

STATUS OF PYROPROCESSING TECHNOLOGY DEVELOPMENT IN KOREA

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The Korea Atomic Energy Research Institute (KAERI) has been developing pyroprocessing technology for recycling useful resources from spent fuel since 1997. The process includes pretreatment, electroreduction, electrorefining, electrowinning, and a waste salt treatment system. This paper briefly addresses unit processes and related innovative technologies. As for the electroreduction step, a stainless steel mesh basket was applied for adaption of granules of uranium oxide. This basket was designed for ready handling and transfer of feed material. A graphite cathode was used for the continuous collection of uranium dendrite in the electrorefining system. This enhances the throughput of the electrorefiner. A particular mesh type stirrer was designed to inhibit uranium spill-over at the liquid Cd crucible. A residual actinide recovery system was also tested to recover TRU tracer. In order to reduce the waste volume, a crystallization method is employed for Cs and Sr removal. Experiments on the unit processes were tested successfully, and based on the results, engineering-scale equipment has been designed for the PRIDE (PyRoprocess Integrated inactive DEMonstration facility).

KEYWORDS : Spent Fuel, Pyroprocessing, Electrolytic Reduction, Electrorefining, Electrowinning, Waste Salt

1. INTRODUCTION

Nuclear energy has recently received more attention as an effective energy source, since it is believed to be compatible with a green energy paradigm wherein carbon dioxide emissions into the environment are reduced. Based on this environmentally friendly aspect, numerous nuclear power plants are under construction or being planned worldwide [1]. However, an important intrinsic issue must still be resolved, i.e. spent fuel management. Spent fuel will increase with the number of nuclear power plants. A recent projection puts spent fuel accumulation at 445,000 tHM in 2020 [2].

The methods of treating spent fuel can be divided into two groups, aqueous processes and pyroprocesses. PUREX is a typical aqueous process that uses an aqueous solution to treat spent fuel. A pyroprocess uses molten salt instead of an aqueous solution. Aqueous processes are more proliferative than the pyroprocess, as the former is able to separate pure Pu, whereas the latter recovers Pu together with other impurities, such as minor actinides (MA).

The basic concept of pyroprocessing is group recovery, which enhances the proliferation resistance significantly, as sole Pu cannot be separated. Pu with minor actinides, which comprise 1.4% of spent fuel, is recovered as a group. A part of U recovered from spent fuel is blended

with this Pu and MA mixture, and the blended material is fabricated as the fuel of a sodium-cooled fast reactor (SFR). The Pu and MA mixture is burnt out in the SFR, resulting in transmutation of the long half-life nuclides. This reduces the waste management period by 1/1000 from 300,000 years.

Cs and Sr, which are major components regarding heat load in spent fuel, are recovered during pyroprocessing, stored separately, and subsequently disposed of. The removal of transuranic elements (TRU), Cs, and Sr from spent fuel allows the repository burden to be reduced by 1/100, compared with the case without removal. The fission products (FP) are recovered and transferred to a repository. As a result of pyroprocessing, both repository efficiency and U usage are increased up to 100-fold.

2. UNITS OF PYROPROCESS

2.1 Electrolytic Reduction Process

As shown in Fig. 1, KAERI is currently developing an electrolytic reduction system, which is the front end of the pyroprocess, to demonstrate the laboratory scale operation of an electrolytic reduction process, and produce engineering data to be utilized in the design of the equipment, instruments, and facilities for the PRIDE and ESPF (Engineering Scale Pyroprocess Facility).

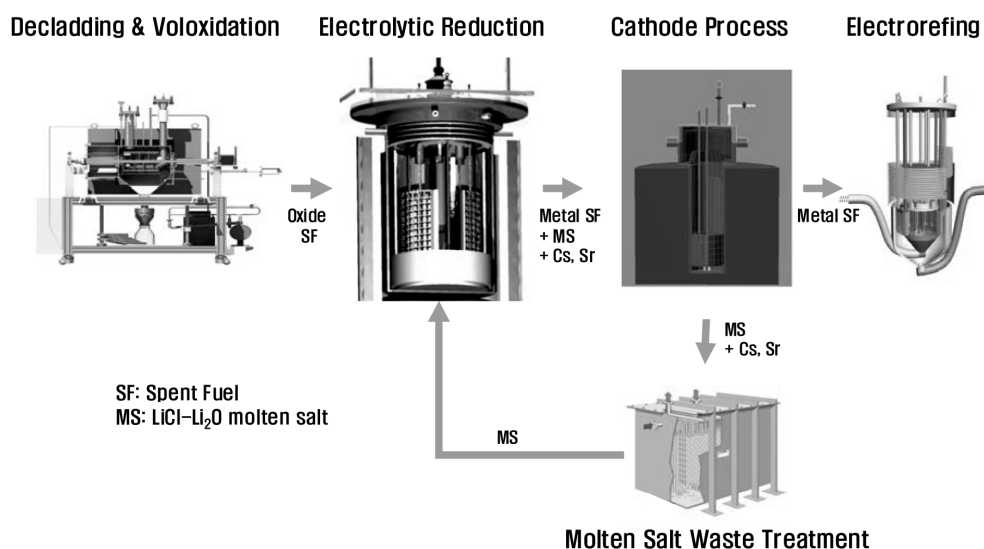


Fig. 1. Electrolytic Reduction System

In the electrolytic reduction process, the spent fuel oxide material from voloxidation is prepared for use in the electrorefiner by reducing the oxide to a metal [3-5]. The electrorefining process cannot accept oxide nuclear fuels directly, because the actinide oxides do not dissolve into the chloride salt. Also, in order to be used in an electrorefiner, materials must be electrical conductors. The metallic form produced by the electrolytic reduction process is suitable for use in the electrorefining process. In the electrolytic reducer, the feed material is placed in a fuel basket. A voltage is applied between the fuel basket cathode and a platinum anode. This process uses a molten LiCl salt electrolyte with a small amount of Li₂O in solution at 650 °C. Spent fuel metals are produced in the cathode basket and oxygen is evolved from the anode. Fission products, such as Cs, Sr, and Ba, are dissolved into the salt in this process, forming chloride compounds in the electrolyte salt. The metal that is collected in the cathode basket contains all of the actinides, lanthanides, and metallic fission products present in the spent fuel. After the electrolytic reduction process, the residual salt material is ~ 20 wt% of the cathode material. The cathode process for the removal of residual salts in the cathode basket of the electrolytic reducer can be added to ease the burden of the salt management process. The resulting metal is suitable for direct introduction into the electrorefiner.

2.1.1 Electrolytic Reduction

The oxide reduction process was widely studied as a front end of the pyroprocess, and KAERI launched an oxide reduction program in 1997. First, the Li-based reduction process of a spent fuel was developed, as shown in Fig. 2.

