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## ABSTRACT

This report summarizes the treatment and waste form options for waste streams resulting from the electrochemical pyroprocessing of used oxide nuclear fuel. The waste treatment options presented reflect many years of research conducted both in the United States (U.S.) and South Korea (Republic of Korea – ROK). Both nations are evaluating similar advanced fuel cycles involving the treatment used nuclear fuel (UNF) for recycle, isolation of fission products for disposal, and collection of the transuranic elements (TRU) from the used fuel for transmutation in a ‘burner’ type fast reactor. South Korea and the U.S. have developed different management strategies for waste streams generated from the pyroprocessing of UNF. The U.S. approach involves immobilizing spent electrolytic salt containing oxidized fission products into a ceramic waste form (CWF) and both the contaminated cladding hulls and metallic fission products into a metal waste form (MWF). Both of these waste forms were developed as part of the Experimental Breeder-II (EBR-II) sodium-bonded metallic fuel treatment program. The ROK approach emphasizes product recycle and waste form volume minimization by segregating fission products recovered from process streams for immobilization in separate waste forms. This includes head-end thermal treatment of the UNF to collect volatile and semi-volatile fission products, cladding recycle, and fission product concentration or separation from LiCl or LiCl-KCl salt streams. This allows for salt recycle and for higher fission-product loading in the final waste form. A novel aspect of the ROK waste-stream management process is dechlorination of the salt waste stream performed either prior to or during waste form fabrication for a substantial reduction in waste volume.

The U.S. and the ROK have initiated a collaborative research effort called the Joint Fuel Cycle Study (JFCS) to better coordinate development of UNF treatment by pyroprocessing. As part of this 10-year collaborative study, an Integrated Recycle Test (IRT) will be performed to evaluate the technical, economic and safeguard aspects of pyroprocessing for large-scale treatment of UNF. The IRT will demonstrate, as closely as possible, the ROK used fuel treatment process. The IRT demonstration will be conducted at Idaho National Laboratory (INL) using commercial pressurized water reactor (PWR) fuel. Several waste forms will be produced from the IRT waste streams and evaluated.

While this report summarizes the overall treatment of UNF by pyroprocessing, the focus is on the waste-stream treatment processes being developed primarily at the Korean Atomic Energy Research Institute (KAERI). Detailed descriptions are provided regarding corrosion characteristics of the CWF, MWF, and advanced pyroprocessing waste forms being developed at KAERI and the Pacific Northwest National Laboratory (PNNL). The waste-stream treatment and waste form testing activities that are planned as part of the IRT are also described. An important component of this report is a description of the scientific basis and experimental strategy for the determination of the expected long-term performance of these waste forms in a geological repository. This testing strategy will be applied to evaluate candidate waste forms during the IRT.

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## ACRONYMS AND ABBREVIATIONS

AE	alkaline earth (element)
AM	alkali metal (element)
ANL	Argonne National Laboratory
AgX	silver ion-exchanged zeolite
CGR&D	critical gap research & development
CRIEPI	Central Research Institute of Electric Power Industry
CWF	ceramic waste form
DF	decontamination factor
DOE	Department of Energy
DUPIC	Direct Use of PWR spent fuel in CANDU
EBR	experimental breeder reactor
ER	electrorefiner
EW	electrowinning
FPs	fission products
GBS	glass-bonded sodalite
ICP-MS	inductively-coupled plasma mass spectrometry
INL	Idaho National Laboratory
HLW	high-level waste
IRT	Integrated Recycle Test
JFCS	Joint Fuel Cycle Study
KAERI	Korean Atomic Energy Research Institute
LABS	lanthanide (alumino) borosilicate
LLW	low-level waste
MT	metric ton
MTU	metric ton uranium
MWD	megawatt day
MWF	metal waste form
NM	noble metals
OP	option
OR	oxide reduction
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
ppm	parts per million

PWR	pressurized water reactor
RAR	residual actinide removal
RE	rare earth (element)
REO <sub>2</sub> or RE <sub>2</sub> O <sub>3</sub>	Rare-earth (lanthanide) oxide
REOCl	oxychloride
ROK	Republic of Korea
RN	radionuclide
SAP	silica-alumina-phosphate composite (waste form)
SEM	scanning electron microscope
SFR	sodium fast reactor
TG	thermogravimetric
TGA	thermogravimetric analysis
TRU	transuranic elements
UDS	undissolved solids
UNF	used nuclear fuel
U/TRU	combined uranium and transuranium elements
WLDC	Wolsung LILW Disposal Center
XPS	X-ray photoelectron spectroscopy
ZIT	zinc titanate composite (waste form)

# **Waste Stream Treatment and Waste Form Fabrication for Pyroprocessing of Used Nuclear Fuel**

## **1. INTRODUCTION**

Pyroprocessing of used nuclear fuel is advancing from the developmental stages to implementation on an industrial scale. As with any industrial venture, and in particular for energy production, the recovery of the useful products results in unusable waste products that must be accounted for in terms of protecting the human population and the environment. The emphasis of this report is to describe pyroprocessing waste-stream treatment options and waste forms that have been developed in the ROK and the U.S. that allow for the responsible disposal of wastes from pyroprocessing treatment of used nuclear fuel. The primary goal of waste-stream treatment is to effectively isolate and contain the hazardous fission-product components and to minimize the volume of waste requiring disposal. The purpose of the waste form is to contain hazardous components in a chemically and physically durable material for long-term disposal in a geological repository.

The Joint Fuel Cycle Study is a collaborative project underway between the U.S. and the ROK to evaluate the technology, economics, and methods of safeguarding nuclear material associated with the transition to advanced treatment of used nuclear fuel. The major technologies associated with advanced used-fuel treatment by pyroprocessing will be demonstrated at the engineering scale during the Integrated Recycle Test (IRT) as part of the greater JFCS project. The IRT will demonstrate (1) pyroprocessing technologies specifically suited to the ROK and U.S. nuclear fuel cycles involving the separation of usable fuel material from fission products, (2) collection and fabrication of transuranic elements into advanced fuels for subsequent irradiation and transmutation of TRU to shorter-lived radionuclides, (3) treatment of the waste streams for waste volume minimization, and (4) production of durable waste forms. The advanced nuclear fuel cycle concept adopted by the U.S., ROK and a number of other countries, involves electrical-power production with PWR-type reactors using oxide fuel followed by treatment of the used fuel to recover the TRU. The recovered TRU is incorporated in a metallic fuel and transmuted to generate fission products with shorter half-lives using advanced ‘burner’ type fast reactors. The metallic UNF from the burner reactors is treated electrochemically to recycle reusable fissile materials. The U.S. favors aqueous-based treatment for used PWR fuel, whereas the ROK has investigated an electrochemical pyroprocessing method to treat PWR fuel. Both the ROK and the U.S. are evaluating the use of pyroprocessing methods for the treatment of the burner reactor UNF. The rationale for transmutation of TRU separated from UNF is to reduce the engineering requirements and costs and to increase the safety margin of geological repositories by excluding long-lived TRU elements.

The U.S. and the ROK have developed different pyroprocessing waste-stream strategies tailored to each country's primary need. In the U.S., treatment of pyroprocessing streams followed development of a treatment process for EBR-II Na-bonded metallic fuel, which results in a small radionuclide inventory and is suitable for a radiological facility of limited size. The philosophy of EBR-II used fuel treatment was to simplify waste processing by developing the minimum number of waste forms requiring minimal treatment. The two waste forms that were developed are the CWF that incorporates spent electrorefiner salt containing oxidized fission product wastes and the MWF that incorporates fuel cladding and metallic fission product wastes. The CWF and MWF are very durable waste forms that have undergone the greatest degree of characterization, testing and performance modeling of any pyroprocessing waste form being considered. These waste forms are being optimized for industrial-scale reprocessing in the U.S.

Pyroprocessing waste-stream treatment schemes developed in the ROK, primarily at KAERI, are focused on UNF treatment at the commercial level, where the waste-stream quantities and radionuclide

inventory will be much greater than those considered for EBR-II. Additionally, the TRU component from the UNF is to be recovered for subsequent transmutation in a burner reactor. The primary objective of the ROK approach is to minimize the volume waste requiring disposal, and thereby minimizing the size of the geological repository required to store the waste at the expense of a greater number of waste-stream processing steps. The ROK process also recycles as much material as possible back to the treatment process to minimize waste.

This report summarizes the overall treatment processes being developed at KAERI and waste form development in the ROK and U.S. Detailed descriptions are provided regarding the corrosion characteristics of the CWF and MWF, advanced waste forms being developed at KAERI and the Pacific Northwest National Laboratory (PNNL) for pyroprocessing waste-streams, and the waste form testing activities being planned as part of the IRT. An important component of this report is a description of the scientific basis and experimental strategy for determining the expected long-term performance of these waste forms in a geological disposal system. This testing strategy will be applied to candidate waste forms for evaluation during the IRT. The report is organized by tracking the wastes from the waste streams generated during the pyroprocessing operations, through treatments to segregate waste constituents destined for different waste forms, the production of waste forms from the resulting waste streams, and testing to measure durability of those waste forms and support performance modeling. These are discussed in the following sections:

**Pyroprocessing of Used Oxide Nuclear Fuel** – Section 1.1 describes the generalized process of electrolytic reduction of oxide UNF followed by electrorefining of the actinide and fission products that are soluble in molten salt. Pyroprocessing waste streams are described in Section 1.2. These include metallic hardware housing the used fuel that becomes radioactive while in the reactor, the volatile fission products that are released from the fuel during treatment, the electrolyte salt waste streams that contain dissolved (oxidized) fission products and actinide components from the used fuel, and the insoluble (metallic) fission products.

**Waste Treatment Processes** – Section 0 describes fission product separation and concentration methods applied to various process streams with the goal of waste stream minimization.

**Pyroprocessing Waste Forms** – Section 0 details waste forms developed for EBR-II wastes and advanced waste forms being developed and investigated in the ROK and the U.S. Detailed discussions address the development of several advanced waste forms.

**Waste Form Performance** – Section 0 discusses waste form testing methods used to determine corrosion mechanisms and measure radionuclide release from the waste form. This information is used to develop release models and predict waste form performance in various geologic repositories.

**Integrated Recycle Test** – Section 0 describes studies that are being planned to evaluate waste-stream treatment methods for fission-product separation, waste volume minimization and the technical feasibility of implementing the various methods in a hot cell environment. Advanced pyroprocessing waste forms with promising performance characteristics will be fabricated and evaluated during the demonstration.

## **1.1 Pyroprocessing of Used Oxide Nuclear Fuel**

Pyroprocessing of used oxide nuclear fuel consists of a series of electrochemical processes that reduce most constituents in the fuel to the metallic state and allow application of separations methods developed for the treatment of EBR-II fuel. For the treatment of oxide fuel, there are many options on fuel pre-treatment, electrolytic cell configuration, electrolyte, fission-product separation, and actinide recovery methods. The strategies being developed in the ROK and U.S. are summarized below.

A research priority at the KAERI involves minimizing the volume of high-level waste (HLW) that requires disposal in a geological repository. This is done by separation of fission products and the

Development of pyroprocessing technologies for the treatment of used oxide fuel at KAERI consists primarily of: (1) head-end processes including high temperature treatment to remove volatile and semi-volatile radioisotopes from the fuel, (2) electro-reduction process with specific cell materials and structure, (3) electrowinning (ER) process with a graphite cathode and a semi-continuous ER operation, and (4) a series of electrowinning (EW) processes. This approach is used to minimize the amount of TRU in waste streams as well as to effectively recover U and TRU for reuse.

The common goals of the U.S./ROK JFCS are to demonstrate advanced pyroprocessing technologies and waste stream management, evaluate the economic viability of pyroprocessing, and demonstrate safe-guard technologies to prevent diversion of accountable material during the pyro-treatment of used oxide fuel.

Six primary high-level radioactive waste streams are expected to be generated during the pyroprocessing of used oxide fuel, (1) contaminated fuel assembly hardware, (2) fuel cladding, (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) processes. A depiction of the pyroprocessing flowsheet is shown in Figure 1.1 and a brief description of each waste stream is given in Table 1.1. These waste streams are discussed in more detail in the following sections.

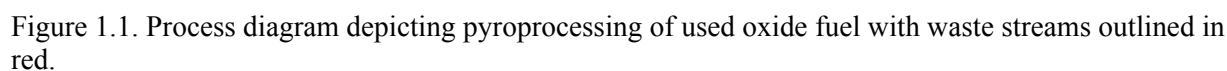


Table 1.1. Summary of pyroprocess-treated UNF waste streams.

Waste	Components
Hardware	Structural parts of spent fuel bundle including grid, guide tube, springs, etc., contaminated with activation products.
Cladding	Zircaloy 4 or stainless steel cladding contaminated with actinides, fission products, and activation products.
Filter media	Filters (fly ash for Cs, calcium for Tc and AgX for I trapping) for selective off-gas trapping during high temperature voloxidation process.
LiCl waste salt	Salt from electrolytic reduction containing heat-generating Group I (Cs, Rb), Group II (Sr, Ba) fission products (*if performing high temperature voloxidation in head-end process, only Group II fission products are present in LiCl waste salt).
LiCl+KCl waste salt	Salt from electrorefining and electrowinning (drawdown) containing lanthanides and trace amounts of actinides.
UDS	Undissolved solids (UDS) from electrolytic reduction and electrorefining containing noble metal fission products (i.e., Tc, Zr, Mo, Ru, Rh, Pd, and Te) and oxide residue.

### 1.2.1 Hardware

The hardware from the used nuclear fuel assembly is removed prior to pyroprocessing and 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. The hardware waste represents about 30% of the total metal waste mass from the treatment of 10 MT UNF to be disposed of and about 64% of the waste volume. Although the hardware waste is categorized as non-fuel bearing component, the radioactivity of the waste was calculated to exceed the intermediate-/low-level waste disposition regulation due to Ni-59 and Nb-94 generated by neutron activation. For example, KAERI evaluated the characteristics of radioactivation for top/bottom nozzle and support grids using KENO-VI/ORIGEN-S modules. The calculated radioactivity was consistent with the result of quantitative measurements for support grids. Generally, the hardware waste is treated by mechanical compaction or melting for volume reduction.

### 1.2.2 Cladding Hulls

Nuclear fuel is separated from cladding in a mechanical or oxidative decladding process. The separated cladding remains contaminated with residual nuclear materials and is radioactive from activation products produced in the cladding from neutron absorption. Two concepts have been researched for cladding disposal: once-through and reuse. Once-through is aimed at volume reduction by compaction or melting for alloy formation. Compaction can achieve about 60-70% volume reduction whereas melting has a higher volume reduction. Alloys made with mixtures of Stainless steel cladding with 15% zirconium (SS-15Zr) and zirconium cladding with 8% stainless steel (Zr-8SS) were shown to have multi-phase microstructures that aid in immobilizing other elements (McDeavitt et al., 1998). The main objective of the reuse option for cladding hulls is minimization of high-level hull waste. As Zircaloy-4 and Zirlo cladding both consist of about 98% Zr, the recovery and reuse of Zr would significantly reduce the amount of hull waste requiring disposal.

Cladding hull waste was not a major issue in the countries that performed or are performing hydrometallurgical, or aqueous reprocessing, although it is classified as a Greater than Class C waste (U.S.) or Intermediate-Level Long-Lived radioactive waste (France) waste due to residual contamination. The Wolsung LILW Disposal Center (WLDC), now in operation in Korea (Song, 2013), performed a preliminary study on the radioactivation of cladding hull materials revealed that Nb-containing cladding



hulls cannot meet the criteria of WLDC because of Nb-94 generation (Jeon et al., 2012; Jeon et al., 2014). The calculation results showed that for the Nb-containing cladding materials (ZIRLO, HANA-4, and HANA-6) a decontamination factor (DF) of 4,900 must be achieved to meet the acceptance limit of WLDC. On the other hand, it was suggested that Zircaloy-4 can be accepted to WLDC if complete removal of used nuclear fuel (UNF) is guaranteed. Here, it should be noted that the complete removal of UNF from the cladding hull waste is unrealistic because it was already identified from the wet processing that even acid washing cannot achieve such a high DF. These facts suggest that the cladding hull waste generated from the pyroprocessing should be disposed of in a HLW repository based on Korean and U.S. regulations.

### **1.2.3 Off-Gas Filter Media**

Various radioisotopes present in a used oxide fuel will be released as a gas or particulates during mechanical de-cladding, low and high temperature processing, electrolytic processing and solidification that must be captured by filters. In the KAERI pyroprocessing flowsheet, volatiles (e.g., Kr, Xe, C-14, H-3) and semi-volatiles (Cs, Tc, I, et al.) are vaporized during the head-end high temperature processing and captured by a series of filter media. Most waste form production processes start by pulverizing the salt wastes and handling them at relatively high temperatures. During these operations, particulates or volatile radioisotopes would be released from the equipment. For this reason, almost all waste form fabrication processing equipment is equipped with a HEPA filter or a specific adsorption system. Except for the KAERI filter media used in the voloxidation step of pyroprocessing, all the filter media are considered as secondary wastes whose amount and radioactivity is not greater than those of original radioactive materials or wastes.

The adaption of high-temperature treatment in KAERI (Park et al., 2010) has several advantages: (1) a greater fraction of the fuel can be separated from the cladding, (2) the particle size of spent fuel material can be better controlled to improve the efficiencies of subsequent process, and (3) 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 adverse effects of volatile and semi-volatile FPs. Therefore, if considering high-temperature treatment process as a head-end option, an off-gas treatment system for selective trapping of volatile fission products such as I, Tc, and Cs is essential. In the off-gas capturing system developed at KAERI, a fly ash filter is used to capture Cs, a silver ion-exchanged zeolite (AgX) is used for I capture, and a calcia filter is used for Tc capture. The solidification methods for disposing these used filters are under development at KAERI.

### **1.2.4 Waste Salt**

Significant differences exist in the radioactive waste management of waste streams between pyroprocessing and aqueous reprocessing. Chloride-based wastes generated during pyroprocessing are comprised of highly ionic compounds with high volatilities above the melting temperature of the electrolyte salt. Due to the properties of metal chlorides, different treatments methods are required for the separation and immobilization of fission-product chlorides than those used for aqueous-based processes.

