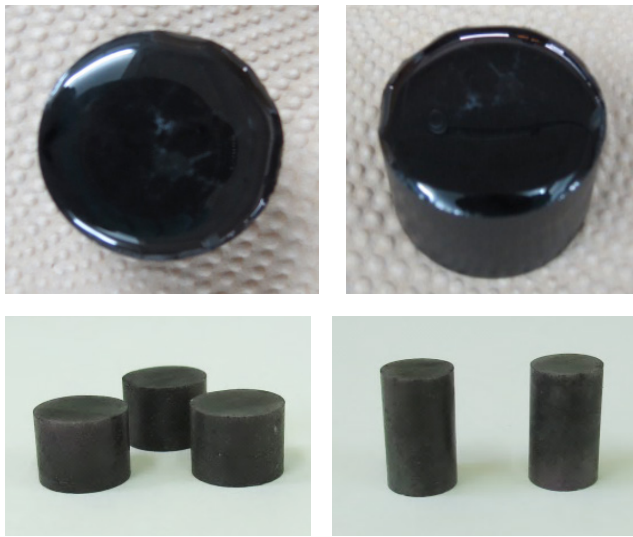
Waste Material System	LiCl-KCl		Additive	Binder	Remark
	Purification System	Waste loading			
ZIT ZnO-TiO ₂ -SiO ₂ -CaO-B ₂ O ₃ -P ₂ O ₅	Oxygen	~40wt%	Oxide Oxychloride	No	KAERI
A-ZIT ZnO-TiO ₂ -Al ₂ O ₃ -Fe ₂ O ₃ -P ₂ O ₅	Hybride (O ₂ +Phosphate)	~40wt%	Oxide Oxychloride Phosphate	Binder	KAERI
LIPS PbO-Fe ₂ O ₃ -P ₂ O ₅	Phosphate	~40wt%	Phosphate	No	Well known matrix
Li(K)-SAP Li(K) ₂ O-SiO ₂ -Al ₂ O ₃ -P ₂ O ₅	Phosphate	Not defined	Phosphate	No	KAERI

or phosphates are chemically durable and thermally stable. In this respect, waste loading and processing temperatures are more important than the selection of immobilization matrix. Table 4 shows the development history of ZIT type waste forms developed at KAERI [14].

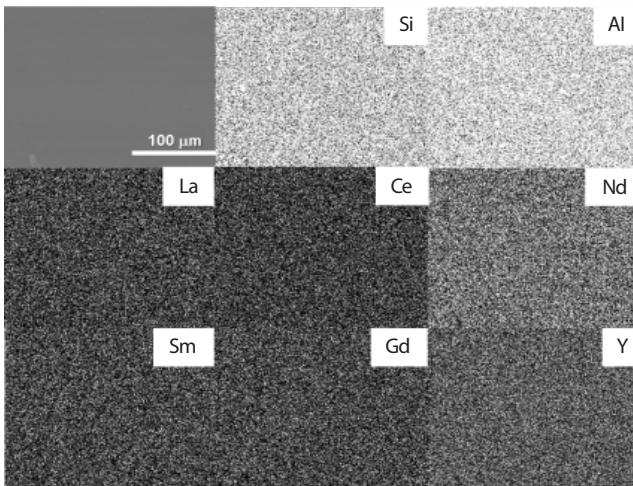
In the case of oxide form of lanthanides as precipitates, a specific glass matrix, LABS (lanthanide borosilicate) glass is very useful. It can be made with high loadings of lanthanide oxides (up to 50-60 mass%) and exhibits high chemical durability [18]. However, a high processing temperature of about 1450°C is required. For this reason, a ZnO-TiO₂ based matrix referred to as ZIT was developed and it can be processed at relatively lower temperatures (~1200°C), with a high waste loading and reasonable chemical durability. It was designed to immobilize lanthanides in a monazite (LnPO₄) host phase that is encapsulated by an inert matrix in a monolithic form. The ZIT composite is prepared by mixing several compounds (ZnO, TiO₂, B₂O₃, SiO₂ and CaHPO₄) and heat-treating them at 600°C. The Ln waste form can be prepared by mixing the composite with Ln oxides (oxychlorides) and heat-treating at 1200°C. Based on the X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis, Ln-rich phases are surrounded by Ti-rich and Zn-rich phases, where Zn preferentially interacts with Si. The

major crystalline phases are LnPO₄, Zn₂TiO₄ and Zn₂SiO₄. ZIT waste loading is about 40 mass% and it has good leach resistance. In phosphate precipitation, the monazite form is the target host matrix of the ZIT waste form. Lanthanide phosphate (monazite) is a very stable compound with high density. The ZIT composition was modified to lower P content in the composite; however, it was found that the modified ZIT composition was not good for phosphate precipitates, as the resulting ZIT waste form exhibited high porosity and a relatively low density. Another approach is to use durable phosphate glass (lead iron phosphate) to produce monolithic waste forms, referred to as LIPS waste forms. The monolithic waste form with 40 mass% LnPO₄ was prepared at 1,000°C. In this case, macro pores were not detected but relatively small pores were present in the top layers of the waste form. Based on experimental results, it is believed that the tested binder or matrix cannot dissolve or solvate phosphate and hence, Ln phosphate is precipitated at the bottom of the glass. Therefore, LABS and ZIT waste forms are applicable for Ln oxides precipitates while the LIPS waste form is no longer being considered a viable waste form.