While performing inactive tests for the Li-based reduction process, KAERI developed and demonstrated

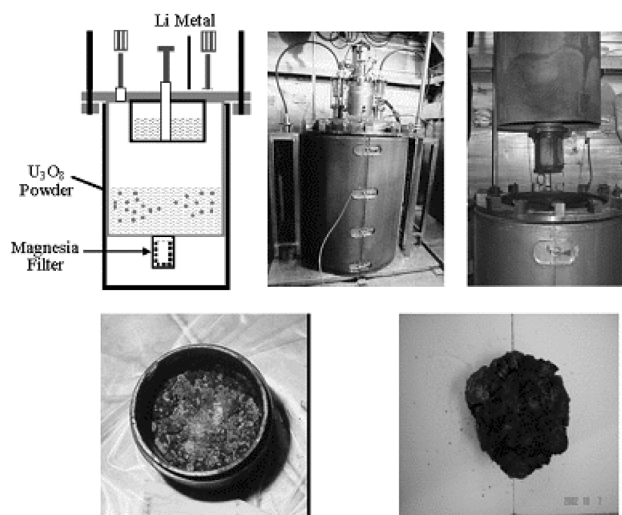


Fig. 2. Li reduction System with a Magnesia Filter

an electrolytic reduction process, using an innovative concept, with a porous magnesia filter. With this concept, KAERI installed an electrolytic reducer in the ACPF and performed seven inactive tests with fresh U₃O₈ and SIMFUEL. A LiCl-Li₂O molten salt was used as an electrolyte and the electrochemical reactions were tested. As the test results showed no LiCl decomposition, the stability of the LiCl molten salt was ensured. Each run was performed with ~10 kg of fresh U₃O₈ or SIMFUEL. The extent of the fuel reduction and the distribution of stable fission products between the salt and fuel phases were determined. A reactor model was developed to assess scale-up issues for a high through-put electrolytic reducer. During these inactive tests, more than a 99% reduction

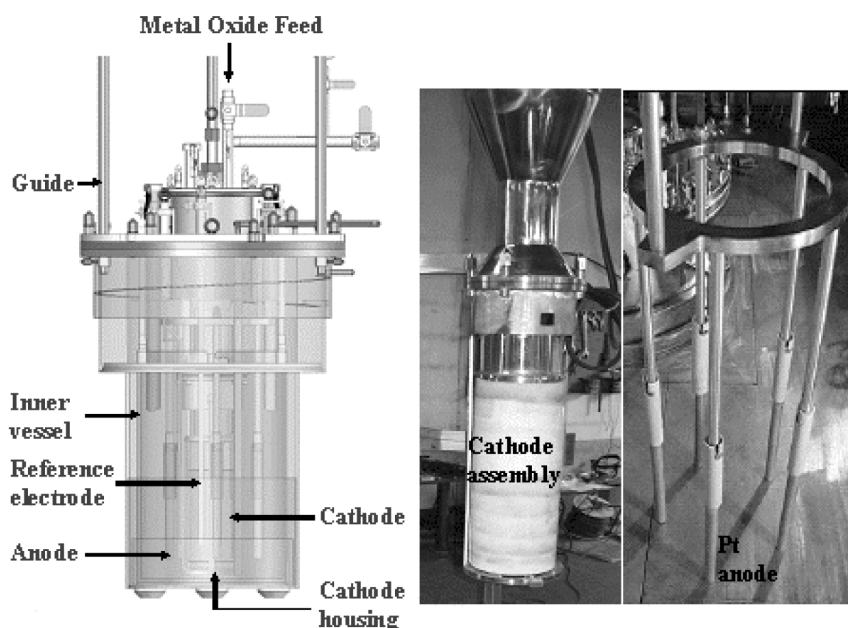


Fig. 3. Electrolytic Reducer with a Magnesia Cathode Basket

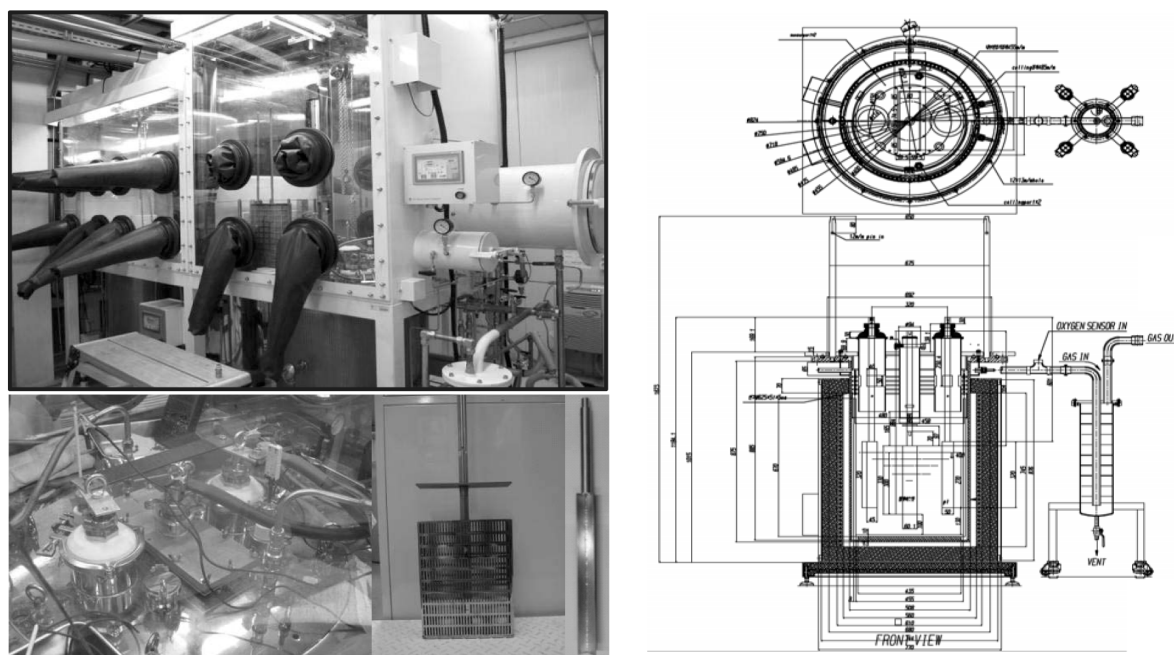


Fig. 4. Electrolytic Reducer with a Metal Cathode Basket

yield and anode current density higher than 100 mA/cm^2 were obtained (See Fig. 3).

A new electrolytic reduction system equipped with a metal cathode basket, which can be linked to the electrorefining process, was developed. The technology to suppress the vaporization of molten salts and enable reuse of the molten salts was verified. The bench-scale

tests showed that the current density on the anode was increased from $\sim 100 \text{ mA/cm}^2$ (old electrolytic reducer) to $\sim 500 \text{ mA/cm}^2$ (new electrolytic reducer), thus enabling high speed electrolytic reduction.

An electrolytic reduction run ($17 \text{ kg UO}_2/\text{batch}$), using the new electrolytic reducer with a metal cathode basket, was successfully tested, showing an average anode current

density of $\sim 250 \text{ mA/cm}^2$ (See Fig. 4), and the basic design of an engineering scale electrolytic reducer ($\sim 50 \text{ kg UO}_2/\text{batch}$) was completed.

2.1.2 Cathode Process

In the processing of cathode material from the electrolytic reduction process, the material is placed in a process crucible and then heated. The salt material in the sample is boiled off of the material and distilled for recycling. To prevent reoxidation of metal products by Li_2O in the residual salt, the process should be carried out below 900°C [6].

The cathode process of the electrolytic reduction is characterized by salt recovery in powder form, which is easy to handle in remote operation conditions. The underlying principle of this process is the condensation of LiCl vapor as a solid in the cold region of the cathode processor. In an experiment of reduced pressure ($\sim 20 \text{ inHg}$) at 700°C , the distilled salt was recovered in a solid powder form at the receiver of the cathode processor, as shown in Fig. 5.

The recovered salt will be sent to the waste salt regeneration process and then recycled to the electrolytic reduction process for reuse.