Two chloride based waste streams are generated during pyroprocessing: a LiCl stream from the reduction of used oxide fuel and a LiCl-KCl stream from the treatment of metallic fuel. Generally, during the treatment of used oxide fuel, the group I and II fission products (Rb, Cs, Sr and Ba), I, Se, and Te accumulate in the LiCl salt during the oxide reduction step, while the lanthanide fission products and trace amounts of actinides partition to the LiCl-KCl salt during the electrorefining step. For the treatment of metallic fuel waste, all these fission products accumulate in the 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, perhaps, a tellurite glass. Alternatively, separation of fission products concentrated into a reduced volume of electrolyte allows for recycle of the remaining salt.

### **1.2.5 Undissolved Solids**

Undissolved solids including Tc (if it is not removed during head-end, high-temperature voloxidation), 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 could be recovered from the anode basket and the anode basket reused. To immobilize the noble metal fission products, the noble metals could be processed directly to form an epsilon-phase alloy waste form (Strachan et al., 2011) or alloyed with added steel to produce a metallic waste form similar to the treatment of EBR-II used fuel cladding (Simpson, 2012, Westphal, 2013). However, uranium oxide and other oxides not recovered in the electrorefining process will remain with the noble metals in the anode basket. Whether or not these oxides would be incorporated into either of these metallic waste forms remains to be determined. The amounts of residual oxides will depend on the operating conditions of electrorefining process.

## 2. WASTE TREATMENT PROCESSES

### 2.1 Off-gas Treatment

Fuel pre-treatment using a high-temperature head-end process removes volatile fission products (e.g., Kr, Xe, C-14, and H-3) and semi-volatile fission products (e.g., Cs, Tc, and I) from the waste that can be captured for immobilization. Head-end removal of the volatile and semi-volatile fission products can reduce the operational burden of the subsequent electrochemical treatment. KAERI has proposed an off-gas trapping system to capture the Kr, Xe, H-3 (as water), C-14 (as CO<sub>2</sub>), I (as AgI) and the semi-volatile fission products such as Cs (as CsI, Cs<sub>2</sub>TeO<sub>4</sub>, Cs<sub>2</sub>UO<sub>4</sub>, and Cs<sub>2</sub>MoO<sub>4</sub>), and Tc [as Ca(TcO<sub>4</sub>)<sub>2</sub>] from the decladding and head-end, high-temperature off-gas process (Park et al., 2010). Table 2.1 summarizes the off-gas trapping technologies proposed by KAERI for various volatile and semi-volatile fission products released in the high-temperature thermal process.

Table 2.1. Off-gas trapping materials for volatile and semi-volatile fission products.

Nuclides	Trapping media	Chemical form of nuclides trapped filter
Cs, Rb, Cd	Fly ash filter	<b>Cs:</b> CsAlSi <sub>2</sub> O <sub>6</sub> $\text{Cs}_2\text{O (g)} + \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2(\text{s}) = 2\text{CsAlSi}_2\text{O}_6(\text{s})$ <b>Rb:</b> RbAlSi <sub>2</sub> O <sub>6</sub> <b>Cd:</b> CdAl(SiO <sub>4</sub> ) <sub>2</sub>
Tc, Mo, Sb, Te, Se	Calcium-based filter	<b>Tc:</b> Ca(TcO <sub>4</sub> ) <sub>2</sub> , Ca <sub>5</sub> Tc <sub>2</sub> O <sub>12</sub> $\text{Tc}_2\text{O}_7(\text{g}) + \text{CaO}(\text{s}) = \text{Ca(TcO}_4)_2(\text{s})$ $\text{Tc}_2\text{O}_7(\text{g}) + 5\text{CaO}(\text{s}) = \text{Ca}_5\text{Tc}_2\text{O}_{12}(\text{s})$ <b>Mo:</b> CaMoO <sub>4</sub> <b>Sb:</b> CaSb <sub>2</sub> O <sub>7</sub> , CaSb <sub>2</sub> O <sub>6</sub> <b>Te:</b> CaTeO <sub>3</sub> , CaTe <sub>2</sub> O <sub>5</sub> <b>Se:</b> CaSeO <sub>3</sub> , CaSe <sub>2</sub> O <sub>5</sub>
I, Br	AgX (or Bi-based sorbent)	<b>I:</b> AgI $\text{Ag}_2\text{O} + \text{I}_2 = 2\text{AgI} + 0.5\text{O}_2$ <b>I:</b> BiI <sub>3</sub> , BiOI $\text{Bi} + 3/2\text{I}_2 = \text{BiI}_3$ , $\text{Bi} + 1/2\text{O}_2 + 1/2\text{I}_2 = \text{BiOI}$ <b>Br:</b> AgBr
H-3	Zeolite 4A	HTO
C-14	Calcium-based filter	CaCO <sub>3</sub> $\text{CO}_2(\text{g}) + \text{CaO}(\text{s}) = \text{CaCO}_3(\text{s})$

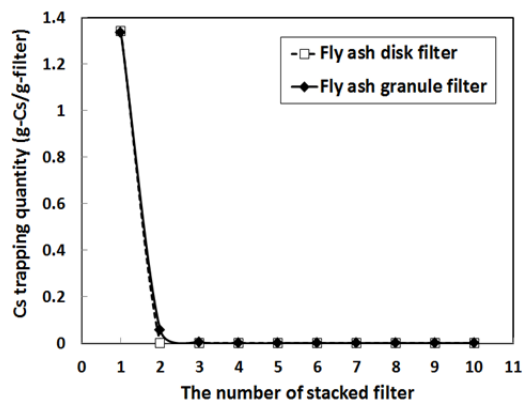
Disk-type fly ash filters have shown good performance for the capture of gaseous Cs generated from the head-end, high-temperature treatment of spent nuclear fuel (Shin et al., 2009; Westphal et al., 2008). Five types of granule filters, including a ball type, tube type, and sponge structure type have also been evaluated (Park et al., 2013). The sponge-structure type granule filter shown in Figure 2.1a had the highest trapping capacity for Cs at 0.42 g-Cs/g-granule. The performance of stacked (multiple filters) sponge-structure type filters was then compared to stacked disk-type filters in a two-zone tube furnace with the results shown in Figure 2.1b. The Cs trapping profile of the sponge-structure type granule filters was indistinguishable from that of the disk-type fly-ash filters. For both filter types, Cs was successfully trapped within the second filter.

Various types of calcium granule filters have also been developed and evaluated including three ball types and a sponge-structure (Park et al., 2013). The sponge-structure type granule filter shown in

Figure 2.1d had the highest trapping capacity for Re at a capacity of 0.62 g-Re/g-granule. The sponge-structure type granule filter was also compared to the disk-type filter tested using a two-zone tube furnace, as shown in Figure 2.1d, the Re trapping profile of the sponge-structure type granule filters was broader than that of the disk-type fly ash filters. This might be due to lower gas-solid contact efficiency of the granule filter compared to that of the disk-type filter and a lower reaction rate than that of Cs with fly-ash. Experiments with radioactive gases on fly ash and calcium granule filters will be conducted in the DUPIC Fuel Development Facility hot-cell at KAERI.



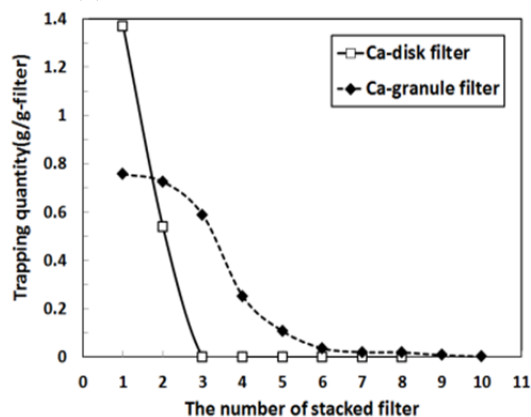
(a)



(b)



(c)



(d)

Figure 2.1. Images and capturing results of (a) fly ash granules, (b) cesium trapping profile of disk and granular fly ash, (c) calcium filter granules, and (d) rhenium trapping profile of disk and granular calcium filter.

Conventionally, radioactive iodine (I-129) off-gas has been removed by using silver-exchanged zeolites (AgX, AgZ) (Haefner and Tranter, 2007). Although these materials show high removal efficiencies of I-129, zeolite-based sorbents cannot exclude physical sorption of iodine (Goossens et al., 1991). Weakly bound iodine is fatal in view of long-term storage since physically adsorbed iodine would be easily dissolved in groundwater, or released at elevated temperatures. Furthermore, a process using silver is not favorable in terms of economics considering high price of silver. In this regard, KAERI has been studying the development of new sorbent for I-129 off-gas removal. Bismuth is being employed to induce chemisorption of iodine. Bismuth-based iodine waste forms have been extensively studied by Taylor et al. (Taylor and Lopata, 1985; Taylor et al., 1989; Taylor, 1990). They studied hydrolytic stability of bismuth iodine compounds in various conditions, proposing that bismuth oxyiodide could be a candidate waste form for I-129. Preliminary study of KAERI was focused on the synthesis of porous

bismuth granules by using polyvinyl alcohol as a sacrificial scaffold (Yang et al., 2015). Adsorption capacity of iodine as-synthesized samples is approximately two times higher than that of commercial AgX. In addition, iodine was retained by forming BiI<sub>3</sub> or BiOI compounds that are thermally stable up to 300°C, suggesting that I physical sorption could be successfully avoided. Fundamentally, iodine chemisorption can be enhanced by using host matrices with large pore sizes. KAERI is now employing mesoporous silica as a substrate incorporating bismuth. Mesoporous silicas have high surface area and uniformly distributed mesopores, facilitating molecular diffusion (Ryoo et al., 2000). One of the most important factors affecting iodine adsorption is the degree of bismuth incorporation. Facile adsorption of bismuth into the host matrix was successfully performed by functionalizing the surface of mesoporous silica with thiol group. Another factor related with adsorption is particle size. High-temperature processing will lead to the agglomeration of bismuth particles, resulting in poor performance. Therefore, this conglomerate is studying the effect of particle size at different temperatures. Maximum I<sub>2</sub> adsorption studies have shown that bismuth-incorporated silica could capture approximately 435 mg-I<sub>2</sub>/g-sorbent in static air. Additional optimization studies at KAERI are expected to increase the capture efficiency of iodine in these systems.

## 2.2 Cladding Hull Treatment

Dealing with cladding hull waste is a heavy burden for large-scale treatment of UNF because of the large volume of cladding (2.5 m<sup>3</sup> for every 10 MT of UNF). This is especially true for the ROK, which has limited space for a HLW repository. KAERI has invested extensive effort to develop methods to minimize the amount of high-level cladding hull waste. This effort at KAERI has included the characterization and treatment of actual UNF cladding hulls.

### 2.2.1 Cladding Hull Treatment by Chlorination

Chlorination is one of the approaches being pursued to minimize the amount of HLW generated from the cladding hull waste. The chlorination process employs a simple chemical reaction between metallic zirconium and chlorine gas as follows:



Characteristic merits of the chlorination process are a simple reaction process and the separation of the ZrCl<sub>4</sub> reaction product from most radioactive impurities 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 UNF. As zirconium represents about 97 mass% of cladding hull material, it is expected that the amount of high-level cladding waste can be reduced to 1/10 of total waste, including Zr oxide and alloying elements, upon meeting 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 (Jeon et al., 2012a).

At the KAERI, a quartz reactor system was employed for preliminary experiments. A schematic diagram of the system is shown in Figure 2.2. The quartz reactor has a porous quartz frit in the middle to hold 3-cm long pieces of cladding hulls in the hot zone while allowing reactant gases and gaseous products can pass through it. Using the quartz reactor system, various experiments were performed, including experiments to study the effect of oxide layers on the hulls. In previous work, the effect of oxidation conditions on the chlorination reaction of Zircaloy-4 was investigated (Jeon et al., 2012b). After being oxidized at either 500 or 600°C for 5 hr, or at 500°C for 24 hr under an air atmosphere, hulls were still reactive with chlorine gas at 380°C. However, hulls that were oxidized at 700°C were not reactive with chlorine gas. These results indicate that oxide layers formed on cladding during oxidative decladding at 500 or 600°C might not hinder the chlorination reaction. Perhaps this is due to the exposure of fresh cladding surfaces formed during the decladding process that might provide reaction pathways for chlorination. Surface analysis using the X-ray photoelectron spectroscopy (XPS) technique showed that the reaction temperature significantly changes the oxidation state of the Zircaloy-4 cladding hull surface, which is considered as a major factor affecting the oxidation rate (Jeon et al., 2012b).

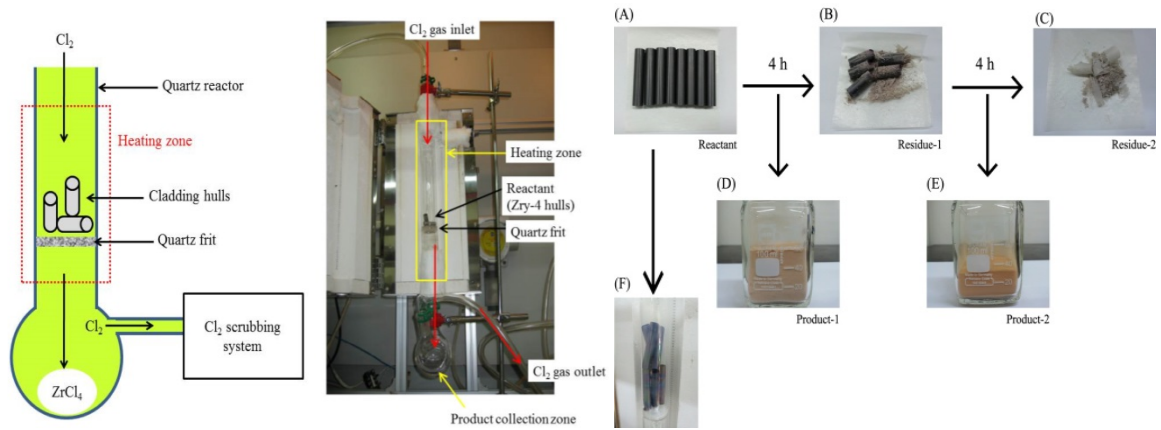


Figure 2.2. Schematic diagram (left), the quartz reactor system for the chlorination (middle) and picture of samples before and after reactions [3]; the pictures of (A) reactants (Zircaloy-4 hulls), (B) Residue-1, (C) Residue-2, (D) Product-1, (E) Product-2, and (F) reactants loaded in the quartz reactor (right) (Jeon et al., 2013).

Using the quartz reactor system, a preliminary test for complete chlorination of 50 g of cladding oxidized at 500°C for 10 hr in air was investigated (Jeon et al., 2013). The amount of reaction residue was only 0.95 mass% of the initial weight. Final recovery ratio of metallic zirconium was about 95 mass%, with 3% zirconium oxide and an experimental loss of about 2 mass%. Iron and tin were identified as minor impurities, with a Zr purity of 99.8 mass% in the recovered ZrCl<sub>4</sub>.

With the successful demonstration of the chlorination process, KAERI is now focusing work on two key issues for the chlorination process. The first is to verify fundamental data such as reaction kinetics and effects of reaction parameters, and the other is scale-up that considers purification of recovered zirconium tetrachloride. On the fundamental research aspect, a thermogravimetric analysis (TGA) system was developed that can employ cladding hull pieces up to 5-cm long using a quartz basket. Using Zircaloy-4 cladding hulls, the effects of total flow rate, chlorine partial pressure, and reaction temperature were investigated. The experimental results revealed that the chlorination reaction of Zircaloy-4 cladding hulls can be explained by the volumetric reduction model (A Khawam, 2006). In the volumetric reduction model, the influence of chlorine partial pressure and reaction temperature on the chlorination reaction kinetics is expressed by the following equation:

$$\frac{d\alpha}{dt} = 3 \times \left( 1.16 \times e^{-\frac{26.2}{RT}} \times pCl_2^{0.669} \right) \times (1 - \alpha)^{2/3} \quad (2.2)$$

where the term alpha is the conversion fraction, which changes from 0 to 1 as the reaction proceeds.

### 2.2.2 Cladding Hull Treatment by Electrefining

As another approach for Zr recovery, electrefining can be used for the treatment of cladding hull materials such as Zircaloy-4 and Zirlo. Electrefining process is the method that selectively recovers Zr by the difference of Gibbs free energy of metal chloride formation in high temperature molten salts (Ackerman, 1991; Inoue, 2002). 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 the electrefining process have been done based on the concept depicted in Figure 2.3. During the electrefining 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 compared to that of Zr. Residue UNF will dissolve into the salt after being chemically chlorinated by  $\text{ZrCl}_4$ , which is used as an initiator for Zr electrefining in chloride-based molten salts. The radioactive nuclides from residue fuel dissolve into the salt for subsequent waste salt treatment. The recovered Zr can be reused as an additive for metal waste forms or disposed as low-level waste.

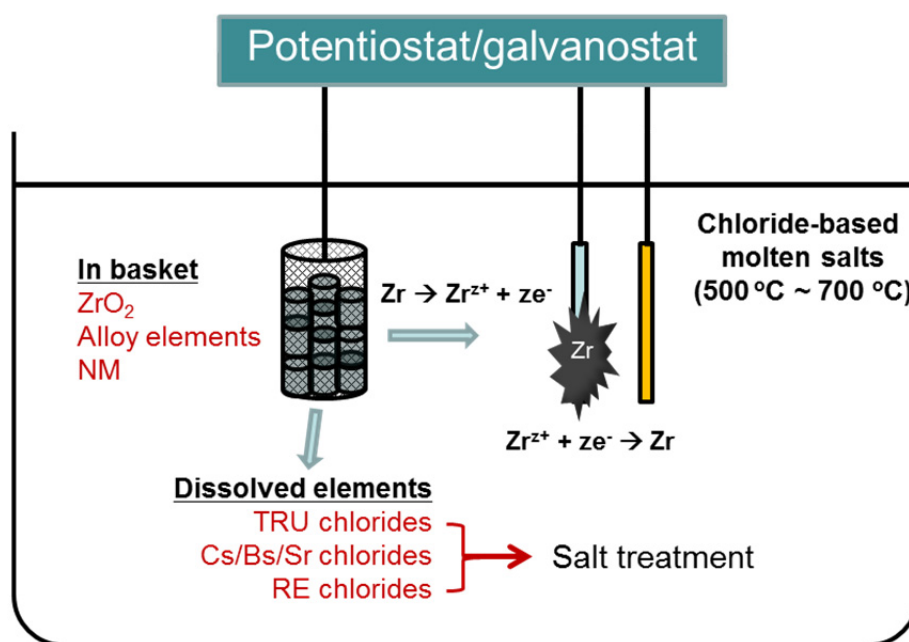


Figure 2.3. A conceptual diagram of the Zr electrefining process at KAERI.