The general approach to waste form processing consists of mixing waste and a solidification matrix followed by heat-treatment. In the case of phosphate solidification,



(a) LABS glass waste forms



(b) Electron mapping image of Ln nuclides

Fig. 13. Typical LABS glass waste forms and distribution of Ln elements.

mechanically mixing immiscible (incompatible) materials is not effective for producing a homogeneous form because phosphates do not dissolve in the melt phase. If a phosphate precipitation agent is distributed in desirable solidification matrix, separation and solidification can be performed using one material and the resulting waste form would be uniform. To achieve this, using a Li(K)-based composite,

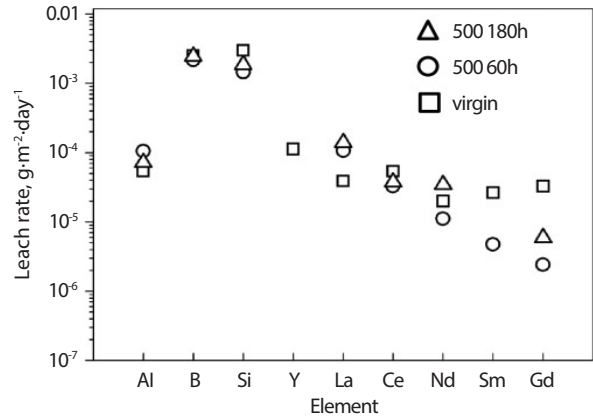


Fig. 14. Leach rates of the LABS waste forms by the PCT method.

Li(K)-Al-Si-P, a series of separation and consolidation tests are being conducted to develop monazite-based waste forms. In a similar vein, a Si-B-Al composite for producing LABS glass with high waste loading of up to 50 wt% is under development [18]. Fig. 13 represents a typical LABS waste form in which Ln nuclides are uniformly distributed. Fig. 14 shows the results of PCT leaching tests; the normalized leaching rates of surrogate nuclides, such as La, Ce, Nd, Sm and Gd, were about 10⁻⁴ ~ 10⁻⁶ g·cm⁻²·day⁻¹.

3.4 Metallic waste forms fabrication technologies

This section summarizes KAERI activities in developing metal waste treatment technologies by melting cladding hull with added noble metals or hardware components and fabricating metal waste form alloy with excellent corrosion resistance. An alternative technology considered is Zr recovery from zircaloy cladding hulls that can reduce the amount of high-level waste and reuse expensive Zr metal via recycling process.

3.4.1 Recovery of Zr from cladding hull treatment

KAERI has invested much time and effort into developing methods to minimize the amount of cladding hull waste by Zr recovery using chlorination and electrorefining techniques. These research efforts also included the

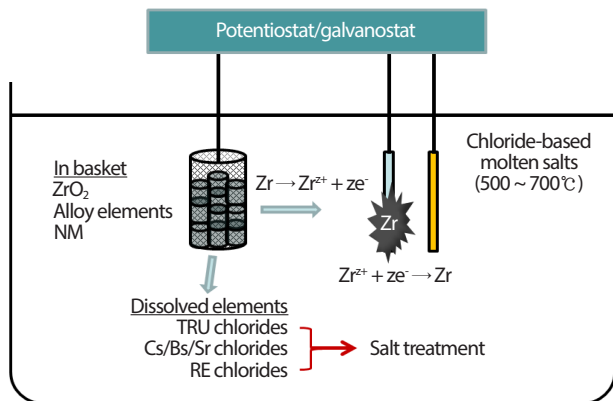


Fig. 15. A conceptual diagram of the Zr electrorefining process at KAERI.

characterization of actual cladding hulls at DFD (DUPIC Fuel Development Facility) [19].