2.2 Electrorefining Process

2.2.1 CERS

The CERS (Continuous ElectroRefining System), which recovers pure uranium from reduced spent fuel, is composed of an electrorefiner, a salt distiller, and a melting furnace. A U-chlorinator (UCl_3 making equipment) and a transportation system are also needed to operate the CERS. In the electrorefiner, uranium deposition is initiated in molten LiCl-KCl salt with about 9 wt% UCl_3 . Uranium

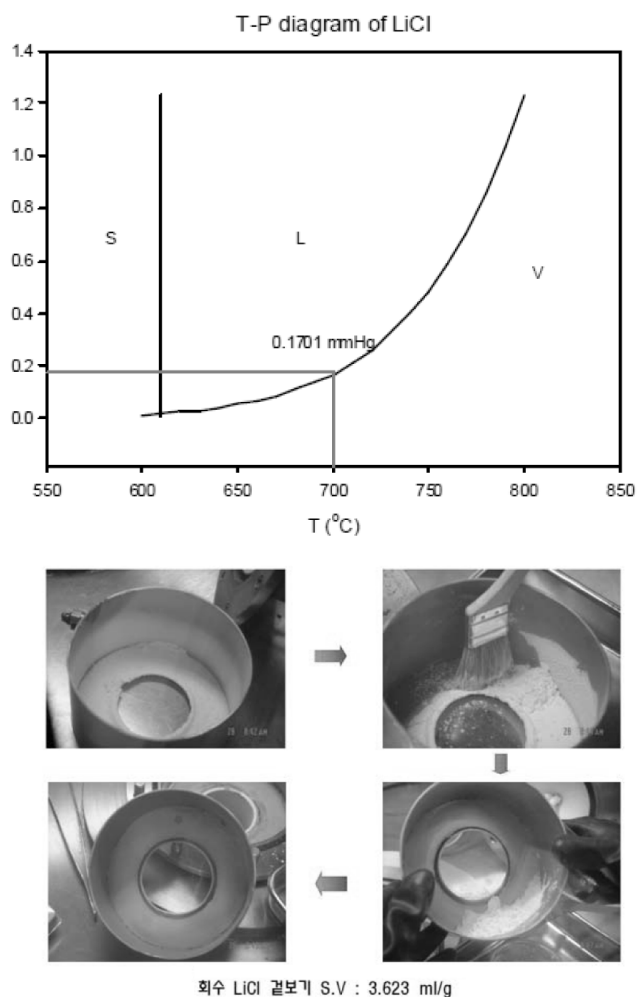


Fig. 5. P-T Diagram of LiCl and the Photo of the Recovered Salt

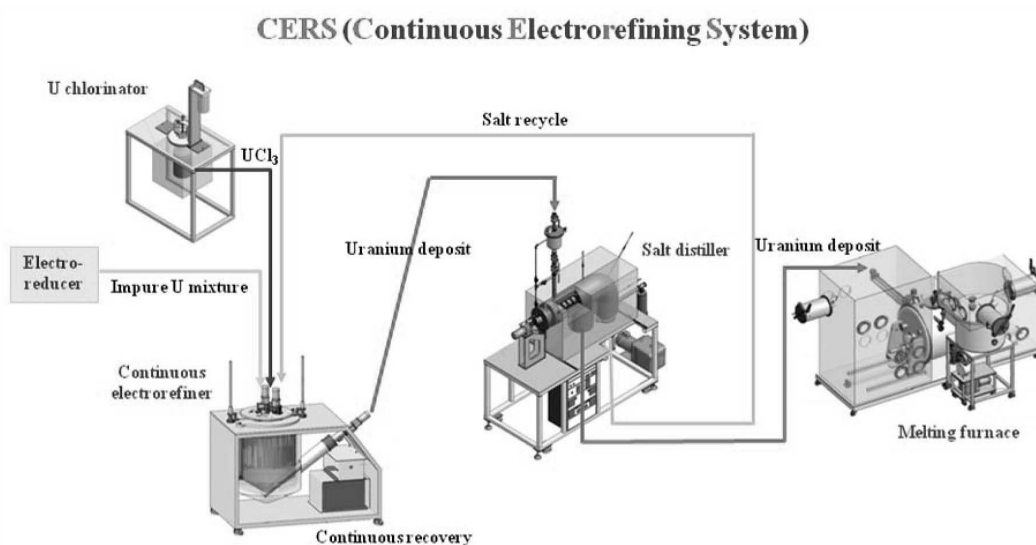


Fig. 6. Schematic Illustration of the Continuous Electrorefining System

dendrites are then deposited and fall from the electrode spontaneously [7], and are finally collected at the bottom of the reactor. The collected uranium deposits are transferred with a screw to a container. The uranium deposits are fed into a salt distiller, and salt in the uranium deposits is distilled by using a salt distiller. The salt-distilled uranium is melted and subsequently reformed to ingots for storage or for future use. The CERS was designed to continuously operate with a capacity of 20 kgU/day, as shown in Fig. 6.

2.2.2 Electrefiner

The role of an electrefiner is to recover uranium from the impure uranium mixture that is the product of the electrolytic reduction system. The currently installed HT (high throughput) ER is designed to have a capacity of 20 kgU/day, which has been simulated by ANSYS CFX [8,9]. A photograph of the HTER is shown in Fig. 7.

The reduced uranium metal from the electrolytic reduction system is fed into an anode basket, which is placed at the periphery of the reactor. It rotates in order to enhance mass transfer. The cathodes, at which the uranium dendrites are deposited, are located in the core part of the reactor. At the center of the reactor is a scraper used to collect the uranium deposits that fall to the bottom of the reactor. The salt is a LiCl-KCl eutectic solution. It also contains UCl_3 in order to initiate deposition of the uranium on the solid cathode. The deposited uranium at the cathodes falls spontaneously from the solid cathode at an operation condition of 500°C . It is continuously conveyed by screw and transferred to a container. The remaining materials after depletion of the uranium from the feed material at the anode basket are noble metals, such as Fe and Mo.

To determine the operational conditions of the electrefiner, the current-potential curves of the electrefiner, with a 17.3 kg uranium pellet in the anode basket and 4.6 wt% UCl_3 in the salt, were measured, and the results are shown in Fig. 8. From the results, the upper current limit for the electrefiner was determined to be 125 A according to the cut-off voltage of the anode (-0.5 V vs. Ag/AgCl). The optimal operation conditions for 20kgU/day throughput should be secured by controlling the applied current with respect to the anode cut-off voltage and the UCl_3 concentration.

2.2.3 Salt Distillation

Uranium deposits, generated from an electrefiner, contain more than 30 wt% salt. In order to recover a pure U metal ingot, the retained salt should be removed from the uranium deposits. Above 99 wt% salt removal from the uranium deposits should be achieved prior to the following step of uranium metal casting. A vacuum evaporation technique was applied to the removal system and the behavior of salt evaporation from uranium deposits has been studied using a bench-scale salt distiller. The characteristics of salt evaporation depend largely on the vapor pressures of the components and the temperature.

The vacuum pressure and the hold temperature are the key factors of the evaporation process.

From the results of the bench-scale distiller, a high throughput lab-scale salt distiller for 28.57 kg U deposit/day capacity has been developed, as shown in Fig. 9. A performance test of the lab-scale salt distiller was carried out.