To examine the electrochemical behavior of Zr, cyclic voltammetry was performed in  $\text{LiCl-KCl-ZrCl}_4$  molten salts using a tungsten wire cathode and Zr rod anode. In the absence of  $\text{ZrCl}_4$ , the residual current flown was less than 0.5 mA, which indicates that there are no significant side reactions associated with the reduction/oxidation of electrolyte components and the tungsten working electrode and Zr counter electrode over the potential range of -0.2 V to -1.8 V vs.  $\text{Ag/Ag}^+$ . In the presence of  $\text{ZrCl}_4$ , multiple reduction processes occur that are attributed to the existence of various valence states of Zr, as shown in Figure 2.4. The respective reduction processes are considered to correspond to the following reactions (Lee et al., 2012; Sakamura, 2004).

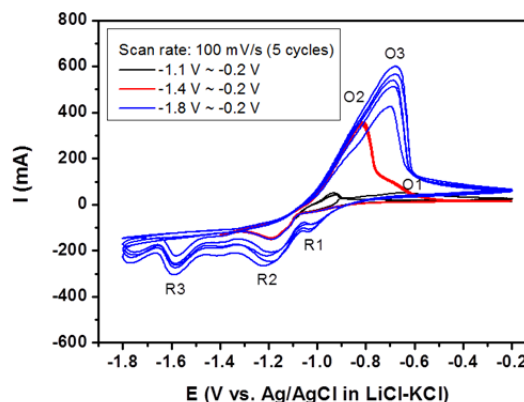
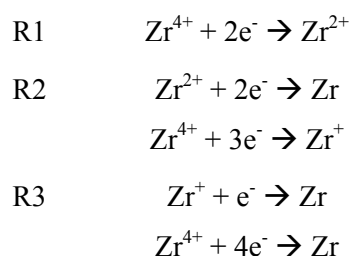


Figure 2.4. Cyclic voltammograms for tungsten electrode at various scan ranges at a scan rate of  $100 \text{ mV s}^{-1}$  in  $\text{LiCl-KCl-ZrCl}_4$  molten salts at  $500^\circ\text{C}$ . Tungsten wire with an exposed area of  $0.942 \text{ cm}^2$  was used as a working electrode and Zr rod was used as an anode. Each scan was repeated 5 times and the working electrode area was  $0.942 \text{ cm}^2$  (Lee et al., 2012).

In the Zr electrorefining experiment at  $-1.15 \text{ V vs. Ag/Ag}^+$ , Zr with a purity of 99.44 mass% was recovered on the cathode as Zr and  $\text{ZrCl}$  with 0.56 mass% Sn, excluding the incorporated salts. However, a significant amount of salt ( $\sim 94 \text{ mass\%}$  salt) was included in the Zr product, which might be attributed to a powder-type deposition characteristic of Zr generally found in all-chloride based salts. This is one of the most challenging issues in the Zr electrorefining process with respect to the recovery yield. Although all-fluoride based molten salts are known to form a coherent or dendritic Zr deposit (Gurklis et al., 1952; Mellors et al., 1966), the use of Zr electrorefining is not promising because of the high operating temperature required and severe corrosiveness. In addition, salt waste treatment processes for fluoride-based salts have not been established yet. Therefore, research on the development of mixed chloride-fluoride salts for Zr electrorefining process is now underway at KAERI to enhance the Zr recovery yield by the modification of Zr deposition morphology as shown in the flow diagram in Figure 2.5.

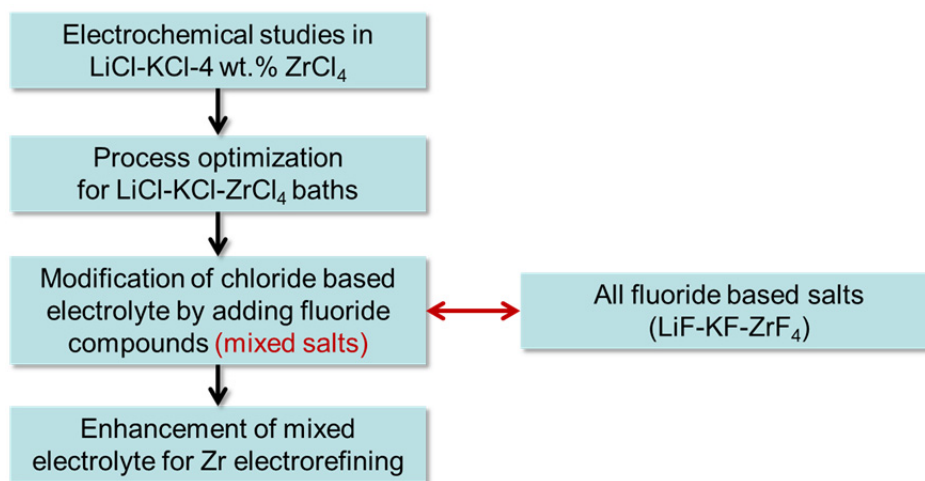


Figure 2.5. Flow diagram of high-throughput Zr recovery process.



The process condition for Zr electrorefining in the LiCl-KCl-  $\text{ZrCl}_4$  salt as shown in Figure 2.5 was optimized by examining the effects of process parameters such as  $\text{ZrCl}_4$  concentration, temperature, applied potential, etc. with respect to the electrorefined Zr deposit content and morphology. The Zr content in the electrorefined Zr was slightly increased to  $\sim 10$  mass% at lower  $\text{ZrCl}_4$  and applied potential. The second phase, based on the initially optimized conditions (e.g.,  $\text{Zr}^{4+}$  concentration; 0.07 M), involved addition of fluoride compounds to the LiCl-KCl salt to act as reaction initiators, such as  $\text{ZrF}_4$  instead of  $\text{ZrCl}_4$  or as a separate component such as LiF with  $\text{ZrCl}_4$ . The operating temperature was set to  $600^\circ\text{C}$  due to higher eutectic points of mixed salts. The voltammetric behavior of Zr in LiCl-KCl-0.07 M  $\text{ZrF}_4$  revealed to be similar with that of LiCl-KCl-0.07 M  $\text{ZrCl}_4$ , whereas the multi-step reduction process completely changed to a single step process associated with a direct reduction of  $\text{Zr}^{4+}$  to metallic Zr in LiCl-KCl-0.07 M  $\text{ZrCl}_4$  with the addition of excess LiF (0.84 M). The morphological feature and crystallinity of electrorefined Zr in the optimized mixed salts were greatly improved showing the Zr content of  $\sim 70$  mass%, which is comparable to  $\sim 80$  mass% Zr that was achieved in an all-fluoride salt without a subsequent salt distillation.

The effect of Zr oxide coatings on Zr electrorefining was also studied (Lee et al., 2012b). The electrochemical measurements were performed for Zircaloy-4 cladding tubes oxidized for 5 hr at various temperatures from  $400^\circ\text{C}$  to  $600^\circ\text{C}$  under air atmospheric conditions. The anode current transients at a dissolution potential of  $-0.78$  V vs.  $\text{Ag}/\text{Ag}^+$  revealed a different incubation time for the onset of electrochemical dissolution depending on the oxidation temperature of the cladding tubes, as shown in Figure 2.6a. However the electrochemical dissolution of oxidized Zircaloy-4 tubes could be initiated by a salt treatment under an open circuit potential for a certain length of time and the incubation time was accelerated by applying a dissolution potential. The reduction-oxidation changed from passive to active after the salt treatment, as shown in Figure 2.6b. The electrochemical dissolution was experimentally confirmed for oxidized 10 g cladding tube segments and resulted in recovered Zr with over 99 mass% purity.

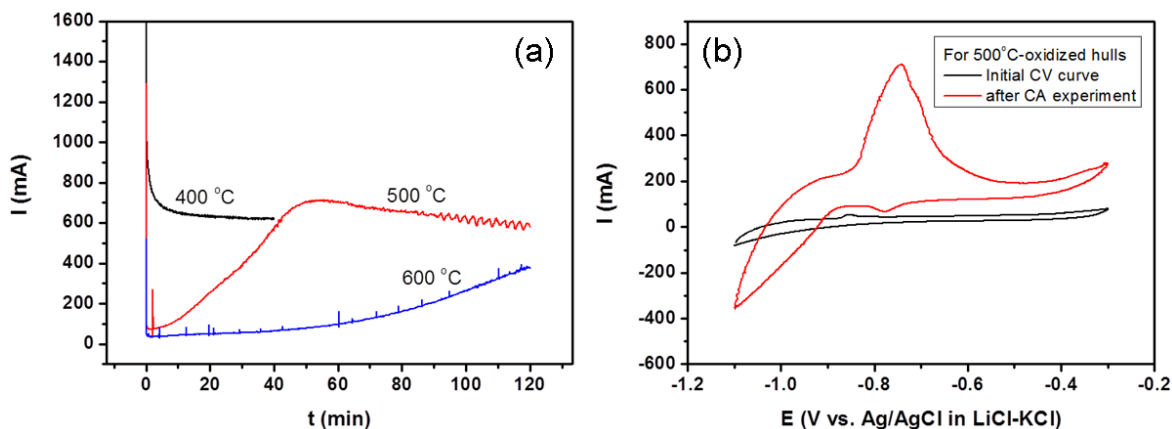


Figure 2.6. (a) Current transients in LiCl-KCl- $\text{ZrCl}_4$  at  $500^\circ\text{C}$  for Zircaloy-4 hulls that were previously oxidized at various temperatures for 5 hr, and (b) cyclic voltammograms for Zircaloy-4 hulls oxidized at  $500^\circ\text{C}$  for 2 hr before and after the chronoamperometric experiment. The scan rate was  $20 \text{ mV s}^{-1}$  (Lee et al., 2012b).

In addition, the effects of residual fission product oxides was studied for Zr recovery by electrochemical measurements in chloride-based molten salts containing surrogate FP oxides of  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ . The results indicate that there was no perceptible change in the voltammograms and that the concentration of surrogates FP included in the recovered Zr deposit was lower than the measurement detection limit.

The technology development for Zr reduction process is not only applicable to the recovery from cladding hull wastes, but also to the conversion of  $\text{ZrCl}_4$  to metallic Zr when combined with the chlorination process, and for treating undissolved solids that contains a significant amount of Zr.

## **2.3 Waste Salt Minimization**

Pyroprocessing of UNF utilizes a series of electrolytic processes and two molten-salt electrolyte systems. Fission-product partitioning into the process-salt streams depends of the type of fuel (oxide or metallic) and on fuel pre-treatment. Impurities in chloride electrolytes can modify the physical and chemical characteristics of the salt, such as changes to the system melting point, and this can alter processing performance. Therefore, chloride electrolytes must be replaced periodically for the optimal electrochemical operation of pyroprocessing. The electrolyte to be replaced due to high fission product concentrations is referred to as waste salt. Since waste salt is heat-generating, radioactive, and highly soluble in water, it must be further treated to produce a durable waste form suitable for long-term geological disposal.

A general approach to minimize the waste salt volume is selective separation of FPs from the bulk salt waste and recycling the purified salt back to the main process. 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 with these processes is to concentrate the FPs for waste form volume minimization and salt recycle.

Pyroprocessing development in the U.S. has been focused on the treatment of used metallic fuel and two waste forms were developed for fission product immobilization: the ceramic waste form (CWF) and the metallic waste form (MWF). A once-through salt treatment approach was developed for the limited metallic UNF inventory in the U.S. Here, salt waste containing fuel/cladding bond sodium, FPs and TRU elements are processed into the CWF without further treatment or salt recycle. While this process leads to overall process simplicity, it also results in a significant waste volume with low fission-product loading. The MWF produced from treated cladding containing residual second row, transition metal FPs (noble metals that are insoluble in the electrorefining process) does allow for significant cladding hull volume reduction, but with low FP loading.

Pyroprocessing in the ROK has focused on treatment of used oxide fuel requiring the treatment of two salt process streams, fission-product off-gas from fuel pre-treatment, cladding, and an undissolved solid (UDS) component. The ROK approach to waste stream treatment emphasizes waste volume reduction in exchange for overall waste treatment complexity.

Three primary salt/FP separation technologies have been developed at KAERI: (1) Melt crystallization using a phase equilibrium between liquid and solid phases, (2) Selective distillation using a phase equilibrium between liquid and gas phases, and (3) selective reaction in  $\text{LiCl-KCl}$  salt. Melt crystallization concentrates FP-bearing compounds in the melt by solidifying the pure salt ( $\text{LiCl}$  or  $\text{LiCl-KCl}$ ). The regions of contaminated and pure salt are then physically separated. Distillation uses the difference of vapor pressure between metal chlorides and host salt to separate the FPs. When the difference is not sufficient to separate some specific metal chlorides, it is possible to obtain higher separation efficiency by converting the targeted metal chlorides into compounds that are insoluble in the melt, in other words, selective chemical reaction in the melt. In this section, the progress of research addressing each method will be described in detail.

### **2.3.1 Melt Crystallization**

Chemical approaches, such as ion-exchange or selective reaction, to separate Cs and Sr from  $\text{LiCl}$  systems have been investigated; however, results from these studies indicate that the chemical methods are not effective for FP separation in the  $\text{LiCl}$  system (Harrison et al., 2008). Melt crystallization methods for  $\text{LiCl}$  purification have been extensively studied at KAERI with initial investigations based on the Bridgeman or Czochralski methods. While these processes result in extremely pure products, very long

crystal growth times and specialized, precision equipment are required. KAERI then experimented with simpler melt crystallization systems with excellent results.

For treatment of used oxide fuel, the LiCl system is used for the reduction of the oxide fuel prior to electrorefining in a LiCl-KCl eutectic salt. The primary FPs that accumulate in the LiCl salt are Cs and Sr. Melt crystallization treatment of LiCl waste salts results in the collection of a relatively pure LiCl solid, while most of the Group I and II fission products are concentrated in the remaining LiCl melt. The solid, purified LiCl fraction is then removed from the contaminated liquid fraction for recycle. The contaminated fraction of much reduced volume is then diverted to waste form fabrication. The separation efficiency of Group I and II elements from LiCl molten salt by melt crystallization is determined from the temperature-composition phase diagram of the LiCl system (Cho et al., 2010).

The melt crystallization method developed at KAERI is a simple process that uses cooled plates immersed in a molten salt. A solid crystalline phase (clean LiCl) grows as a compact layer on the cooled plate surface. Melt crystallization experiments were carried out in a lab-scale apparatus (shown in Figure 2.7) with a maximum capacity of 4 kg-LiCl/batch. The apparatus consisted of two furnaces, three crystallizers, crystallizer moving system and a coolant input system.

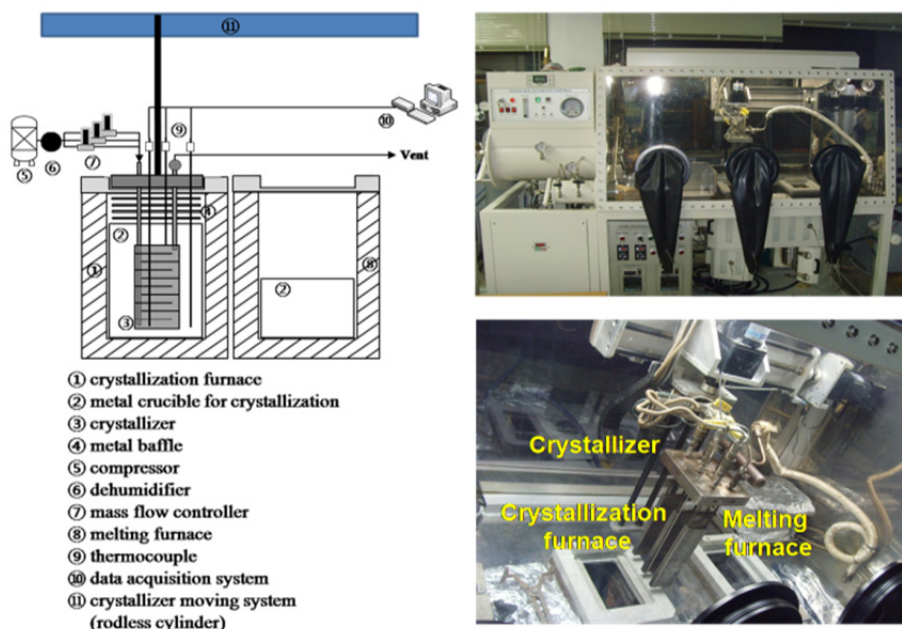


Figure 2.7. KAERI Lab-scale melt crystallization apparatus.

Since the melt crystallization process is based on the growth of a solid layer on a cooled surface, the crystal growth rate affects the formed crystal structure and the amounts of an impurity in the crystal. Impurities are not incorporated into the highly ordered crystal structure as long as the growth is slow. On the other hand, fast crystal growth results in the liquid phase impurities being entrapped in the crystal mass. Based on a series of experiments, the optimized flux in the developed lab-scale equipment was below  $0.04 \text{ g min}^{-1} \text{ cm}^{-2}$  resulting in 90% of separation efficiency for FPs in the crystallization temperature range of 590–650°C.