The chlorination process to recover Zr from cladding tube employs a simple chemical reaction between metallic zirconium and chlorine gas as follows: $Zr(s) + 2Cl_2(g) \rightarrow ZrCl_4(g)$. The characteristic merits of the chlorination process are that it is a simple reaction process and the separation of the $ZrCl_4$ reaction product from most radioactive impurities can be easily carried out owing to its low sublimation temperature (331°C). In other words, zirconium of high purity can be recovered from a mixture of cladding hull waste that includes a small amount of residual spent fuel materials. As zirconium represents about 97 mass% of the cladding hull material, it is expected that the amount of cladding waste can be reduced to 1/10th of the total waste, including Zr oxide and alloying elements at a 93% of the Zr recovery efficiency. Here, it should be mentioned that oxidized Zr present on the hulls cannot be recovered owing to its extremely low reactivity with chlorine gas [36-38]. In another approach for Zr recovery, electrorefining can be used for treating cladding hull materials, such as Zircaloy-4 and Zirlo. In electrorefining, Zr is selectively recovered by differences in the Gibbs free energy of metal chloride formation in high temperature molten salts [39]. Because metallic Zr is deposited on a cathode, the recovered Zr can

be directly reused after salt distillation without additional processing. At KAERI, research activities on Zr recovery using electrorefining have been conducted based on the concept depicted in Fig. 15 [40]. During the electrorefining process, alloying components such as Sn, Fe, and Cr for Zircaloy-4 and Sn, Nb, and Fe for Zirlo are expected to remain inside the anode basket with undissolved Zr oxide due to their higher reduction potentials when compared to Zr. Residue spent fuel material will dissolve in the salt after being chemically chlorinated by $ZrCl_4$, which is used as an initiator for Zr electrorefining in chloride-based molten salts. Radioactive nuclides from the residue fuel dissolved in the salt are subjected to subsequent waste salt treatment. The recovered Zr can be reused as an additive for metal waste forms or disposed as low-level waste.

3.4.2 Metal alloy solidification for technetium immobilization

Investigations are underway to improve long-term metal waste disposal stability by immobilizing long-lived radionuclides, such as Tc among noble metals in the anode sludge, with a Zr-based metallic alloy from Zircaloy cladding. Recently, KAERI has been developing a solidification technology by recycling Zr cladding as a immobilization host matrix to solidify anode sludge residue which includes Tc and other noble metals (NMs) from electrorefining process [41]. Therefore, main objective of this study is to identify an optimum composition of Zr-Cr-Si-NMs system to produce a stable metal waste form with excellent corrosion resistance and lower melting temperature.

Specimens were prepared by the arc plasma melting method, and the melting temperature was measured by inserting a thermometer after melting in the induction heating system. The corrosion rate was generally lower than $10 \mu m \cdot y^{-1}$ for all the specimens. ZIRLO, INCONEL718, SS-15Zr, ZIR-8SS, ZIR-8SS-5Mo, and ZIR-17Cr-5Mo specimens showed a very low current density, even at 600 mV. It was considered that a stable oxide passivation film was formed uniformly. The results show that the ZIR-8SS,

ZIR-8SS-5Mo, and ZIR-17Cr-5Mo specimens have a high corrosion resistance with a corrosion rate lower than $5 \mu\text{m}\cdot\text{y}^{-1}$. Therefore, the ZIRLO-8SS alloy is the most suitable solidified alloy, but it is limited by the fact that process temperature is higher than $1,450^\circ\text{C}$. ZIRLO-INCONEL718-SS304-based alloys have a low manufacturing temperature under 1200°C , but they have low corrosion resistance due to the non-uniform dispersion of Cr in the microstructure. The corrosion resistance of ZIRLO-8SS based alloys, which have a lower Cr content than ZIRLO-INCONEL718-SS304 alloys, is superior to that of the ZIRLO-INCONEL718-SS304 alloys. The difference in these results can be attributed to differences in Cr elemental distribution, which depends on the uniformity of microstructure.

4. Conclusions

KAERI is developing pyroprocessing for spent fuel recycling to reduce the final waste volume and fabricate waste forms durable in disposal environments. This review focuses on highlighting the recent progress in waste treatment technologies for pyroprocessing.

KAERI uses high-temperature treatment in the head-end process to supply feed materials to oxide reduction process. Various filter types have been developed for capturing volatiles and semi-volatiles evolved at high temperatures. Recently, new filter media have been developed for off-gas capturing, including a kaolinite-based filter to capture gaseous cesium for overcoming limitation of fly-ash filters and bismuth-based adsorbents for the removal of ^{129}I . Immobilization methods for disposing these used filters are being studied at KAERI.

The general approach to minimize salt waste volume is the selective separation of fission products from bulk salt waste and recycling the purified salt back to the main process. Nuclide separation from two kinds of waste salts showed that separation efficiency of over 90% obtained in laboratory scale tests were also achieved in the engineering

scale study. Immobilization technology of residual salt waste has been developed to produce final waste forms for suitable disposal. Extensive research has resulted in the development of two alternative waste forms referred to as U-SAP and LABS.

To develop fabrication technology of metal waste forms, KAERI is studying a simple melting process of cladding hulls added with noble metals or hardware components. It is expected that metal waste form alloy fabricated from the product material shows an excellent corrosion resistance. In addition, a technology has been developed for Zr recovery from zircaloy cladding hulls, reducing the amount of waste and allowing the reuse of expensive Zr metal via recycling process.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT).

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