2.2.4 Melting Furnace

The melting process is performed to consolidate the refined uranium deposits into a solid cylindrical metallic form, which will be used as raw material for SFR fuel, or will be stored for future use. This process is followed by

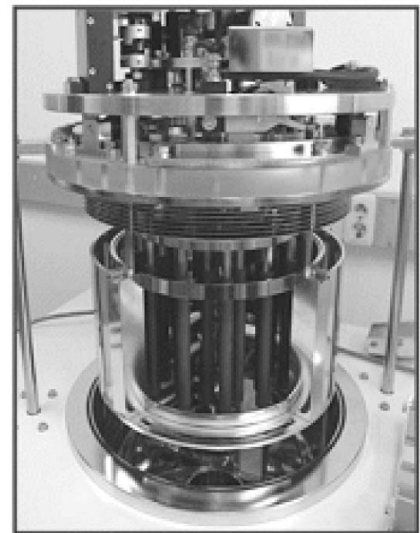


Fig. 7. Continuous-type Electrefiner Equipped with Graphite Cathodes

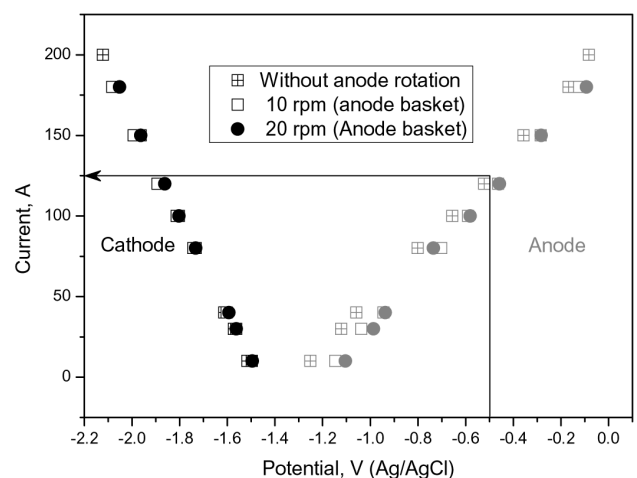


Fig. 8. Current-potential Curves of the Electrefiner

the salt distillation process, where almost 99% of salts mixed with uranium deposits are removed.

The main equipment used for the ingot casting process is a melting furnace, which consists of a vacuum chamber, a charger, a crucible, and a mold. The distilled uranium dendrite is fed to the charger and the uranium dendrite enters the crucible, which is made of graphite coated with zirconia. The vacuum chamber is first evacuated to $\sim 10^{-1}$ torr and then, using an induction coil heater, the temperature of the crucible is increased to 1300°C. The uranium dendrite is melted and then the melted uranium is poured into the mold by tilting the crucible. An engineering-scale U ingot casting equipment providing 50 kgU/day capacity is currently being developed on the basis of the lab-scale equipment, as shown in Fig. 10.

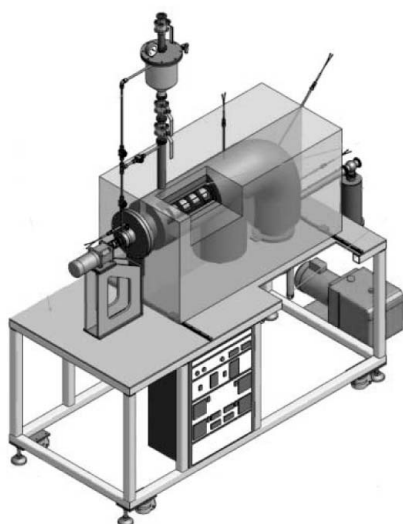


Fig. 9. The High-throughput Salt Distiller

2.2.5 UCl_3 Preparation

The role of uranium chloride salt (UCl_3) is to stabilize the initial cell voltage between electrodes in the electrorefining reactor. The preparation process for a uranium chloride salt includes two steps: reaction of gaseous chlorine with liquid cadmium to form $CdCl_2$ in a Cd layer and then reaction of U with $CdCl_2$ in LiCl-KCl eutectic salt to produce UCl_3 . The apparatus for the reaction consists of a chlorine gas generator, a chlorinator, and a wet scrubber for off-gas treatment, as shown in Fig. 11, and has a capacity of 1.3 kg UCl_3 /batch. The prepared UCl_3 salt in LiCl-KCl eutectic salt is transferred to the electrorefiner.

For the transfer of LiCl-KCl molten salt, which contains UCl_3 , to the electrorefiner, we have developed a



Fig. 10. The Lab-scale U Ingot Casting Equipment

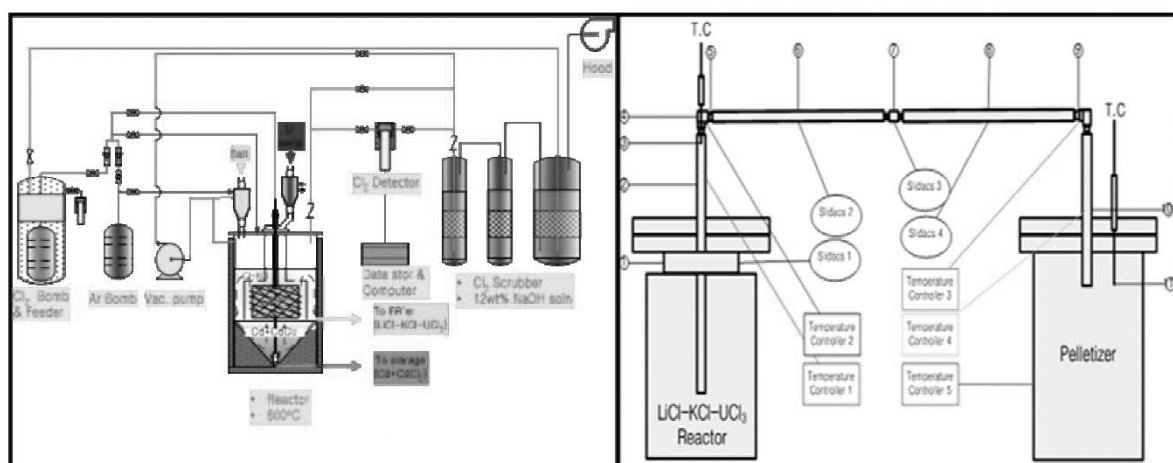


Fig. 11. Schematic Diagrams of the U-chlorinator (Left) and Salt Transfer (Right)

pelletizing process. This process consists of two steps: transportation of the molten salt to a pelletizer and solidification of the molten salt in a mold. Because chlorine gas is used during the manufacture of UCl_3 , which is melted in LiCl-KCl eutectic salt, and the molten salt is strongly sensitive to moisture, the transportation of the molten salt and the pelletizer operation should be carried out under an inert gas such as Ar. The molten salt transportation is driven by pressurization of the reactor vessel while maintaining temperature above the melting point, as shown in Fig. 11.

2.3 Electrowinning System

Electrowinning technology is implemented to recover TRU from the molten salt system, a major process in the pyroprocessing technology, with proliferation resistance. Electrowinning technology of LCC is employed to recover group actinides such as uranium and TRU (Np, Pu, Am, Cm) in the molten salt (LiCl-KCl) transferred from the

electrorefining process, which collects uranium of high purity. A cadmium distillation technology is also used to separate Cd and actinides from recovered actinide/Cd products by LCC, while residual actinide recovery (RAR) is incorporated for treatment of spent salt with low concentrations of actinides, as shown in Fig. 12. Finally, computer analysis technology is utilized to simulate the electrolytic process of the molten salt system for TRU recovery.