Temperature control of the Ar-cooled melt crystallization apparatus is crucial for adequate separation efficiency. Critical thermocouple components required to control the crystallization process are indicated in Figure 2.8 and include: (1) cooling plate thermocouple to determine the end-point of crystallization, (2) thermocouple between cooling plates to monitor excessive crystallization that results in low separation efficiency, and (3) the melt temperature thermocouple outside the crystallizer that is used to monitor the state of melt. Crystallization plates are chilled by a cooled argon recirculation system. This method is

applicable for the recovery of LiCl from LiCl-CsCl, LiCl-CsCl-SrCl<sub>2</sub>, LiCl-SrCl<sub>2</sub>-BaCl<sub>2</sub>, LiCl-CsCl-SrCl<sub>2</sub>-BaCl<sub>2</sub> or LiCl salt containing other metal halides. The separation efficiency depends on the concentration of FPs in the salt. Based on the experiments, it is possible to concentrate up to about 30 mass% of Sr(Ba)Cl<sub>2</sub> in a molten system of LiCl-CsCl-SrCl<sub>2</sub>-BaCl<sub>2</sub> with a minor quantity of CsCl contamination in the solidified product.

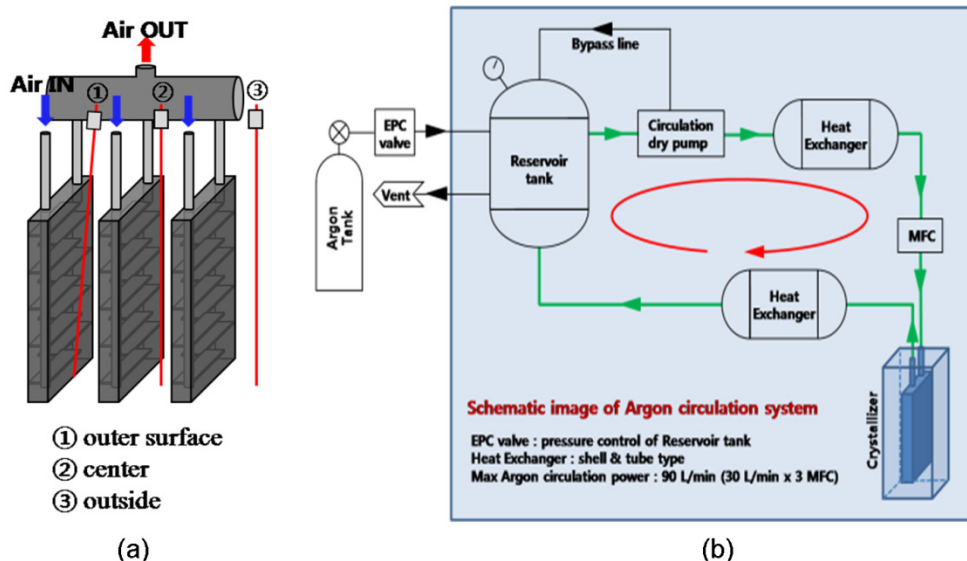


Figure 2.8. Schematic description of key components in a layer crystallization; thermocouple location for controlling layer crystallization (a) and Ar cooling/recirculation system (b).

### 2.3.2 Selective Distillation

Salt distillation is frequently used during pyroprocessing treatment of UNF to separate salt from the product of an electrolytic process. This concept was applied to recover pure salt from the mixture of lanthanide products and electrolyte. As another conceptual approach, selective distillation is possible to separate FPs from a waste salt. This selective distillation is possible due to differences in the vapor pressures of various metal chlorides. If there is a large difference in the vapor pressure, selective distillation provides an efficient means for the recovery of pure salt and separation of FPs.

Figure 2.9 shows the vapor pressure of various metal chlorides as a function of temperature. As shown in Figure 2.9, there are large vapor pressure differences between LiCl and BaCl<sub>2</sub> or SrCl<sub>2</sub>. This is a good condition for the application of selective distillation. Based on the vaporization results and the vapor pressures of BaCl<sub>2</sub> and SrCl<sub>2</sub>, vacuum distillation tests of LiCl- and LiCl-KCl-BaCl<sub>2</sub>-SrCl<sub>2</sub> systems were carried out using specific vacuum thermal gravimetric furnace equipment. BaCl<sub>2</sub> and SrCl<sub>2</sub> were very stable at 750~900°C and 1 Torr pressure. The vaporization tendency of LiCl (or LiCl-KCl)-BaCl<sub>2</sub>-SrCl<sub>2</sub> system seemed to be very similar to the pure LiCl (or LiCl-KCl eutectic salt) vaporization results. The results of the experiments indicated very little co-vaporization of BaCl<sub>2</sub> or SrCl<sub>2</sub> with LiCl (or LiCl-KCl eutectic salt) vapor (Eun et al., 2012a).

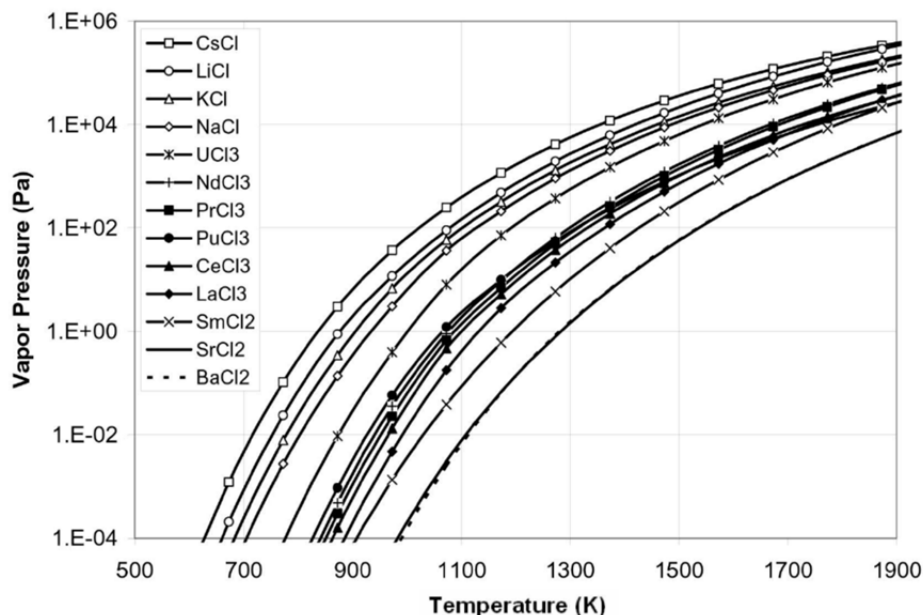


Figure 2.9. Vapor pressures for metal chlorides (Westphal et al., 2008).

A preliminary vaporization test of the  $\text{LiCl-KCl-NdCl}_3$  system was practiced to apply simple selective distillation to the separation of  $\text{RECl}_3$  from  $\text{LiCl-KCl-RECl}_3$  system. It was confirmed that the system was separated into a  $\text{LiCl-KCl}$  salt fraction and a  $\text{NdCl}_3$  fraction at  $750^\circ\text{C}$  and 0.5 Torr. However, the test required a relatively long operation time, and the co-vaporization of  $\text{NdCl}_3$  with  $\text{LiCl-KCl}$  was somewhat higher than that of  $\text{BaCl}_2$  or  $\text{SrCl}_2$ . Further tests will be performed to determine an efficient condition for the selective distillation of  $\text{LiCl-KCl-RECl}_3$  system.

For salt mixtures with small differences in vapor pressure, it is difficult to apply the selective distillation method. In this case, however, it is possible to convert FPs chlorides into compounds (i.e., oxides, oxychlorides, or phosphates) with higher melting temperatures or low volatilities, followed by distillation recovery of  $\text{LiCl}$  or  $\text{LiCl-KCl}$ .

A selective distillation test of  $\text{LiCl-KCl}$  eutectic salt containing rare-earth (RE) oxides or phosphates was performed in the lab-scale vacuum distillation system as shown in Figure 2.10 (Eun et al., 2012b). This distillation system can be operated in a closed loop condition with the operation subjected to the force of a temperature gradient at a reduced pressure. Experimental results indicate that approximately 99% of  $\text{LiCl-KCl}$  eutectic salt was recovered with a purity of 99.9%. The rare-earth oxides or phosphates remained in the sample boat in particle form of various sizes and with very little residual salt remaining.



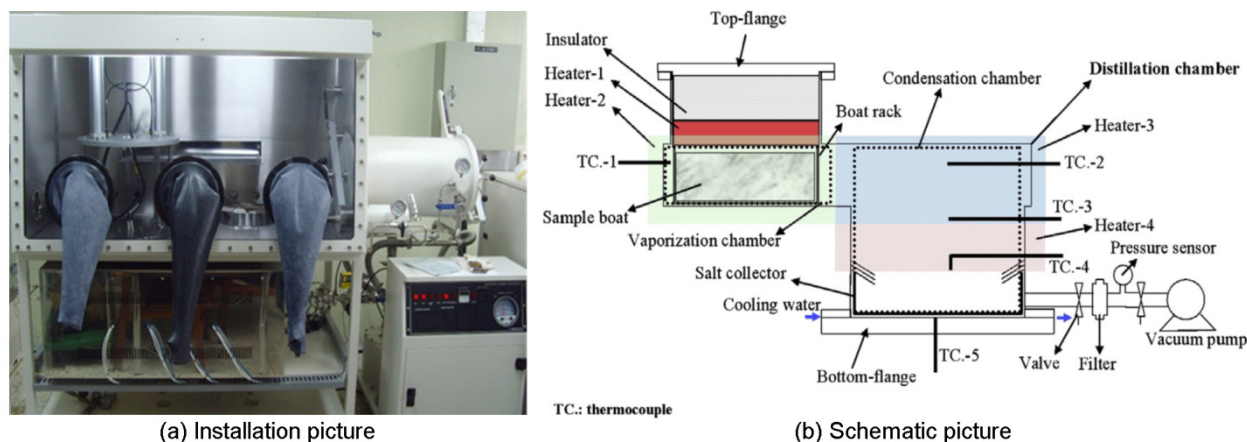


Figure 2.10. Lab-scale vacuum distillation system.

### 2.3.3 Selective Reaction (Precipitation)

In the selective precipitation process, lanthanide fission-product elements that accumulate in the LiCl-KCl eutectic salt are converted to insoluble precipitates by reaction with oxygen gas or phosphate agent in a precipitation step. After a full precipitation of these lanthanide oxides or phosphates, the eutectic salt waste is allowed to solidify and the salt ingot is separated by cutting into two layers: an upper pure (or purified) salt layer and a lower salt layer containing the fission product precipitate layer. The upper pure salt layer is then recycled back to the electrorefiner; whereas, the lower, contaminated layer undergoes distillation to separate the eutectic salt from the non-volatile lanthanide precipitate. The salt vapor is allowed to condense and then is collected for recycle back to the ER. Finally, all the remaining lanthanide precipitates are immobilized by fabricating into a durable waste form. By adopting the eutectic salt waste treatment technology, the amount of final wastes can be reduced drastically (Kim et al., 2008). This method has been performed to separate lanthanide elements from eutectic salt waste by using the lab-scale oxidative precipitation apparatus indicated at Figure 2.11 (maximum batch size: 4 kg/batch). The apparatus is consisted of three parts: an oxidative precipitation reactor, a solid salt separation device, and a layer separation device.

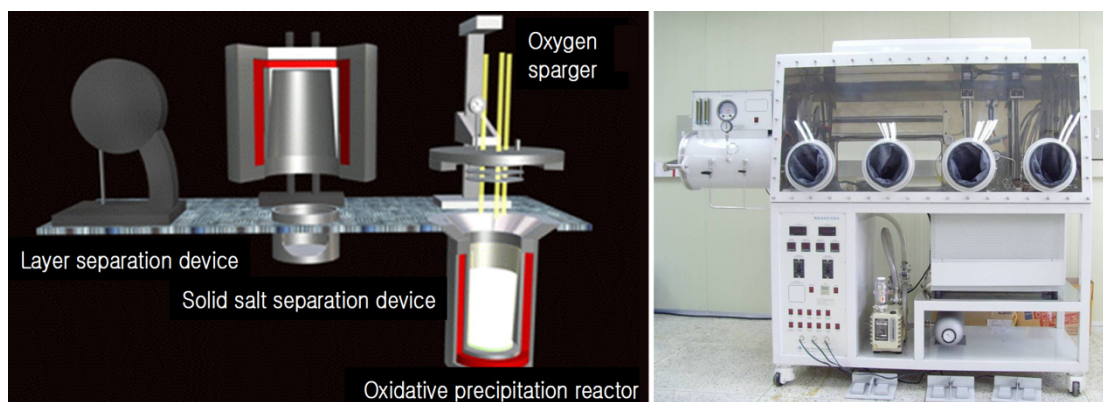
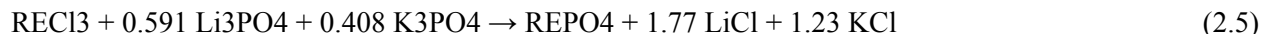


Figure 2.11. Lab-scale oxide precipitation apparatus.

For even oxygen sparging, three vertical-type sparger that has dozens of 2-mm ID holes in the bottom part of sparger was used. Due to severe corrosion during an oxygen sparging operation, the oxidation reaction was carried out in a tantalum crucible (Cho et al., 2006). In the oxygen sparging process, an even distribution of oxygen is a very important experimental variable. Rare-earth (lanthanide) oxide ( $\text{REO}_2$  or  $\text{RE}_2\text{O}_3$ ) or oxychloride ( $\text{REOCl}$ ) forms were the dominate reaction products when the oxygen potential of

the chemical reaction is between the rare-earth ion and oxygen ions under molten salt conditions. The formed oxide or oxychloride precipitates have very low solubility in the molten eutectic salt. The rare-earth precipitates were a mixture of oxychlorides, i.e., LaOCl, PrOCl, NdOCl, SmOCl, EuOCl, GdOCl and oxides, i.e., CeO<sub>2</sub>, PrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> (Cho et al., 2009).

Phosphate precipitation as a dry purification method has been researched for separating rare-earth fission products from waste salt owing to simple processing and ease of scale-up for large-scale operations. Using the phosphate precipitation method, eutectic waste salt containing rare-earth fission product elements that accumulate from the pyroprocessing of UNF can be also purified. The phosphate reactions of a rare-earth (RE) with Li<sub>3</sub>PO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub> are shown in Equations (2.3) and (2.4), respectively.



The use of a sole phosphate precipitant, Li<sub>3</sub>PO<sub>4</sub> or K<sub>3</sub>PO<sub>4</sub>, forms LiCl or KCl as a byproduct, which can change the original eutectic ratio. If the eutectic ratio change exceeds a certain extent, the reuse of purified eutectic waste salt by phosphate precipitation can cause problems for the normal operation of the electrochemical process. The eutectic ratio of LiCl and KCl salts are generated when stoichiometric amounts of Li<sub>3</sub>PO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub> are used (as in Equation 2.5). This increases the reusability of purified eutectic waste salt (Cho et al., 2013).

The selective precipitation process has advantages and disadvantages for large-scale operation. Almost all lanthanides in the LiCl-KCl salt can be separated and about 99% of the LiCl-KCl salt can be recovered and recycled in the electrolytic process. However, this process requires three or four unit processes, and the mechanical cutting of the pure and impure salt layers can generate significant contamination from the spread of salt particles. While the oxidation of lanthanides by sparging oxygen performed at 700~800°C and it is a very corrosive process, the method does not require accurate salt composition knowledge for complete precipitation and excess sparge oxygen simply diffused out of the salt.

Phosphate precipitation is a very easy process and is performed at a milder processing temperature range than distillation, i.e., 450~550°C. However, it is required that the initial concentration of lanthanide elements in the salt be known so that the excess metal phosphate, or its particulates as a precipitation agent, does not remain in the cleaned salt and interfere with subsequent process operations.

Phosphate or oxide conversion of lanthanide fission product elements in the salt involves somewhat complex processes to separate reaction products from the eutectic. Total distillation of the eutectic salt from lanthanide product can eliminate mechanical separation process of the purified salt from precipitated products.

### 3. PYROPROCESSING WASTE FORMS

Several waste forms have been developed for the metallic and salt waste streams generated during pyroprocessing. The role of the waste forms is to immobilize radionuclides for safe handling and disposal. The major challenge to immobilizing salt wastes is to avoid disrupting the physical and chemical integrity of the host phase(s) for the fission products due to the presence  $\text{Cl}^-$ . Although  $\text{Cl}^-$  is not a radiological concern, it must either be removed during treatment or be accommodated in the waste form without interfering with the formation of phases intended to immobilization of fission products. Dechlorination of waste salts was discussed in Section 2.3, but can also occur during waste form production. The following sections discuss approaches developed to immobilize waste salts in various waste forms. Section 3.1 presents the waste forms developed in the U.S. (at ANL) for EBR-II wastes that are being used as baseline materials for comparison of alternative waste forms. Sections 3.2 and 3.3 present advanced waste forms being developed in the ROK (at KAERI) and U.S. (at PNNL) for salt wastes.

#### 3.1 ANL Developed EBR-II Waste Forms

Waste forms were developed during the treatment of EBR-II sodium-bonded fuel. A glass-bonded sodalite material referred to as the ceramic waste form was developed to immobilize fission products that cumulated in waste electrorefiner (ER) salt and a alloyed waste form was developed for metallic wastes retained in the anode basket (Ebert, 2005; Bateman et al., 2007). These are considered as baseline waste forms for comparing advanced waste forms being developed with higher waste loadings and/or durabilities that are suitable for waste streams from advanced processing and waste treatment methods.

##### 3.1.1 Ceramic Waste Form

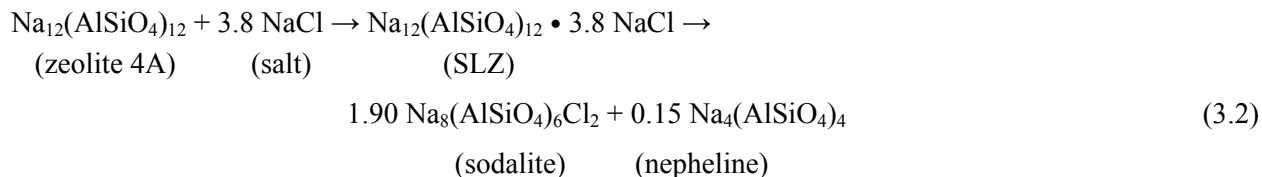
The glass-bonded sodalite (GBS) waste form was designed to incorporate  $\text{Cl}^-$  within the crystal structure of sodalite by reacting waste salt with zeolite 4A and encapsulating the sodalite within a durable glass. The current procedure for producing a GBS waste form involves two steps. Zeolite 4A is first pre-treated with molten salt to occlude the salt in the zeolite cage structure and place these reactants in intimate contact to facilitate the reaction to form sodalite, which is:



The salt-loaded zeolite is then mixed with crushed glass and heated to about 900°C to both generate sodalite and melt the glass to encapsulate it. The glass used to make the GBS waste form is referred to as binder glass because it is used to bind the sodalite particles in a physically stable monolithic waste form. It was later determined that only  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{I}^-$  from the salt waste are retained in the sodalite and the other waste salt constituents either dissolve into the glass or form inclusion phases. The small amounts of residual water in the zeolite were found to oxidize the most reactive salt constituents, which are primarily lanthanide and actinide chlorides, during the salt occlusion step. These oxide crystallites also form inclusion phases within the glass.