2.3.1 Electrowinning Reactor with Liquid Cd Cathode

Presently, a lab-scale electrowinning apparatus with a mesh-type LCC structure is in place. Our present research target is to improve its performance. U and TRU elements show distinct red-ox potential differences on the solid cathode (W, STS, graphite, et al.) and hence U can be preferentially recovered using a solid cathode [10,11]. On

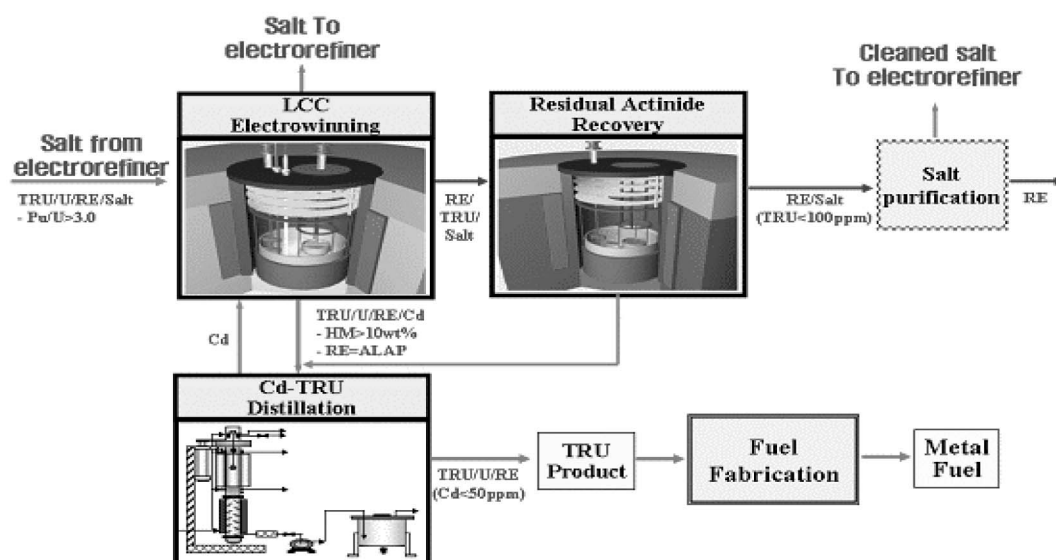


Fig. 12. Electrowinning Process

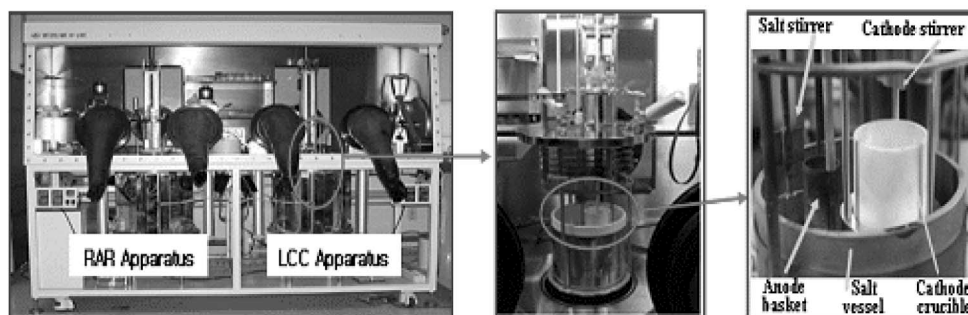


Fig. 13. Lab-scale LCC Electrowinner

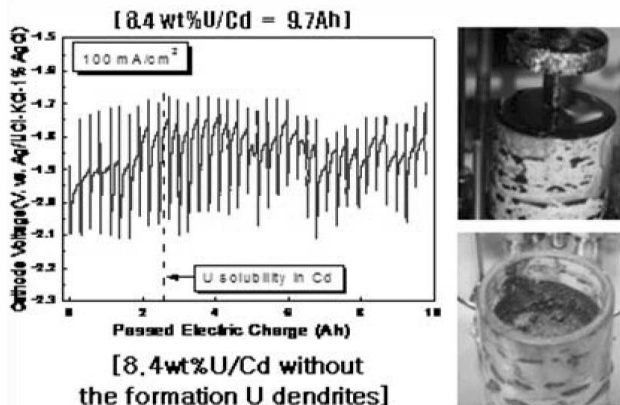


Fig. 14. LCC Performance Test Results Using a Mesh Agitator

the other hand, red-ox potentials of actinide elements are very close on liquid cathodes (Cd, Bi et al.) [12], and therefore it is technically difficult to recover actinide elements separately on LCC, which means the electrowinning process using LCC provides the non-proliferation of pyroprocessing

The electrowinning technique using a LCC is a key step for non-proliferation, because TRU elements could be collected with uranium on the LCC [13,14]. During the electro-deposition of U/TRU elements, however, the uranium ions are deposited in the shape of dendrites on the surface of the LCC [15]. These uranium dendrites hinder co-deposition of U and TRU elements.

We designed and manufactured a lab-scale LCC electrowinner to evaluate the performance of LCC structures such as stirrer-type and mesh-type apparatuses (Fig. 13). The experimental results of the performance tests using a mesh-type LCC structure showed that up to 8.4 wt%/Cd of uranium was collected without the formation of uranium dendrites (Fig. 14).

2.3.2 Cd Distillation

A distillation process was adopted for the separation of cadmium, since this type of physical separation process is more attractive than a chemical or dissolution process as it generates fewer secondary processes [16]. The cadmium separation takes place by evaporation of cadmium in the hot region and condensation of cadmium vapor in the cold region [17]. The condensed solid cadmium is recycled to the electrowinning process for reuse.

The apparent evaporation rate of pure cadmium was measured at various temperatures and pressures. The evaporation rate of pure cadmium was varied from 4.6 to 38.5 g/cm²/h in a temperature range of 500–650°C and in a vacuum pressure range of 0.5 to 10 torr. It increased with increasing temperature and decreasing pressure (Fig. 15). These experimental data should be very useful for designing the distiller and optimizing its operation.

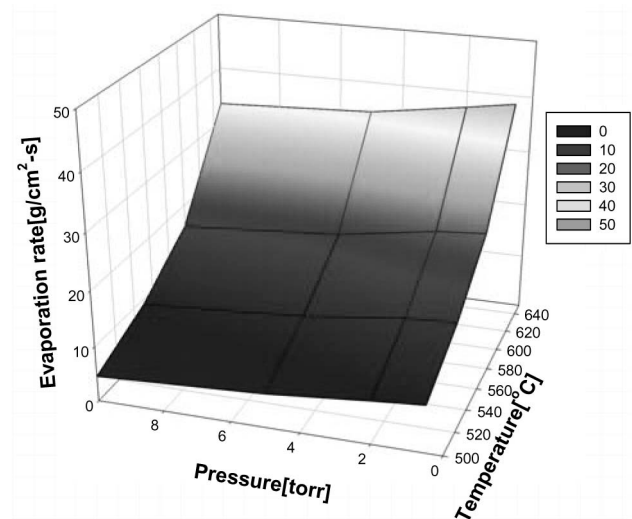


Fig. 15. The Evaporation Rate of Pure Cadmium as a Function of Temperature and Pressure, Respectively

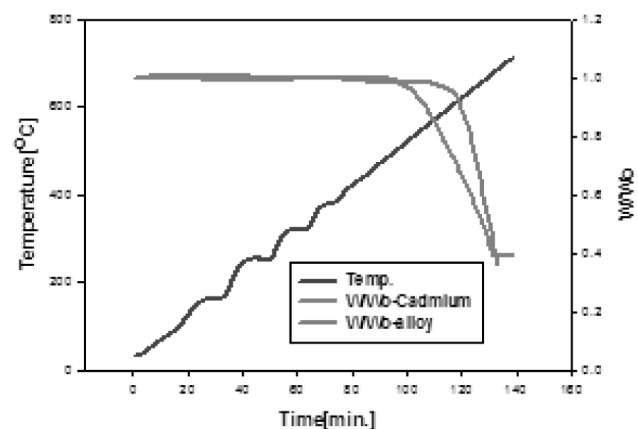


Fig. 16. The Onset Evaporation Temperature of Cadmium Alloyed with Cerium

In a non-isothermal evaporation experiment, the onset evaporation temperature of cadmium alloyed with cerium was higher than that of pure cadmium (Fig. 16). It was inferred from the results that cadmium alloyed with other metals such as LCC deposits can be distilled at a higher temperature than pure cadmium.