The reaction to form sodalite defines the stoichiometric amounts of zeolite and NaCl that form sodalite. Sub-stoichiometric amounts of zeolite result in the formation of halite inclusions and sub-stoichiometric amounts of NaCl result in the generation of nepheline as a zeolite decomposition product. For example, the target salt loading for the EBR-II CWF<sup>1</sup> (10.7 mass% salt in the salt-loaded zeolite) provides 3.8 NaCl per formula of zeolite and 0.15 moles of nepheline are formed per formula as:



The formation of nepheline is detrimental to HLW glasses because it removes equal amounts of Al and Si from the surrounding glass, which decreases the chemical durability of the residual glass. The formation of nepheline is not detrimental to the durability of the glass phase in the GBS waste form because sodalite or zeolite provides the Al and Si for nepheline formation, not the glass. However, the formation of nepheline does decrease the amount of sodalite that can be formed and waste salt that is immobilized. The presence of small amounts of halite inclusions does not significantly impact the waste form performance. I<sup>-</sup> substitutes for Cl<sup>-</sup> in both the sodalite and halite phases, but other cations in the salt waste do not substitute for Na. The other alkali metals (most significantly Li, K, and Cs) may instead react to form aluminosilicates that do not serve the purpose of containing Cl<sup>-</sup> and lower the waste loading.

Two aspects of halite inclusions observed in the glass provide insights into the formation process: the inclusions are nearly spherical and the halite crystals only partially fill the void volume. This indicates that the salt was molten when the glass solidified upon cooling. Glass is observed to have penetrated into the fine porosity between individual sodalite grains, but the sodalite domain sizes are consistent with that of the aggregated zeolite used in the process. This indicates the glass was molten when the sodalite formed.

The glass phase serves three crucial roles in generating an effective waste form. First, it encapsulates the submicrometer-sized lanthanide and actinide oxides that are produced during the occlusion step and the halite that forms during waste form processing in a durable material. Second, Na from the glass exchanges with alkali metal and alkaline earth cations in the salt (most importantly fission products) allowing their incorporation in the glass phase by maintaining charge balance as



Third, the exchanged Na provided by the glass serves as additional reactant to sequester chloride in either sodalite or halite. The Na-content of the glass is important to the chemical role of the glass phase and the amount of glass used to make the GBS waste form is important for the physical role of encapsulation.

The generation of sodalite in the waste form sequesters the chloride and iodide from the salt so a durable glass phase can form with the dissolved radionuclides and other constituents from the waste salt. The glass phase hosts the majority of radionuclides from the waste salt and provides the chemical durability that controls their release. The compositions of halite inclusions indicate the importance and efficiency of the Na provided by the binder glass exchanging with cations in the salt in that halite inclusions are found not to include radionuclides other than iodide. For example, waste forms made with salt wastes having very high Cs contents were found to generate Cs-pollucite in addition to sodalite and to have high Cs concentrations in the binder glass, but no CsCl inclusions or Cs-contaminated halite inclusions were detected (Lambregts and Frank, 2002; 2003).

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1. The specific composition of the GBS material developed for EBR-II salt wastes is referred to as the “ceramic waste form” (CWF) to distinguish it from other GBS materials made with higher waste loadings.

The  $\text{Cl}^-$  content of the salt determines the approximate amount of sodalite required in the waste form and the stoichiometry of sodalite defines the amount of Na required to sequester  $\text{Cl}^-$  in the salt as either sodalite or halite. Glass-bonded sodalite (with 8% salt loading) is a mature waste form that has been thoroughly tested as a waste form for waste eutectic salt. The matrix corrosion and radionuclide release behaviors are understood and a degradation model has been developed (Ebert, 2005). The results of scoping tests suggest that sufficiently durable waste forms can be made having waste salt loadings near 12 mass% by optimizing the relative amounts of salt, zeolite, and glass used to make the waste form and by using a binder glass having a sufficient amount of  $\text{Na}_2\text{O}$  that can exchange with cations in the waste salt. The combined benefits of optimizing the salt loading and the amount of binder glass used remains to be demonstrated.

The GBS may not be an efficient waste form for salt wastes having very low NaCl contents because most or all of the Na required to form sodalite must be provided by the binder glass or as an additive. Using the minimum amount of glass to encapsulate the sodalite made with the stoichiometric amount of NaCl requires a binder glass with enough Na to exchange with an equivalent amount of other alkali metal and alkaline earth metals. Work is in progress to develop such a binder glass.

### **3.1.2 Metal Waste Form**

The metal waste form was developed to utilize hardware and the cladding hulls from the fuel assembly that are added to the electrorefiner with the chopped fuel segments to alloy the residual metallic fuel wastes that were not dissolved into the processing salt during electrorefining. The hardware includes predominantly cladding hulls made of stainless steel or Zircaloy that remain on the fuel segments and contaminated plenums, end pieces, and ducts that may be included as waste to be processed. For waste streams composed predominantly of stainless steel hulls, the relative amounts of steel from the hardware and Zr in the fuel waste are sufficient to directly process the wastes at about  $1650^\circ\text{C}$  in a conventional furnace. This takes advantage of the Fe-15Zr eutectic composition in the binary system to facilitate waste form processing. Metallic constituents of the fuel waste (primarily Zr, Mo, Ru, Rh, Pd, and Tc) dissolve in the molten steel during processing and are incorporated into various intermetallic and solid solution phases as the mixture is cooled. Some constituents of the waste streams (e.g., Zr and Mo) serve as important components of the alloy phases that comprise the metallic waste form, whereas other radionuclides are present as substitutional or interstitial contaminants in those phases. The predominant phases are a  $\text{Fe}_2\text{Zr}$  intermetallic and an iron solid solution phase similar to steel, but small amounts of intermetallic phases of Fe or Zr alloyed with waste constituents can also form, such as  $\text{Fe}_2\text{Mo}$  and  $\text{Pd}_2\text{Zr}$ . Studies have shown that metal waste forms can be made from mixtures ranging from SS-1Zr to SS-42Zr with the resulting composites ranging from almost completely steel to almost completely intermetallic. The phases that form are important because they host the radionuclides in the waste: Tc is sequestered by the steel and  $\text{Fe}_2\text{Mo}$  intermetallic and actinides are sequestered by the  $\text{Fe}_2\text{Zr}$  and  $\text{Pd}_2\text{Zr}$  intermetallics. Waste forms must be formulated to ensure a sufficient amount of each host phase forms to accommodate all of the radionuclides in the waste stream reporting to that phase, which depends on the concentrations and distributions of non-active constituents. Most of the Cr from the steel remains in the iron solid solution phase and  $\text{Fe}_2\text{Mo}$  intermetallic, and much of the Ni is incorporated in the  $\text{Fe}_2\text{Zr}$  intermetallic. Other metals in the fuel waste (e.g., Ru and Rh) are distributed in all phases. The compositional flexibility of those host phases to substitute waste components is expected to accommodate variations in the waste streams that occur during continuous recycling operations. The Zr present in the fuel wastes (or present as an additive) acts as an oxygen getter during waste form processing that protects other metal elements from oxidation. Small amounts of  $\text{ZrO}_2$  are commonly formed on and near the surface of waste forms due to trace amounts of oxygen present in the furnace atmosphere. Scoping studies showed that oxide contents up to 30 vol% could be encapsulated within a multi-phase alloy waste form. Work is in progress to evaluate the corrosion behavior of metal-ceramic composites made with various oxides that may be present as contaminants in a metallic waste stream or added as a separate waste stream, including  $\text{ZrO}_2$ ,

lanthanide oxides, and actinide oxides. These oxides are sparingly soluble in the molten alloy during processing and are expected to remain inert in groundwater during storage.

The most important aspect of waste form performance is mitigating the release of radionuclides into groundwater in a disposal system over its regulated service life (see Section 4.3). The alloy and iron solid solution phases serve as physically, chemically, and radiologically durable host phases for the fuel wastes. The conceptual model for the release of radionuclides into solution as the metal waste form corrodes in a disposal system is a two-step process in which the metal atoms (including radionuclides) must first be oxidized to be freed from the surrounding atoms in the host alloy and the resulting ionic species must then be dissolved. Oxidation of metal atoms in the waste form occurs through electrochemical reactions with the contacting solution at a rate that can be modeled using electrode kinetics theory. Redox-sensitive solutes in the solution establish the corrosion potential at sites on the surface that controls the oxidation rates of the various metal atoms in each alloy. Usually, one alloy behaves anodically and dissolves while the other phases behave cathodically and do not dissolve. The oxidation states of the oxidized radionuclides in the dissolving phase determine their propensity for dissolution in the solution of interest (e.g., sparingly little  $\text{Tc}^{4+}$  will be released but essentially all  $\text{Tc}^{7+}$  will be released). The release of radionuclides into solution over time will be limited by the corrosion behavior of the host phase that encapsulates it. The most important limiting effect is the possible formation of a passivating surface layer that greatly moderates the oxidation rate and radionuclide release. The passivation of stainless steels is due to the formation of a Cr-oxide film that limits transport of oxidants to the bulk metal. This contributes to the durability of waste forms that are made by alloying fuel wastes with stainless steel components of the fuel assembly and other stainless steel hardware. Since Tc and Cr are distributed similarly, Tc-bearing phases are expected to be durable. On the other hand, actinides report to  $\text{Fe}_2\text{Zr}$  intermetallics, which do not contain Cr and do not passivate.

Waste form compositions near the Zr-8Fe eutectic have been proposed for waste streams dominated by Zircaloy cladding and hardware. Scoping studies showed that mixtures ranging from 50 to 92 mass% Zr generate assemblages with differing amounts of  $\text{Fe}_2\text{Zr}$ ,  $\text{Zr}_2\text{Fe}$  intermetallics and  $\alpha\text{-Zr}$  solid solution phases. The Zr-8SS mixture was recommended because composites dominated by intermetallics are more brittle than the Zr-rich alloys (Abraham et al. 1996). The researchers note that the distribution of waste constituents in these materials has not been evaluated. While U and transuranic elements will likely be incorporated into the  $\text{Fe}_2\text{Zr}$  intermetallics as observed in SS-15Zr materials, it is not known if Tc will be sequestered by the phases that form in Zr-8SS or be present as metallic Tc. Although Tc is expected to dissolve in the  $\beta\text{-Zr}$  present at the processing temperature, it may exsolve as that phase converts to  $\alpha\text{-Zr}$  when the waste form cools.

### 3.2 KAERI Developed Waste Forms

In the KAERI pyroprocessing treatment of oxide used fuel, two salt process streams, LiCl from fuel reduction, and LiCl-KCl from fuel electrorefining/electrowinning, will be treated to separate fission products and allow for recycle of the purified salt. 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 salt based on differences in vapor pressure of metal compounds, are under development. The waste salt containing fission products that result from the separation treatments will be processed into final waste forms. For fission product immobilization, possible waste forms include ceramics (such as the CWF), Te-glasses, lanthanide borosilicate glasses, and mineral phases such as apatite, monazite, zircon, hollandite, etc. to immobilize lanthanide fission products. Extensive research at KAERI has resulted in the development of two alternative waste forms referred to as SAP and ZIT. The SAP waste form was developed to immobilize FPs from waste salts. The ZIT waste form was developed to immobilize lanthanide fission products in the oxide, oxychloride, or phosphate form and is based on a monazite host phase.

### 3.2.1 SAP

For waste salt, the baseline approach is direct immobilization of salt by using a compatible ceramic or glass matrix with metal chlorides. This method was developed originally for eutectic salts from the metal fuel pyroprocessing. KAERI adapted another method which can remove the Cl-induced problems like low compatibility of metal chlorides with conventional glass matrices. The chemical conversion of metal borate or metal phosphate has been reported in the literature (Ikeda et al., 1995; Donze et al., 2000). KAERI also adapted the dechlorination reaction with a synthetic composite and applied it to the conversion of metal chloride under oxidative conditions with the release of Cl<sub>2</sub> gas. In the dechlorination method, the main problem is the treatment of chlorine gas stream which includes other radioactive halogens (iodine and bromine). Thus, chlorine gas is treated as a secondary radioactive waste. For this reason, KAERI has investigated a Cl capturing method using a metal oxide that can be converted into metal chloride for recycle in one of the electrolytes. Figure 3.1 shows the conceptual process for dechlorination and chlorination for solidification of waste salt.

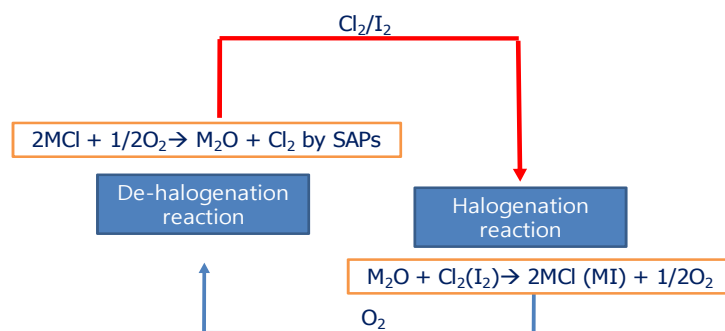
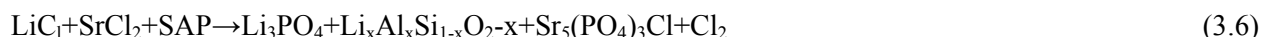
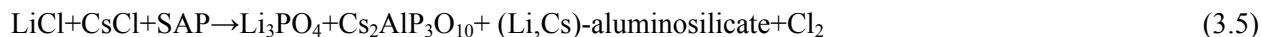


Figure 3.1. KAERI solidification process flow composing of dechlorination-chlorination reaction system for recycling Cl in waste salt.

This conceptual system could be realized by using a SAP (silica-alumina-phosphate) composite as a dechlorination agent of waste salt and a lithium oxide composite for Cl capture. Metal chloride waste is expected to be composed of about 90 mass% of alkali metal chlorides and below 10 mass% of FPs chlorides. The synthetic composite (SAP) was designed to form a conventional glass matrix when combined with alkali metal elements in waste salt. The initial SAP material was composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> for the dechlorination reaction and consolidation experiments. The inorganic composite is synthesized by a sol-gel process using TEOS (tetraethyl orthosilicate), AlCl<sub>3</sub> hydrate, H<sub>3</sub>PO<sub>4</sub> in a EtOH/H<sub>2</sub>O medium. The synthetic products have a sequential domain, -(SiO<sub>2</sub>)-(SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>)-(Al<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>)-(P<sub>2</sub>O<sub>5</sub>), in the tens of nm scale. The reaction is initiated with a breakage of the chemical bond containing phosphates when contacting with a molten salt. During the reaction, metal elements chemically interact with aluminosilicate, aluminophosphate and phosphate in the synthetic composite to produce metal compounds with high thermal stability (Park et al., 2008) as illustrated in Figure 3.2.



Based on the reactivity test, the SAP composite has higher reactivity for LiCl than NaCl or KCl. The proper reaction ratios (SAP/salt in weight) for LiCl and LiCl-KCl salts are about 2 and 3, respectively.

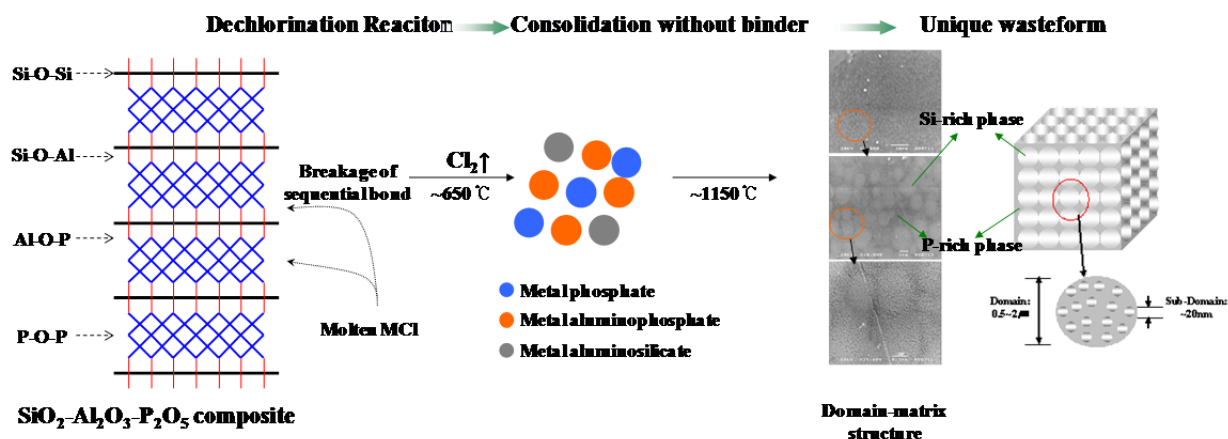


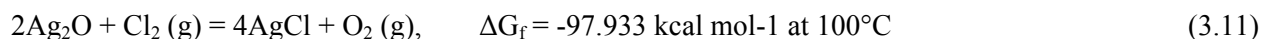
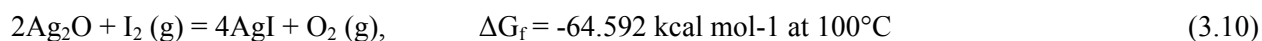
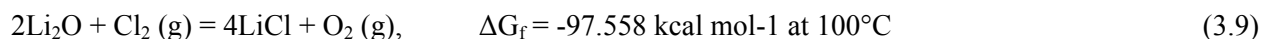
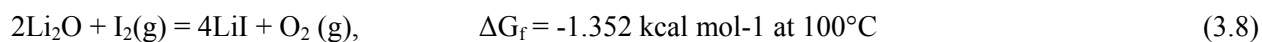
Figure 3.2. Description on the SAP dechlorination process for waste salt.