2.3.3 RAR

For a promising pyro-partitioning process, it is necessary to find an effective method for the recovery of residual actinides from spent salt resulting from the electrowinning step prior to the removal of all the fission products in the waste salt treatment step. KAERI has established a residual actinides recovery (RAR) scheme by combining electrolysis using a LCC and oxidation of rare earth fission products

using a CdCl_2 oxidant [18]. Eventually, the rare earth metal chloride products can be transferred to the waste salt treatment step. The same equipment used for LCC electrowinning can be used for RAR operation. Therefore, the RAR process has promising advantages, such as the use of compact equipment and a simple process, compared to the multi-staged counter-current reductive extraction process [19].

KAERI developed an original hybrid concept using a LCC and an oxidant based on the results of a thermodynamic approach. The approach consists of two steps. The first is a electrolysis using a LCC to collect all the residual actinides and some of the rare earth FPs so as to reduce the concentration of actinides in the molten salt. The second step is selective recovery of parts of the co-deposited rare earth FPs by oxidation (or chlorination) using CdCl_2 from a Cd alloy with the FPs, U, and TRU.

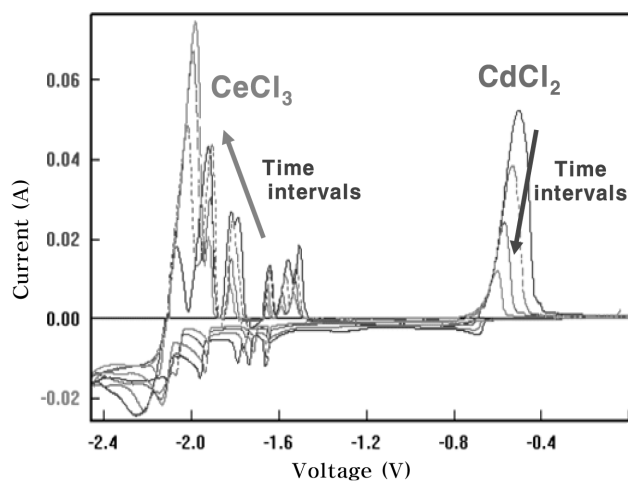


Fig. 17. Cyclic Voltammograms of the Salt Phase at a Time Interval of 30 Minutes during Oxidation of the Ce-U-Cd Alloy

Oxidation experiments involving the addition of CdCl_2 oxidant into a salt containing a molten Cd-metals alloy were carried out to confirm the residual concentration of the actinides in the salt was maintained at a value of less than 0.01 wt% (100 ppm). Fig. 17 shows cyclic voltammograms of the salt phase, which were monitored at a time interval of 30 minutes during the oxidation of Ce-U-Cd alloy with CdCl_2 . Experimental results show that the residual concentration of uranium can be reduced to a value less than 100 ppm. Therefore, it was confirmed that this RAR process could be applicable to the selective removal of the actinides content from the spent LiCl-KCl salt [20].

2.3.4 Computational Simulation

Multi physics electrochemical modeling, in a framework of Computational Fluid Dynamics (CFD) [21] code, has been proposed and dealt with in detail to simulate the electro-transport behavior in a molten-salt electrowinning system. The modeling approach utilized in this study is focused on the mass transport and current arising due to the concentration and the surface over-potential based on the cell configuration and molten-salt electrolyte turbulence. The electrowinning cell model demonstrated here has a concentrically arranged structure with an anode annulus surrounding a LCC crucible inside it (Fig.18). This implementation with the unique feature of a potential-to-current algorithm could provide useful information for more realistic spatial variation of the electrochemical characteristics. This approach will be applied to the design of an engineering scale electrowinning system.

2.4 Waste Salt Regeneration and Solidification System

During the pyroprocessing of LWR spent oxide fuels, two different types of waste salts are expected to be generated: (i) LiCl waste salt containing alkali and alkaline-earth (Group I/II) fission products (FPs) from the electrolytic reduction process and (ii) LiCl-KCl eutectic waste salt containing rare-earth FPs from the electrorefining (winning)