The dechlorination reaction temperature for LiCl salt is about over 610°C while LiCl-KCl salt has two reaction temperature ranges, about 400°C and 700°C. When phosphate present as a reaction initiator in the SAP composite contacts a molten salt, the dechlorination reaction is highly activated. The reaction experiments revealed that the proper reaction condition for LiCl and LiCl-KCl was 650°C for 24 hr, where >99% of waste salts could be dechlorinated. The reaction products could be consolidated at about 1150°C.

Chlorine gas generated from the reaction is easily captured by a metal oxide which is converted into metal chloride. All the alkali metal oxide, hydroxide or carbonate can react with chlorine. Among them, Li<sub>2</sub>O or K<sub>2</sub>O is more favorable in this system because oxide can provide an oxygen gas that is needed in the dechlorination reaction. KAERI are under investigation on the optimum oxide composite for capturing of chlorine gas. Initial test using Li<sub>2</sub>O-Li<sub>2</sub>O<sub>2</sub> composite revealed that the conversion of oxide into chloride (LiCl) is about 98%.

The behavior of Iodine as another halogen in waste salts is important during the dechlorination reaction. In LiCl salt from electro-reduction process after voloxidation, there would be no iodine. But, in the IRT demonstration waste salt or SFR pyro-waste contains some amount of iodine. During the dechlorination reaction at 650°C, almost all iodine is vaporized with chlorine and the halogen is captured by metal oxide to be recycled to the electrolytic process. However, in case of stepwise reaction for LiCl-KCl, iodine can be collected from main gas flow. Considering the melting temperature of LiCl-KCl salt and reactivity of metal chlorides, the dehalogenation reaction starts at about 360°C, where LiCl preferentially reacts with the composite. As the reaction goes on, the fraction of KCl in eutectic salt increases and at a second reaction temperature, about 650~750°C, KCl can be dechlorinated. From the experiments using LiI, KI, or CsI, it was found that almost iodine is vaporized below 450°C. This indicates that most of the iodine can be selectively vaporized, even though some fraction of chlorine in the salt is simultaneously released during the reaction below 450°C.

When SAP contacts with a molten salt, metal iodine in the salt is easily decomposed into iodine gas but the halogenation reaction with metal oxide is different. Chlorine is more reactive to lithium oxide or silver oxide, based on the Gibbs free energy of reaction for halogenations based on thermodynamic calculations (HSC Chemistry 6 - [www.hsc-chemistry.net](http://www.hsc-chemistry.net)).



This indicates that a sequential adsorption process can roughly separate iodine from main chlorine gas flow. In a first stage using lithium oxide as adsorbent, chlorine is preferentially reacted to produce LiCl and in the second stage using silver oxide, iodine and residual chlorine are reacted to produce silver halides. There is the potential for the improvement of iodine separation from chlorine flow by using some engineering concepts. As shown in Figure 3.3, KAERI suggested the conceptual process flow for the recycle of halogen and separation of iodine by using SAP, lithium oxide and transition metal oxides (Park et al., 2012).

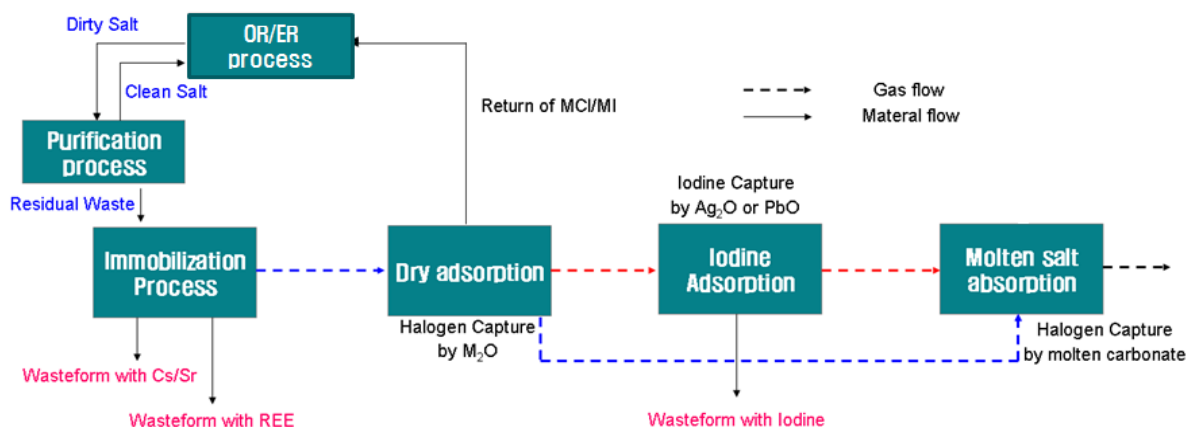


Figure 3.3. Conceptual process flow for the recycle of halogen and separation of iodine.

The composition of initial SAP composite for dechlorination test was adjusted to about 30 mass% SiO<sub>2</sub>, 26 mass% Al<sub>2</sub>O<sub>3</sub> and 44 mass% P<sub>2</sub>O<sub>5</sub>. The reaction product is composed of silicate and phosphate compounds. These two phases are not compatible with each other and it was not easy to obtain a monolithic form at proper consolidation temperature. For consolidation as a monolithic form, it needs a glass binder such as phosphate or silicate glass. KAERI selected a borosilicate glass as a chemical binder in that a conventional borosilicate glass is more durable than a sodium aluminophosphate glass. The SAP waste form by silicate binder has a morphology, “P-rich phase encapsulated by Si-rich phase” in a few μm range.

For higher reactivity and durability, Fe<sub>2</sub>O<sub>3</sub> as a well-known additive for a phosphate glass was added to the initial SAP composite. The modified SAP (M-SAP) prepared by a sol-gel process using Si, Al, P and Fe reagents has a higher reactivity, where proper M-SAP: salt ratio in weight basis was about 1.6 for LiCl, compared with SAP: salt, which was 2. Yet, it still needs glass binder for a monolithic form. Considering resultant composition of monolithic form after solidification by SAP and M-SAP, U-SAP composition without a glass binder for a monolithic form was established with the chemical composition of:

- LiCl waste: 44 mass% SiO<sub>2</sub>, 17 mass% Al<sub>2</sub>O<sub>3</sub>, 25 mass% P<sub>2</sub>O<sub>5</sub>, 11 mass% B<sub>2</sub>O<sub>3</sub>, 2 mass% Fe<sub>2</sub>O<sub>3</sub>
- LiCl-KCl waste: 42mass% SiO<sub>2</sub>, 20mass% Al<sub>2</sub>O<sub>3</sub>, 31mass% P<sub>2</sub>O<sub>5</sub>, 3mass% B<sub>2</sub>O<sub>3</sub>, 5 mass% Fe<sub>2</sub>O<sub>3</sub>

Table 3.1 shows the reaction ratios and the amount of waste form per salt. The value might be slightly changed, depending on the content of FPs.

Table 3.1. Solidification test results of three SAP composite for LiCl and LiCl-KCl salt.

SAP Composite	LiCl		LiCl-KCl		Remark
	Weight Ratio Salt/SAP/glass	Amount of SAP waste form per salt (kg/kg)	Weight Ratio Salt/SAP/glass	*Amount of SAP waste form per salt (kg/kg)	
<b>SAP</b> SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	1/2/1	3.39	1/3/1.9	5.41	Basic material system
<b>M-SAP</b> SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	1/1.5/0.6	2.49	1/2/1.3	3.61	Enhanced reactivity
<b>U-SAP</b> SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	1/2/0	2.39	1/2.8/0	3.32	No glass binder

\*The amount of waste form considered the vaporization of chlorine and oxidation of metal.

Initial SAP waste form has unique morphology at the  $\mu\text{m}$  scale. This is caused by the microstructure of the synthetic composite prepared by a sol-gel process. Virgin SAP consists of a particle (sol) that is an aggregate of sub-micron particle (about tens of nm). Such a structure in virgin SAP was not great changed even after the reaction and consolidation at 650~1150°C, where the structure size in sub-micron scales was preserved. The element distribution in SAP waste form could be found by some experiments on the phase separation from nm scale to cm scale. Strontium and iron are preferentially distributed into the P-rich phase, while cesium is preferentially located in the Si-rich phase. In tens of nm scale of SAP waste form, P-rich phase is encapsulated by Si-rich phase.

The chemical durability of initial SAP was tested by ASTM C1285-02, ASTM C1220-10, and ISO method 6961 – the result revealed that the P-rich phase encapsulated by Si-rich phase is more durable and its leach resistance is comparable to those of other waste forms (Park et al., 2011). As a newly developed waste form, it is important to define its characteristics such as morphology, elemental distribution, thermal properties, and chemical/physical properties. A series of experiments are planned to collect data related with the characteristics of U-SAP waste form.

### 3.2.2 Ln Waste Form

From the LiCl-KCl purification process such as a selective reaction or distillation, Ln precipitates (chloride, oxides, phosphate or some mixed compound) are expected to be present in the waste salt with a minor quantity of actinides. Considering the chemical form of lanthanides as a precipitates, a properly chosen host matrix or waste form is required. Lanthanide oxides, oxychlorides or phosphates are chemically durable and thermally stable. In this respect the waste loading and processing temperatures are more important than the selection of immobilization matrix.

In case of oxide form of lanthanides as a precipitate, a specific glass matrix, LABS (lanthanide borosilicate) glass is very useful in that it can be made with high loadings of lanthanide oxides (up to 50-60 mass%) and have high chemical durability. However, a high processing temperature of about 1450°C is required. For this reason, a ZnO-TiO<sub>2</sub> based matrix referred to as ZIT was developed that can be processed with the waste at lower temperatures (~1200°C), with high waste loading and reasonable chemical durability (Ahn et al., 2009). It was designed to immobilize lanthanides into a monazite (LnPO<sub>4</sub>) host phase that is encapsulated by an inert matrix in a monolithic form. The ZIT composite is prepared by mixing compounds (ZnO, TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaHPO<sub>4</sub>) and heat-treating at 600°C. The Ln waste form can be prepared by mixing the composite with Ln oxides (oxychlorides) then heat-treating at 1200°C. Based on the XRD and SEM-EDS analysis, Ln-rich phases are surrounded by Ti-rich and Zn-rich phases, where Zn has preferentially interacted with Si. Major crystalline phases are LnPO<sub>4</sub>, Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>SiO<sub>4</sub>. Waste loading of ZIT is about 40 mass% and has good leach resistance (Cho et al., 2011).

In a phosphate precipitation, the monazite form is the target host matrix of the ZIT waste form. Lanthanide phosphate (monazite) is a very stable compound and has a high density. The ZIT composition was modified in a way to lower the P content in the composite, but the modified ZIT composition was not good for phosphate precipitates, since the resulting ZIT waste form had greater porosity and showed relatively low density. Another approach was to use a durable phosphate glass (lead iron phosphate) to produce a monolithic waste form, referred to as the LIPS waste form. The monolithic waste form with 40 mass%  $\text{LnPO}_4$  was prepared at about 1000°C. In this case, macro pores were not detected but there is a relatively small pore in the top of the waste form. Based on the experimental results, it is believed that the tested binder or matrix cannot dissolve or solvate the phosphate at a given processing temperature and Ln phosphate is precipitated in the bottom of glass. Therefore, the LABS and ZIT waste forms are applicable for Ln oxides precipitates, but the LIPS waste form is no longer being considered as a viable waste form.

A general approach for waste form process consists of mixing a waste and solidification matrix followed by heat-treatment. In case of phosphate solidification process, mechanically mixing the immiscible (incompatible) materials is not effective for producing a homogeneous form because phosphate is not dissolved in the melt phase. If a phosphate precipitation agent is distributed in a matrix composed of a desirable solidification matrix, separation and solidification can be performed using one material and the resulting waste form would be uniform. For this, by using a Li(K)-based composite, Li(K)-Al-Si-P, a series of separation and consolidation tests are on-going to develop a monazite-based waste form. Following a similar concept, a Si-B-Al composite for producing LABS glass is under development.

### **3.3 PNNL Developed Waste Forms**

PNNL is investigating two primary candidate waste forms for pyroprocessing spent-salt: solution-derived sodalite and tellurite ( $\text{TeO}_2$ )-based glasses. Tellurite-based glasses can accommodate significantly more  $\text{Cl}^-$  in their structures than borosilicate glasses. Traditional CWF fabrication, as described in Section 3.1.1, is applicable for occlusion of the eutectic LiCl-KCl salt into the zeolite structure prior to conversion to sodalite. Fabrication of the CWF from oxide reduction, LiCl salt by occlusion into the zeolite mineral will not produce sodalite, but instead, results in the formation of various lithium aluminum silicates. PNNL has investigated alternative sodalite fabrication methods specifically from LiCl waste streams. Additionally, some preliminary work was done looking at LABS glasses as highly-loaded host waste form for the rare earth fission products in the LiCl-KCl salt.

#### **3.3.1 Tellurite Glass**

Tellurite glasses are being evaluated as a host for the LiCl-KCl eutectic salt waste components because this family of glasses showed promise for moderate-to-high loadings of up to ~15 mass% of the salt and had very high volumetric waste loadings due to the high density of these types of glasses ( $>5 \times 10^3 \text{ kg m}^{-3}$ ) (Crum et al., 2009).

Tellurite glass has many unique properties for a glassy waste form including high halide loadings over a wide range of single and mixed halides and high density (Vogel et al., 1974; Yakhkind and Chebotarev, 1980), which provides a higher volumetric waste loading capacity than the CWF. The primary drawback of a waste form made with these glasses is the high cost and limited commercial availability of  $\text{TeO}_2$ . Another drawback to the use of these glasses is that, since they have not previously been developed for waste form applications, many of the relevant engineering properties either remain unknown or are not yet well understood.

When tellurite glasses were first considered as a candidate waste form for the LiCl-KCl salt waste, a literature study revealed a number of promising tellurite glass compositions that might accommodate the mixed salt. Several different binary and ternary glasses were fabricated without salt and with 10 mass% of the eutectic salt simulants in a scoping study to evaluate the possible use as a waste form. These glasses had a wide range of properties including volatility during melting, density, and chemical durability



(Riley et al., 2010; Riley et al., 2012b). The most promising glass from this study was a lead tellurite glass with the composition of 78/22 TeO<sub>2</sub>/PbO (by mass) so this system was further explored in subsequent years.

Glasses made with different TeO<sub>2</sub>/PbO ratios were investigated as well to see if a higher loading could be achieved and the 78/22 TeO<sub>2</sub>/PbO composition (by mass) was deemed to be the ideal ratio for achieving maximum waste loading of ~13-14 mass% (at air quench rates) without phase separation (Figure 3.4) using the salt composition presented in Table 3.2.

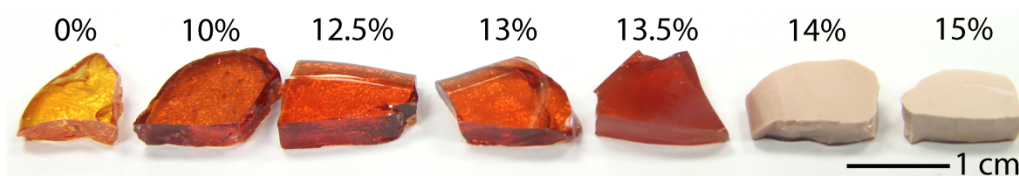


Figure 3.4. Picture ER salt-loaded glasses from a study performed in 2012-2014. The values listed above each glass are mass%’s.

Table 3.2. Reduced composition of ER salt.

Component	Mass%
KCl	52.51%
LiCl	40.64%
NdCl <sub>3</sub>	4.43%
YCl <sub>3</sub>	1.14%
LaCl <sub>3</sub>	0.50%
PrCl <sub>3</sub>	0.45%
SmCl <sub>3</sub>	0.33%
<b>SUM:</b>	<b>100.00%</b>

At the higher salt loadings of  $\geq 14$  mass%, the glass was observed to phase separate where salt droplets comprised mostly of the eutectic salt (with some Pb) precipitated as nanospheres within the glass (Figure 3.5). The structures of glasses made with different salt loadings were analyzed with <sup>207</sup>Pb and <sup>125</sup>Te nuclear magnetic resonance and a systematic shift in the bonding was observed around 14% waste loading (Figure 3.5). The results showed that when salt was added to the glass near the point at which phase separation is observed, the additional salt altered the glass structure and the glass-forming components (Pb in particular) started to interact with the salt differently than they interacted with the glass network. This was also evidenced by a measurable fraction of Pb in the salt droplets revealing that Pb was selectively removed from the glass network during this phase-separation process in the salt droplets. A more detailed summary of the work performed on this set of glasses was provided elsewhere (McCloy et al., 2013; Riley et al., 2014).

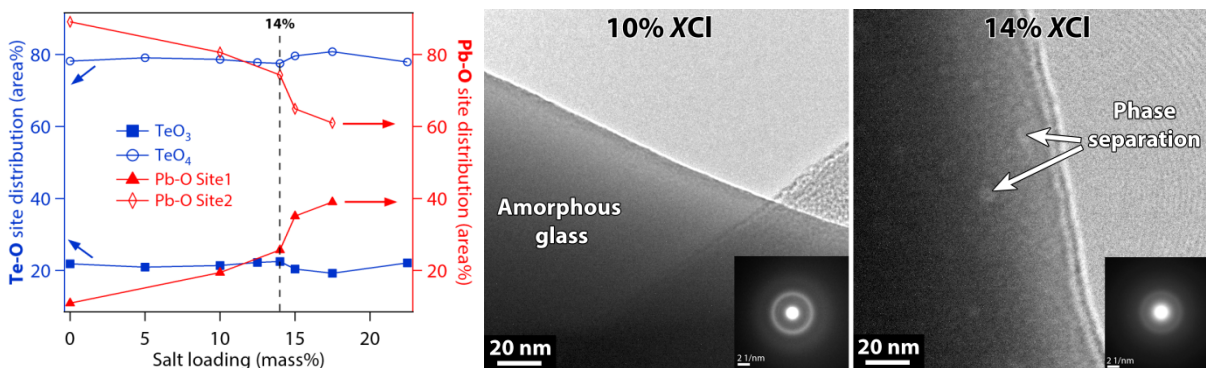


Figure 3.5. (left) Summary of results from  $^{125}\text{Te}$  and  $^{207}\text{Pb}$  NMR experiments showing structural tipping point near the maximum waste loading for the ER salt in tellurite glasses and (right) phase-separated salt droplets found above the salt solubility limit as observed with transmission electron microscopy (McCloy et al., 2013).

Recent work for the tellurite glasses focused on determining the salt loading limits for the LiCl-Li<sub>2</sub>O oxide reduction (OR) salt with fission products of CsCl, SrCl<sub>2</sub>, BaCl<sub>2</sub>, and LiI (see Table 3.3). The waste loading limit was determined to be between 15 and 18 mass% of OR salt based on X-ray diffraction and scanning electron microscopy analyses (Figure 3.6). Chemical durability testing is currently underway on these glasses up to 18% where the phase separation is not visible.

Table 3.3. Reduced composition of OR salt.

Component	Mass%
LiCl	96.27%
Li <sub>2</sub> O	1.97%
SrCl <sub>2</sub>	0.98%
LiI	0.04%
CsCl	0.74%
<b>SUM:</b>	<b>100.00%</b>

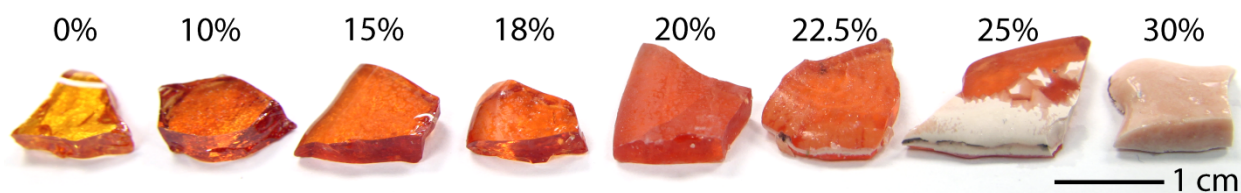


Figure 3.6. Picture of OR salt-loaded glasses. The value listed above each glass is mass%.

Additional work was done looking at the feasibility of immobilizing just the RECl<sub>3</sub> fission products in the baseline 78/22 TeO<sub>2</sub>/PbO tellurite glass. This study showed that the glass can accommodate at least 10 mass% of the mixed RECl<sub>3</sub> mixture, although higher loadings were not investigated.

### 3.3.2 Solution-Based Sodalite

The traditional CWF fabrication with zeolite 4A and waste salt, as described in Section 3.1.1, involves the occlusion of the waste salt into the zeolite structure prior to conversion to sodalite. However, attempted fabrication of the CWF using this approach with the oxide reduction ( $\text{LiCl-Li}_2\text{O}$ ) salt at both KAERI and INL were not successful at producing sodalite. Rather, this process resulted in the formation of various lithium aluminum silicates. Thus, if sodalite is to be made with OR salt, a different approach was needed. PNNL has investigated the application of alternative sodalite fabrication methods developed previously using the eutectic salt to the OR salt.

The solution-based approach to making sodalite has a number of differences from the traditional CWF approach. The primary difference is that the list of potential reactants is flexible but the primary drawback is that the process is aqueous-based and thus introduces some additional complications when implementing this in a hot cell environment. In our previous work, a number of different precursors were evaluated that provided products of different porosities, phase purities, etc. (Riley et al., 2012a; Lepry et al., 2013; Riley et al., 2015). These products were then mixed with a glass binder at different loadings and heat-treated. The heat-treatment can be done in any number of ways including cold-press-and-sintering, hot uniaxial pressing, hot isostatic pressing, or spark plasma sintering. In our experience, hot pressing techniques yielded products with lower porosities than materials made using the cold-press-and-sinter method, where reducing porosity and creating products with maximum sodalite phase purity were the primary goals of the work (Riley et al., 2012a; Lepry et al., 2013; Riley et al., 2015).

The solution-based synthesis approach for making sodalite with the OR salt proved successful, whereas the traditional CWF approach did not. The results from these studies showed that the solution-based approach provided an advantage for salts with high Li contents. However, one drawback to this approach is that lithium silicates were observed to form in addition to sodalite for all of the samples from the study with the OR salt (Figure 3.7). Although it is not chemically durable, this phase might not compromise the durability of a waste form if it is not interconnected throughout the product (Riley et al., 2015).

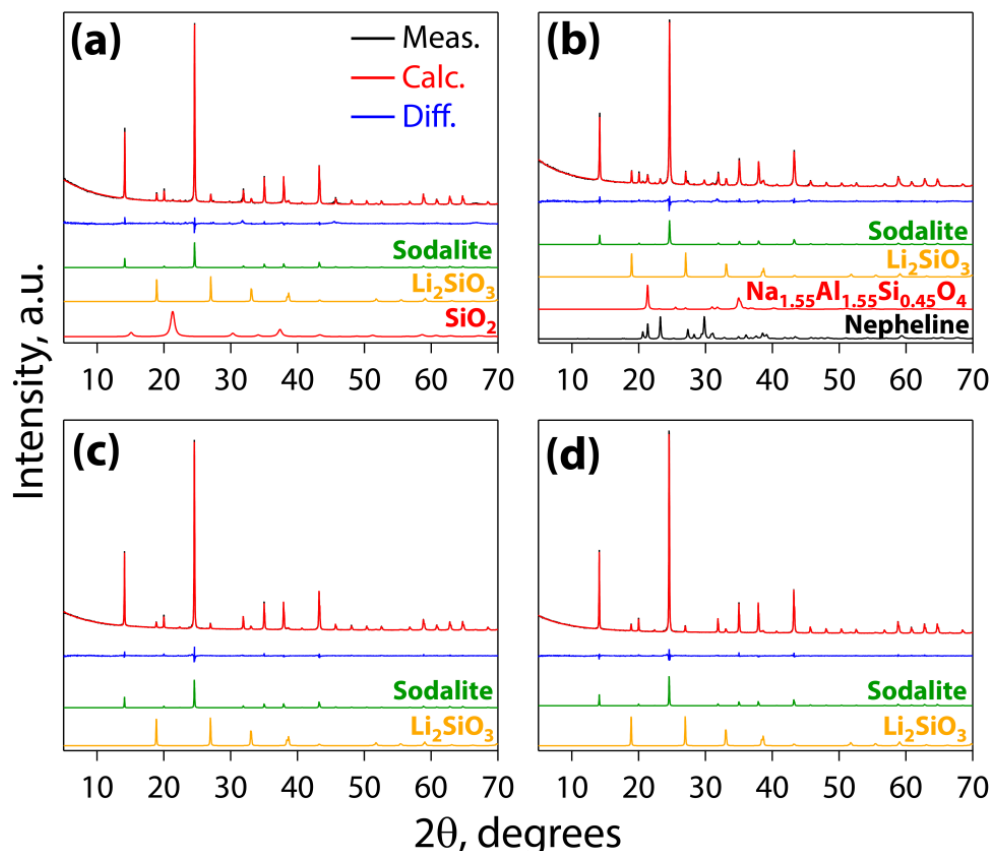


Figure 3.7. Rietveld refinements for (a) TE-SA-CA600-750, (b) CS-SA-CA600-750, (c) TE-SA-CA600-10GB-M-750, and (d) CS-SA-CA600-10GB-M-750, where “TE”=TEOS, “CS”=colloidal silica, “10GB” denotes 10 mass% of SA800 glass binder added, “SA”=NaAlO<sub>2</sub>, “CA600” denotes a calcination step at 600°C, “M”=mixed, and “750” denotes the temperature at which the pellets were fired (750°C) (Riley, 2015).

### 3.3.3 Lanthanide Borosilicate glass

LABS glasses were considered in the late 1980’s as a host matrix to transport actinides from Savannah River to Oak Ridge facilities and later evaluated by DOE as a possible waste form for recovered weapons plutonium. The performance of LABS glasses as high-level radioactive waste forms has been evaluated (Marra and Ebert, 2003; Marra et al., 2006; Ebert, 2006). In the event that the fission products in the ER salt can be completely converted from chlorides to oxides, this oxide waste stream could be immobilized into a LABS glass at very high waste loadings (>60 mass%). The final glass would likely be chemically durability and made at a very low cost. In practice, it is possible that not all of the fission product chlorides would be fully converted into lanthanide oxides, with some remaining as stable intermediate oxy-chlorides, e.g., LaCl<sub>3</sub> (LaOCl), SmCl<sub>3</sub> (SmOCl), and NdCl<sub>3</sub> (NdOCl) (Cho et al., 2006; Hayashi and Minato, 2005). To evaluate the efficiency of the conversion process for the ER salt, the mixture of lanthanide chlorides representing the fractions in the ER salt as is shown in Table 3.4 was heated at 300°C for 2 hr and air-quenched.

Table 3.4. Reduced FP composition in ER salt as chlorides.

Component	Mass%
NdCl <sub>3</sub>	64.71%
YCl <sub>3</sub>	16.70%
LaCl <sub>3</sub>	7.24%
PrCl <sub>3</sub>	6.52%
SmCl <sub>3</sub>	4.83%
<b>SUM:</b>	<b>100.00%</b>

The XRD pattern shows a complete conversion to oxychlorides (Figure 3.8). Hot-stage XRD was performed on an aliquot of this material and the results in Figure 3.8 show that the chloride salt was fully converted to a mixture of oxides at about 1100°C. It is suspected that chlorine gas was evolved.

In order to demonstrate that a glass could be made with this mixture, a glass containing 60 mass% lanthanum oxides corresponding to Table 3.4 where the non-waste component was based off of the Ln-01-2008 glass developed for mixed lanthanide wastes with 41.98% SiO<sub>2</sub>, 41.07% Al<sub>2</sub>O<sub>3</sub>, and 16.95% B<sub>2</sub>O<sub>3</sub> (by mass) (Youchak-Billings et al., 2008). The 60 mass% glass was melted at 1350°C for 1 hr, quenched, ground to a powder, remelted at 1400°C for 1 hr, and then quenched. The product of the second melt was completely homogeneous. It is likely that the glass could be completely homogenized with a single melt at ≥1400°C. Although the LABS glass is a viable option for lanthanide wastes, it is not being pursued as a waste form in either the ROK or U.S.

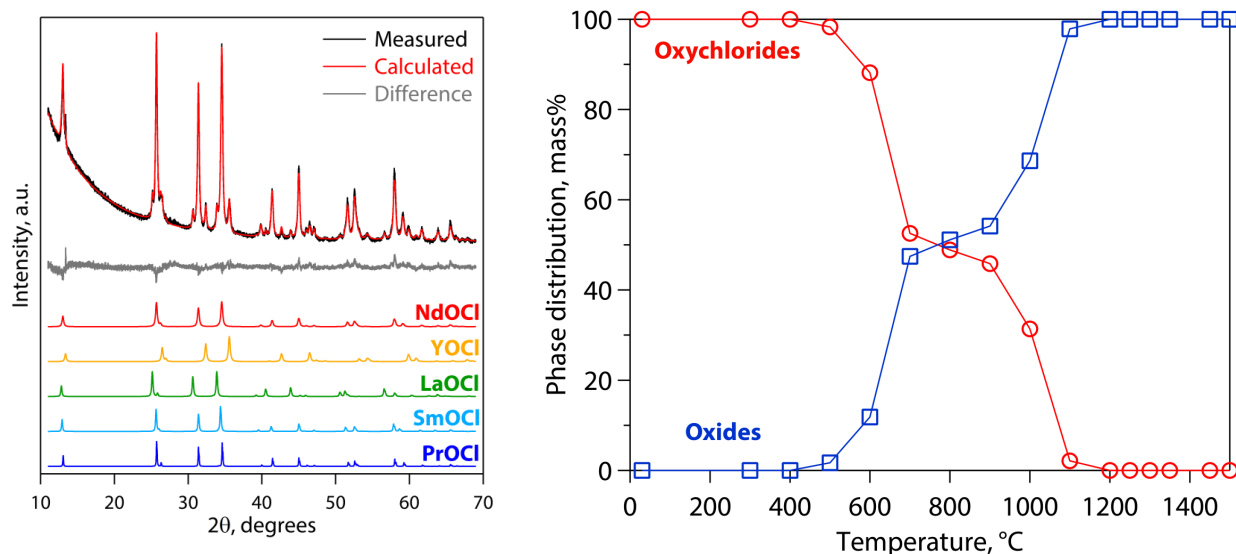


Figure 3.8. (left) XRD pattern of oxychlorides produced from a mixture of lanthanide fission product chlorides after a 300°C dwell for 2 hr. (right) Summary of results from hot-stage XRD run.

## 4. WASTE FORM PERFORMANCE

Waste forms are produced with the primary purpose of mitigating the release of radionuclides to the environment during handling, transport, and storage. Physical and radiological durability are important for handling and short-term interim storage; chemical durability is important for controlling the release of radionuclides during long disposal times in an engineered disposal system. The performance measure for a disposal system is meeting regulatory dose limits at its boundaries. Waste forms are the first of several engineered and natural barriers used to isolate long-lived radionuclides from the biosphere surrounding a disposal site. Although waste forms are developed to sequester radionuclides in durable phases, the ability to reliably predict radionuclide release as those phases degrade under the range of environmental conditions likely to occur over very long disposal times (or to provide an upper bound) is just as important. The chemical durability is a key component of waste form performance in a disposal system and provides the scientific basis for predicting radionuclide release throughout its service life.

When contacted by groundwater, the release of radionuclides from most waste forms is limited by the dissolution rates of the host phases which either break chemical bonds between the radionuclide and host phase or provide a pathway for their diffusional release. The rates at which radionuclides are released from the waste forms must be predicted to provide source terms for use in transport calculations to assess the overall performance of other barriers in the engineered disposal system and ensure that dose regulations will be met over the service life. Host phases are thermodynamically driven to either equilibrate with the solution or transform to more stable phases. Thermodynamically stable phases can equilibrate with the solution or be replaced by a more stable phase through a dissolution/precipitation mechanism. Thermodynamically metastable and unstable phases (including glasses) cannot equilibrate with the solution and the replacement by more stable phases is thermodynamically favored. However, many thermodynamically unstable phases are kinetically persistent due to slow transformation processes or the absence of a pathway for the transformation to occur. For example, glass cannot transform without reacting with water. Therefore, the performance of a waste form is determined primarily by the chemical corrosion resistance of the host phases under conditions relevant to long-term disposal rather than their thermodynamic stability. Corrosion is defined here as the degradation of a material due to interactions with its surroundings. In the thermodynamic sense, degradation lowers the total free energy in the system by transforming a less stable material to a more stable material. Corrosion resistance is due, in large part, to the slow kinetics of processes through which degradation occurs. Understanding the kinetics of processes that lead to corrosion of the host phases and the concomitant release of radionuclides from a waste form provides confidence in the radionuclide source terms calculated for long disposal times.

Incorporating radionuclides in thermodynamically stable phases during production is usually beneficial to waste form performance because there is little or no energetic drive to transform to a more stable material. However, this is impractical for most waste streams due to processing or economic reasons because most waste streams contain several radionuclides with different chemical properties. In most cases, one or more host phases in a waste form will be thermodynamically unstable in the disposal system and energetically driven to transform to a more stable phase or suite of phases. For example, aluminosilicate glasses are driven to transform to clays and zeolites, phosphate glasses are driven to transform to phosphate minerals, and steel/zirconium-based alloys are driven to transform to oxides. The stabilities of these host phases are due to the slow kinetics of processes leading to those transformations or the absence of reaction pathways. For example, lunar glasses have persisted for billions of years due to the lack of water necessary to provide the dissolution/precipitation pathway required for conversion. The kinetic persistence of metastable phases may provide superior chemical durability, since phases that are thermodynamically stable but highly soluble are not desirable host phases.

Models developed to provide radionuclide source term values based on the kinetics of waste form degradation represent the predominant processes affecting the host phase corrosion rates. Because the processes limiting the release of radionuclides may change as corrosion progresses, it is important to understand the corrosion behavior under the full range of conditions relevant to the disposal system in

order to ensure that the model represents the degradation behavior throughout the regulated service life. Tests conducted to support the development of source term models must be appropriate for the distribution of radionuclides between various host phases, the mode by which the radionuclides are released, and effects of environmental variables on the corrosion behavior of the host phases. Separate terms in degradation models may be required to track the releases of radionuclides distributed between different host phases in multi-phase waste forms that are released by different modes, such as from glass and ceramic host phases. Alternatively, one phase and one degradation mode may control the release of all radionuclides. For example, in GBS waste forms, a small fraction of the iodide inventory is present in the halite formed as inclusion phases in the glass during processing, which dissolves immediately when contacted by water. Except for those exposed at the surface of the waste form, the glass must dissolve before water can contact the halite inclusion phases. Likewise, the surrounding glass must dissolve before insoluble oxide inclusions can be released as colloids. Although the same processes control the corrosion behavior of the glass and sodalite phases, sodalite is a thermodynamically stable phase with a limited solubility but glass is not. While the dissolution rates of sodalite and the binder glass are similar in dilute solutions, sodalite dissolution will cease once the solution becomes saturated. Glass dissolution will contribute common ions to the solution (e.g., dissolved Na, Al, and Si) and accelerate saturation of the solution with respect to sodalite. In contrast, glass will continue to dissolve until no glass remains, albeit at a very low rate. The sodalite phase will be practically insoluble in the concentrated solutions expected to occur within a breached waste package as the halite and binder glass dissolve.