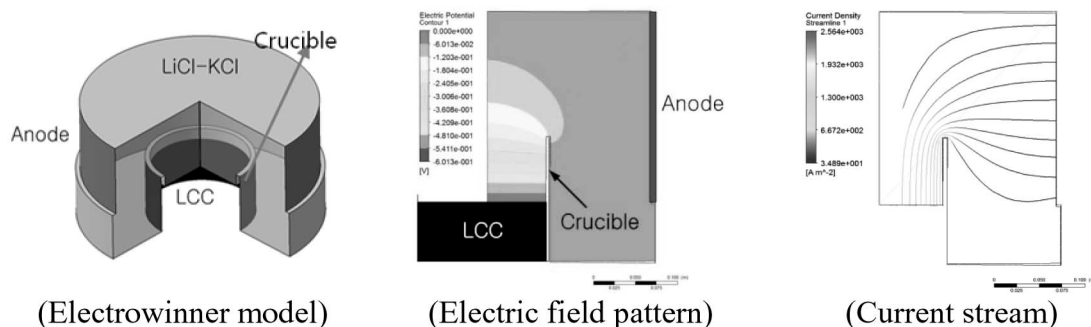


Fig. 18. Electric Field Analysis of Electrowinning System

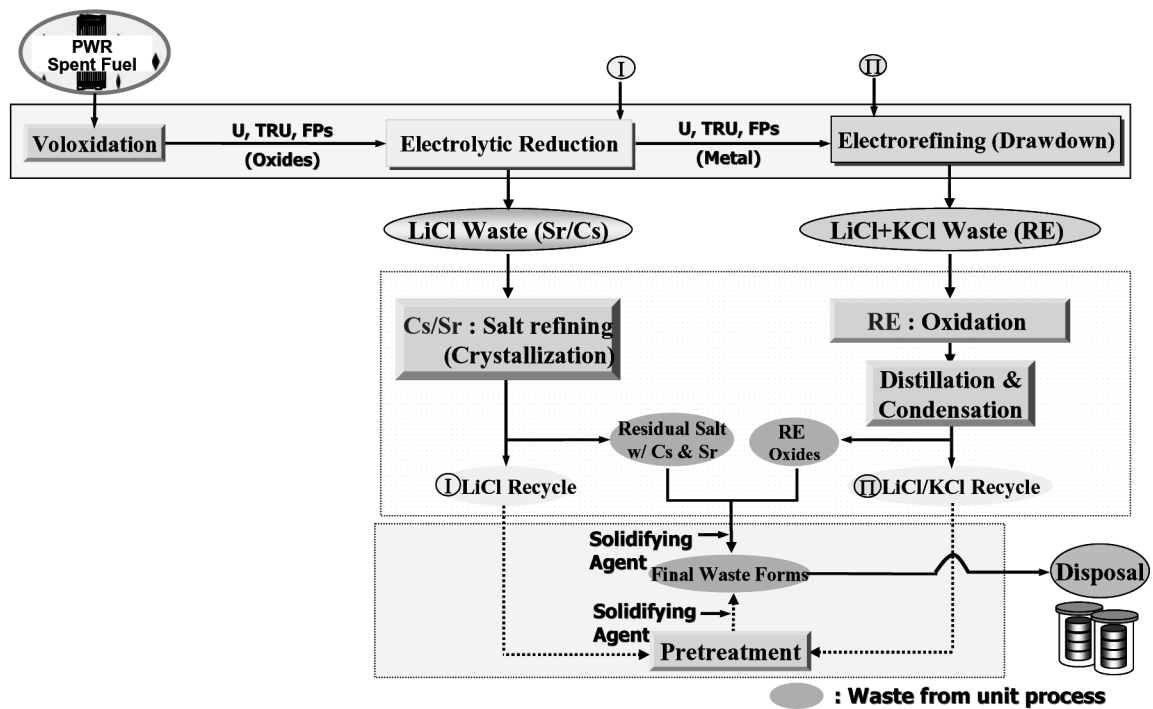


Fig. 19. KAERI's Approach to Effective Management of Waste Salts

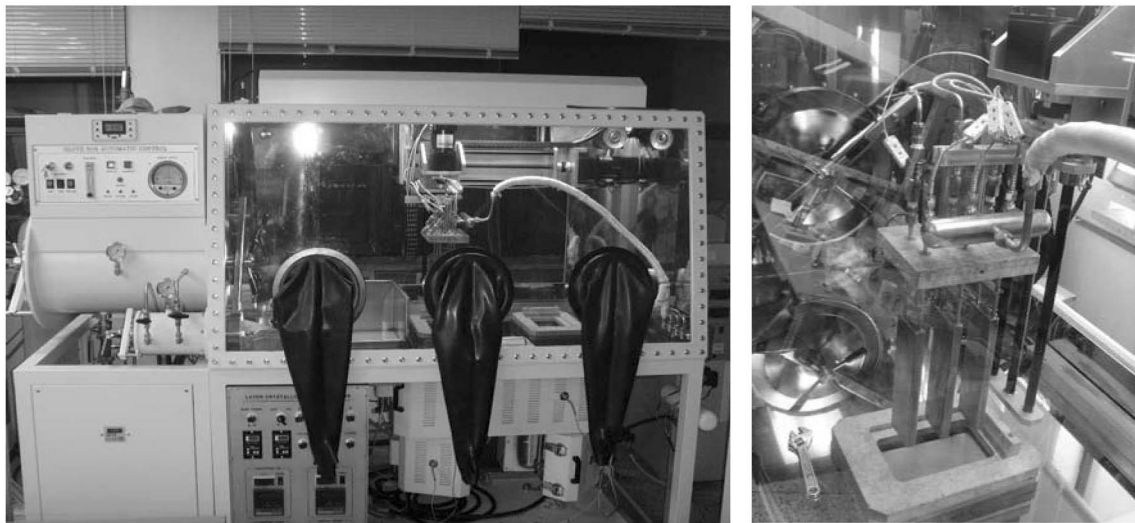


Fig. 20. Lab-scale Layer Melt Crystallization Equipment

process. Since these waste salts are radioactive, heat-generative, and highly soluble in water, they must be fabricated into durable waste forms that are compatible with the environment inside a geologic repository for a long time [22]. Current technology for disposing of waste salts from pyroprocessing involves non-selective total incorporation of waste salts in a zeolite matrix to form a

ceramic waste form (glass-bonded ceramic waste form), which results in a significant increase of the final waste volume for disposal [23].

KAERI is working on two key R&D concepts for the development of innovative waste salt treatment technologies. The first is the minimization of waste salt generation by the removal of fission products in the waste and then

recycling the cleaned salt to the main pyroprocesses. The second is an increase of safety during interim storage or final disposal by the fabrication of high-integrity final waste forms. Accordingly, KAERI has been developing various FPs removal and waste solidification technologies such as melt crystallization, oxidative precipitation, and SAP/ZIT solidification (Fig.19). The performance was found to be successful in small scale equipment. In addition, construction and performance evaluation of lab-scale equipment was completed in 2009. Research on modifications and resultant operation characteristics of the salt regeneration and solidification equipment will be performed in a stepwise manner according to KAERI's long-term R&D plan, which is financially supported by the national long-term nuclear R&D program.

2.4.1 Waste Salt Regeneration

For the regeneration of waste LiCl salts, group I/II FPs involved in the waste salt are separated by using a melt crystallization process such as a layer melt crystallization method. This technology does not require any foreign additives or adsorption agents such as zeolite. The operation principle is based on the solubility difference of solutes (e.g. CsCl and SrCl₂) between molten salt and solid states. In this process, the group I/II radionuclides are concentrated in the melt phase, while the other solid phase contains relatively purified LiCl salt. This crystal phase contains a very small amount of group I/II FPs and is recycled to the

electrolytic reduction process for reuse [24]. A preliminary experiment with a lab-scale apparatus showed that about 80-90 % of total waste salt could be recovered in the form of a refined LiCl crystal containing less than 10-20 % of the initial CsCl and SrCl₂ (Fig. 20).

In the case of rare-earth FPs involved in waste LiCl-KCl eutectic salts, they are removed from eutectic salt by oxidative precipitation and the refined salt is recovered by a salt distillation process (Fig. 21). The rare-earth chlorides react with an oxygen bubble to convert their chemical forms into oxides or oxychlorides. After oxidation, if the molten salt settles for several hours, the oxidized rare-earth products are precipitated, and phase separation into an upper pure salt phase and a lower precipitate phase occurs [25]. The upper part can be directly recycled to the electrorefining process. The lower part is a mixture of rare-earth precipitates and residual salt. The residual salt is recovered as a pure salt by using a vacuum distillation process and is then recycled to the electrorefining process for reuse. Based on the characteristics of salt vaporization and condensation, a salt vacuum distillation and condensation apparatus incorporating a distillation and condensation chamber was designed and its operation characteristics were determined [26]. This apparatus was subjected to the force of a temperature gradient (40 °C to 920 °C) at a reduced pressure (< 10 Torr) as a closed type of system. It was possible to collect the vaporized salts in only one spot, thereby minimizing salt loss and apparatus corrosion.

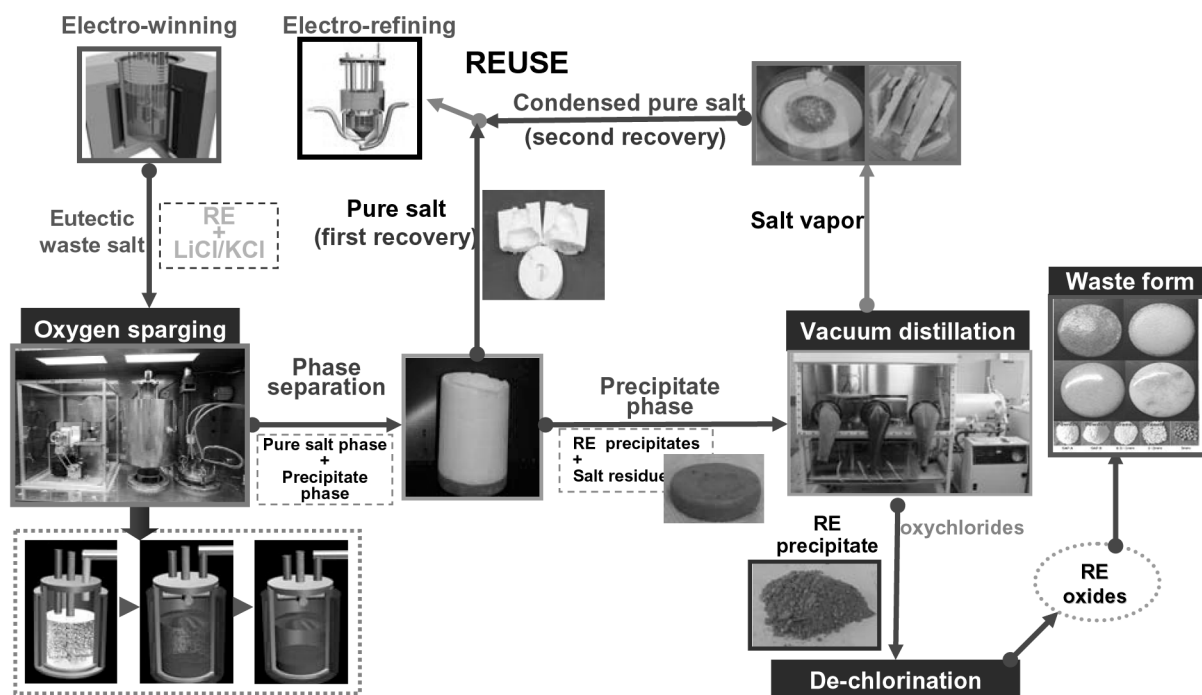


Fig. 21. Regeneration Process of Waste Eutectic Salt

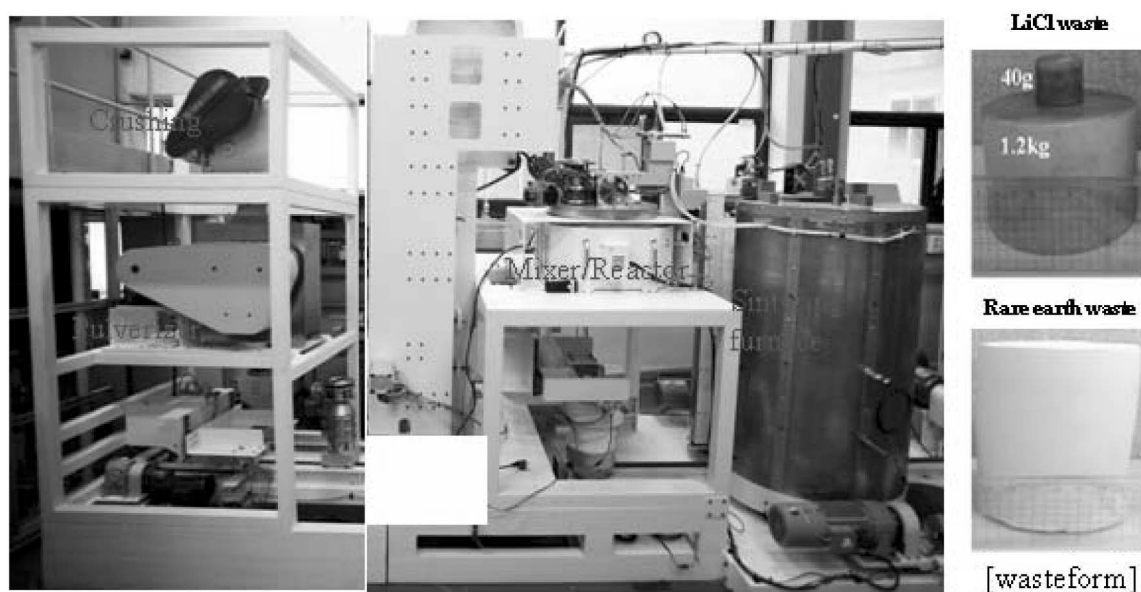


Fig. 22. Waste Salt Solidification Process and Monolithic Waste Forms

The residual salts were vaporized and were completely separated from the rare-earth precipitates, and over 99% of the vaporized salts were recovered. During distillation, carry-over of rare-earth precipitates was not observed and the recovered salt had nearly the same composition as that of the fresh eutectic salt.

2.4.2 Waste Solidification

From the regeneration process for dirty salts, two kinds of wastes, LiCl salt residue with concentrated Group I/II FPs and rare-earth oxides, are generated. For the immobilization of waste salt, a zeolite process, developed by Argonne National Laboratory in the U.S.A., is considered a practical method for LiCl-KCl salt. Also, sodium aluminophosphate glass is well known as a glass matrix that is compatible to metal chloride, especially NaCl-KCl. Zeolite-4A containing a α -cages occludes metal chlorides and is converted into sodalite as a host phase for waste salt after heat-treatment. A phosphate glass with a relatively low melting point has a high compatibility with metal chlorides, treating the waste salt at relatively higher waste loading. However, one important disadvantage of the zeolite process is a substantial increase of the final waste volume due to a limitation of the maximum salt loading into the zeolite structure. Also, when using phosphate glass for waste salt, its chemical durability is about ten times lower than that of the zeolite method. To overcome this problem, KAERI has developed an alternative technology to the zeolite process. This process, called SAP solidification, uses a new inorganic composite of silicone, aluminium, and phosphorous oxide, which can provide a series of chemical routes to stable chemical

forms for waste salts [27,28]. The SAP material is prepared by using a conventional sol-gel method, and then mixed and reacted with molten salt residue for 16 hours at 650°C. The reaction product undergoes a final heat treatment step with the addition of glass frit for 4 hours at around 1,150 °C to form a durable ceramic waste form (Fig. 22).

The rare earth oxides separated from LiCl-KCl salt can be immobilized into a durable silicate glasses or specific ceramic materials, but severe processing conditions are required to obtain a consolidated form with high waste loading. To alleviate the processing conditions, an inorganic composite (ZIT), composed of transition metal oxides and phosphates, has been developed. The composite can convert the rare earth oxides into monazite (LnPO_4) and the mixture can be consolidated at about 1100°C, resulting in a durable waste form with a high density and high waste loading.

We conducted experiments applying the SAP solidification technology, and found that it provided around 3 times higher loading of waste salt into the SAP structure, thus resulting in a smaller final waste volume, while maintaining higher chemical durability and thermal stability compared to the zeolite product. The inorganic composite (ZIT) for the immobilization of rare earth oxides can alleviate the processing conditions and provide a durable waste form.

To realize the immobilization method, KAERI has developed a lab-scale solidification process that consists of crushing, pulverizing, mixing/reacting, and sintering equipment. Thus far, development of the unit equipment has been ongoing to obtain proper performance and the processing conditions have been investigated to abstract the scale-up factors. The unique waste forms fabricated

from this process need to be further characterized and qualified to examine whether they meet the requirements for final disposal; this work is still in progress.

3. CONCLUSION

The main goals of pyroprocess R&D in KAERI are to increase equipment throughput and to reduce the volume of final waste to be disposed of. Application of innovative technologies such as adoption of a graphite cathode in the electrorefiner and waste salt regeneration by a crystallization method was tested. Based on the results of bench- and laboratory-scale tests, an inactive engineering-scale integrated pyroprocess (PRIDE) facility with a capacity of 10 tons-U per year is planned to be constructed and operated by the end of 2016. Active tests in an ESPF (Engineering Scale Pyroprocessing Facility) will follow.

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