Confidence in the long-term predictions of waste form degradation models is derived from a scientific understanding of the mechanisms by which host phases degrade and radionuclides are released. That understanding is developed through laboratory tests that identify controlling processes for the relevant range of conditions, identify alteration phases, and identify and quantify the dependencies on environmental variables. The general hierarchy for testing is to first identify the host phases for key radionuclides and the likely release modes such as:

- Must the phase dissolve or are radionuclides leached?
- Will the phase equilibrate with the solution or continuously transform to alteration phases?
- Must the host phase and radionuclides be oxidized prior to release?
- Do the controlling processes change as the waste form surface and solution compositions evolve?

A conceptual model is developed based on insights from these tests. The conceptual model identifies the processes to be represented by the analytical model where oxidation, diffusion, and surface reactions, and environmental variables are likely to be important. Test methods appropriate for the degradation and release modes that have been determined are then used to measure the degradation kinetics. These results are used to develop analytical expressions that quantify the dependencies of host phase corrosion rates on environmental variables. Although the degradation rate of the host phase determines the availability of the radionuclide, radionuclide transport depends on various properties of the radionuclide in the solution.

The release rates of radionuclides used as source terms are usually calculated as the products of the waste form dissolution rate, the surface area of the waste form, and the inventory of the radionuclide of interest in the waste form. Calculating source terms for multi-phase waste forms in which radionuclides are distributed between several host phases that have different dissolution rates is more complicated and may require the use of an additional term to represent the relative efficiency of releasing each different radionuclide based on the properties of its host phase. Derivation of the radionuclide source terms from the waste form degradation model is probably the most important aspect of developing a waste form degradation model and the laboratory testing protocol that supports that model.

The overall dissolution behavior of all waste forms is expected to be different in dilute and concentrated solutions due to the changing contributions of the component phases as well as chemical and physical changes that occur at the waste form surface. Although tests are needed over the full range of

conditions to understand the degradation and radionuclide release processes, it is important that the model represent the behavior under conditions expected after long disposal times. Since the model parameters derived from test results are semi-empirical and may represent the net effect of several processes and dependencies, it is crucial that appropriate test methods and test conditions be used and that the results be interpreted based on a good understanding of the degradation mechanism. The responses of most test methods represent the early stages of waste form degradation with regard to the solution or the surface, and modifications to test methods may be needed to study the behavior of corroded waste form surfaces in concentrated solutions that are relevant to long disposal times. Confidence in long-term predictions requires both an understanding of the dominant degradation process and the method to measure the kinetics of that process under the appropriate conditions.

The consistency of waste form products is an important practical aspect of waste form performance because all of the testing conducted with prototype waste form materials and model parameterization based on those test results are intended to be applicable to a large number of waste forms produced with wastes from recycling operations conducted over many years. Confidence that waste forms made in the future will perform as well as the prototype materials used to develop the model is derived from the consistency of the assemblage of host phases and the flexibility of those phases to accommodate various amounts of waste constituents while maintaining chemical durability. Therefore, the test or analysis used to demonstrate product consistency must address a characteristic that can be related to waste form performance.

The study of waste form degradation is most advanced for borosilicate glass waste forms, as this is the currently the primary HLW waste form being produced in the U.S. and internationally. Many of the methods developed as part of glass waste form studies are being applied for the analysis of several advanced waste forms, including glass/ceramic composites, ceramic, and metallic waste forms with the goal of developing quantitative models for degradation and radionuclide (RN) release over a range of waste form compositions and disposal environments. Utilizing the benefits of improved waste form performance to lower the cost of engineering systems requires an understanding of the degradation behavior of waste forms in the disposal environment to establish the scientific underpinning for radionuclide source-term estimates, reduce the conservatism in performance estimates, and allow for development of optimized waste forms

## **4.1 Performance of Glass Waste Forms**

Glasses are thermodynamically driven to convert to a suite of alteration phases through various aqueous and solid-state processes. The rate at which the transformation occurs is limited by the kinetics of the processes involved for both glass dissolution and secondary phase precipitation, reaction pathways by which matter can be transferred from the glass to the secondary phases, and the availability of those secondary phases. Because radionuclides distributed throughout the glass structure become available for transport as the glass dissolves, either because bonds with the glass are broken or a diffusion path is established for radionuclides to be leached, predictions of the long-term release of radionuclides are based on the glass dissolution rate and the processes affecting that rate. Alkali borosilicate glasses have been studied extensively and degradation models are available, but the corrosion behaviors of phosphate and tellurite glasses are not as well-characterized. It is not certain if the reaction affinity for the dissolution of these glasses and transformation to secondary phases will be as dominant (and complicated) as it is for silicate glasses. That is, the dissolution rates of alkali borosilicate glasses may become coupled with the precipitation rates of secondary phases. In that case, the dissolution rate of a glass measured in short-term tests prior to secondary phase formation will not represent the rate when coupled to secondary phase precipitation rates. It remains to be determined if the dissolution rates of phosphate and tellurite glasses likewise become coupled with the precipitation rates of their secondary phases.



Dissolution models usually include separate terms to represent the kinetic controls on dissolution and moderating effects of the thermodynamic reaction affinity due to the overall free energy of the system and the mass transport of reactants and products to and from reaction sites. The key aspects of glass dissolution models are the dependences of the dissolution rate on the temperature and pH of the contacting solution and the dissolved concentrations of major glass constituents (e.g., dissolved Si, P, and Te or Pb for silicate, phosphate, and lead-tellurite glasses, respectively) and changes in the composition and structure of the near-surface region as corrosion proceeds. These may affect both the kinetic and thermodynamic terms of the dissolution model.

Lead-tellurite glasses are the only homogeneous glass waste forms being considered in Phase IIB, although salt inclusion phases may form in glasses produced with high waste loadings. It is important for long-term modeling to determine if dissolution of the lead-tellurite glass is controlling the release of radioactive constituents in the waste salt. For testing purposes, it is prudent to treat the lead-tellurite waste forms as if they contain salt inclusions and determine experimentally the effect (or lack of effect) that these have on the release of waste constituents.

## **4.2 Performance of Glass-Ceramic Waste Forms**

The dissolution behaviors of crystalline phases embedded within a glass phase are affected by the glass dissolution rate chemically through common ions in the solution and physically by the glass shielding those phases from water. Solid-state reactions between glass and crystalline phases will be important during waste form production when the phases in the waste form are generated, but are expected to be negligible as the waste form corrodes under disposal conditions. The primary interactions between phases in a waste form will occur through the solution. The crystalline phases are expected to dissolve and equilibrate with the solution simultaneously as the glass dissolves. Dissolved glass constituents that are also present in the crystalline phases (such as silica and phosphate) will accelerate the solution becoming saturated with respect to that crystalline phase and slow its dissolution. Changes in the pH due to the dissolution of one phase will affect the dissolution rates of other phases. This will probably be an important effect in the corrosion of SAP and ZIT waste forms due to the simultaneous dissolution of silicate and phosphate glasses and crystalline silicate and phosphate phases that comprise those waste forms. One of the challenges in testing multi-phase waste forms is relating changes in the solution composition to the degradation of individual phases. Unless a dissolved species is unique to a phase of interest, solids analyses are needed to supplement the solution analyses to distinguish the extents of dissolution for the constituent phases. Although the performance is based on the combined releases of radionuclides from all host phases, modeling that performance requires an understanding of the dissolution behaviors of the individual host phases.

For the purpose of the radionuclide source term model used for performance assessment, it is expected that the glass degradation model can be used for both glass and oxide phases waste forms by using empirical parameter values that represent the combined dissolution rates of all phases. That is, waste forms comprised of several phases that are distinguishable on the small scale (e.g., millimeters) can be represented as homogeneous materials for the purpose of modeling full-size waste form products. This is the basis of the continuum modeling approach, wherein the overall properties of a representative volume of a heterogeneous material are treated as representing a homogeneous material. In this case, the property of interest is radionuclide release. The test specimens used to determine the empirical model parameter values must provide the relative surface areas of the constituent phases representative of the waste form to upscale laboratory results to the full-size waste forms. This is best done by conducting tests with several specimens and pooling the results to generate a statistical range of parameter values. This imposes restrictions on the laboratory test methods that can be used to measure model parameters. In particular, methods such as the PCT that use crushed and sized materials are of limited use because the relative surface areas of the different phases in the sample tested are impossible to control or determine. (Nevertheless, PCTs and similar tests with crushed material provide valuable qualitative insights into corrosion mechanisms.) Instead, test methods using monolithic specimens are preferred because the phase

compositions and microstructure of the reacted surfaces can be characterized before and after testing to identify the reactive phases for comparisons made with solution results.

Two standardized tests that use monolithic test specimens are recommended for studying multi-phase waste forms. ASTM C1308 is a semi-static replacement test that measures dissolution over a series of intervals. The surface corrodes throughout the test but the solution composition remains nearly constant because the solution is frequently replaced with fresh leachant. This test can be used to distinguish the relative importance of surface dissolution reactions and mass transport through the surface corrosion layers that form (e.g., leaching). ASTM C1220 can be conducted as a series of static batch tests to track the evolution of the solution composition as the surface corrodes over long durations to complement the ASTM C1308 tests. Both ASTM C1308 and ASTM C1220 tests can be conducted using leachants that impose a particular pH or solute concentration on the system and at different temperatures to quantify these effects. Changes that occur in the solution composition and at the waste form surface during these tests can be used to assess and quantify the dissolution behaviors of the constituent phases. It is expected that fairly aggressive conditions may be required to differentiate the extents of dissolution of some phases (e.g., various ceramic phases), whereas the dissolution of other phases will be more obvious and could occur during specimen preparation (e.g., halite inclusions in CWF). Special methods may be required to avoid dissolving the salt during specimen preparation.

Although the performance of a multi-phase waste form depends on the combined release of radionuclides from all phases, the relationships between the constituent phases must be known to model the performance. The performance model will likely be simplified and not include separate terms for release from each host phase, but the simplified approach that is used must be justified. Therefore, laboratory tests are used to provide measures of both the overall radionuclide release rates and the contributions of each phase. Use of the conceptual model and testing protocol developed for the CWF is recommended for all waste forms for salt waste initially. Key aspects of this approach are to (1) perform specimen cutting, grinding, and polishing operations using absolute ethanol or an equivalent water-free solvent to mitigate dissolution of soluble inclusion phases, (2) characterize the microstructure of specimens before and after testing, and (3) relate elemental releases to host phases based on stoichiometry, when possible. Test methods that highlight differences in the dissolution rates and solubilities of the constituent phases are used to relate radionuclide releases to host phases. Results of previous tests with CWF materials are used to show the conceptual approach relating test results to corrosion behavior and radionuclide release.

For CWF materials, dissolution of halite inclusions releases Na and Cl, dissolution of sodalite releases Na, Cl, and Si, and dissolution of the binder glass releases Na, B, and Si. The B concentration provides a unique measure of the extent of glass dissolution, but Na, Cl, and Si are contributed by the dissolution of two or more phases. The solubility of sodalite is much lower than the solubilities of the binder glass and halite, and saturation of the solution with respect to sodalite occurs rapidly as these three phases dissolve. Figure 4.1 shows the surface of a CWF specimen reacted in an ASTM C1220 test with demineralized water conducted at 120°C for about 3 months. The surfaces of the sodalite and glass domains are pitted, but the interfacial regions have dissolved preferentially relative to both. This provides a useful measure of waste form degradation, but few insights into the mechanism needed to formulate a degradation model. Figure 4.2b shows a cross section of a specimen reacted in an ASTM C1308 test conducted with 110 ppm  $\text{H}_4\text{SiO}_4$  at 90°C for a total of about 6 months with 5 solution exchanges every 10 days followed by 6 solution exchanges every 21 days. The high Si content of the leachant was intended to demonstrate that saturation prevented the dissolution of sodalite but not the dissolution of the glass. As shown in Figure 4.2a, the B release was linear at  $0.20 \text{ g m}^{-2} \text{ d}^{-1}$  for the first 50 days at the higher exchange frequency of 10 days and  $0.13 \text{ g m}^{-2} \text{ d}^{-1}$  at the lower exchange frequency of 21 days. The linearity indicates glass is dissolving by surface dissolution and B is being released without mass transport limitations. The dependence of the B release rate (i.e., the glass dissolution rate) on the exchange interval is attributed to the small increase in dissolved Si concentration that occurs during each interval as a small

amount of glass dissolves. The glass dissolution rate decreases during each interval but is reset when the solution is replaced with fresh leachant; the total amount of glass that dissolves is greater over the longer exchange intervals and the average rate decreases. The original surface is indicated by the flat edges of the sodalite domains at the top of the micrograph in Figure 4.2b. Glass near the sodalite domains has a much higher concentration of halite inclusions that generate porosity and physically promote the amount of glass dissolved (and the dissolution rate) due to the greater surface area. The resulting surface with preferential dissolution at the sodalite/glass interface is consistent with that generated in the ASTM C1220 test.

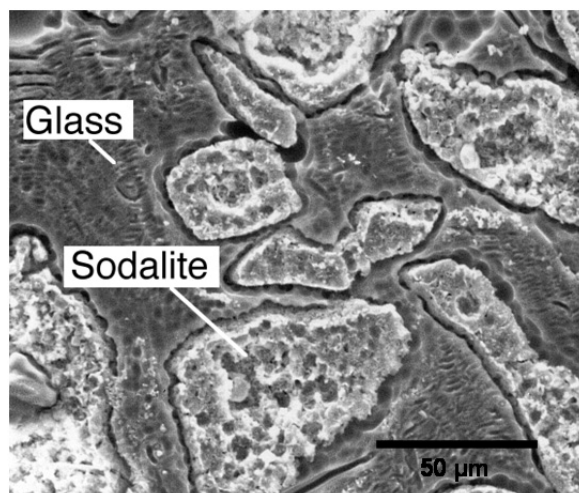
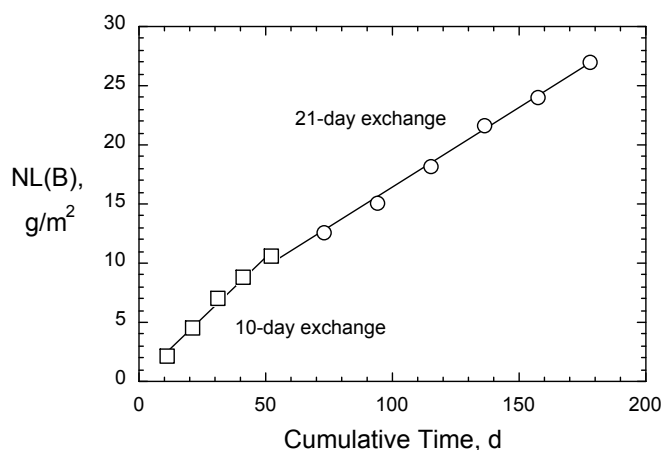
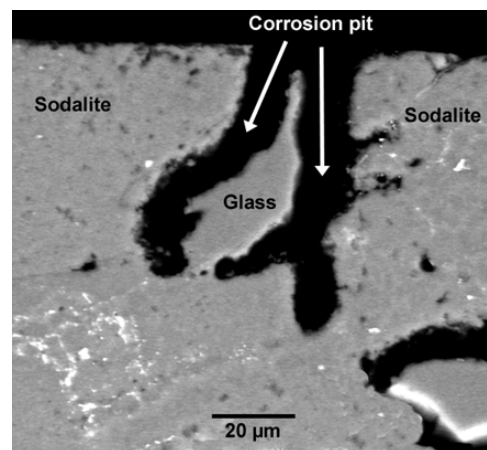


Figure 4.1. Corroded CWF from an ASTM C1220 conducted in demineralized water at 120°C for about 3 months (surface view).



(a)



(b)

Figure 4.2. Results of ASTM C1308 test conducted with 110 ppm  $\text{H}_4\text{SiO}_4$  at 90°C for about 6 months (a) cumulative B release, and (b) scanning electron micrograph of cross-sectioned specimen at end of test.

Additional insights regarding the degradation behavior of a multi-phase material are provided by comparing the solution analyses of tests conducted under different conditions with the compositions of the constituent phases. The halite release is characterized by solution results based on the immersion time and test conditions. Figure 4.3a and Figure 4.3b show the results of a series of ASTM C1220 and ASTM C1285 tests conducted with the CWF, respectively. The ASTM C1220 test provides a solution-dominated system that remains fairly dilute as the waste form dissolves; the test response is dominated by the waste

form dissolution kinetics. The ASTM C1285 test provides a waste form-dominated system in which the solution becomes highly concentrated as the waste form dissolves; the test response is dominated by solution feed-back and reaction affinity. The ASTM C1285 tests (PCTs) in Figure 4.3b show the same high Na and  $\text{Cl}^-$  concentrations for all test durations and an increase in the B concentration over time. The changes in solution composition can be related to dissolution behaviors of the constituent phases based on the composition and abundance of each phase. The CWF is composed of about 70 mass% sodalite, 25 mass% binder glass, and 3 mass% halite. Table 4.1 summarizes the mass fractions of the major elements in the halite, sodalite, and binder glass phases and their ratios.

Table 4.1. Elemental compositions of constituent phases and ratios.

Element	Halite	Sodalite	Binder Glass
Elemental Distribution in Each Phase (mass fraction)			
Na	0.074	0.849	0.077
Cl	0.258	0.742	—
Si	—	0.627	0.373
B	—	—	1.00
Elemental Concentration Ratios			
Cl/Na	3.5	0.87	—
Na/Si	—	1.3	0.2
B/Si	—	—	2.7
B/Na	—	—	13

The relatively high and constant  $\text{Cl}^-$  concentrations seen in Figure 4.3b are due primarily to halite dissolution, and the observation that  $NL_B > NL_{\text{Si}}$  indicates the extent of glass dissolution was greater than the extent of sodalite dissolution. The observation that the Cl/Na ratio in solution (which is 3.6) is about the same as that ratio in halite indicates the extent of sodalite dissolution is negligible; the ratio would be higher if an appreciable amount of sodalite had dissolved. (Note that the Si concentration generated in the 7-day PCT, which was  $32 \text{ mg L}^{-1}$ , was the basis for selecting a  $110 \text{ mg H}_4\text{SiO}_4 \text{ L}^{-1}$  leachant to mitigate sodalite dissolution in the ASTM C1308 tests discussed above.) In contrast, Figure 4.3a shows that the releases of all species increase over time in dilute solutions. The increasing  $\text{Cl}^-$  concentration is due primarily to sodalite dissolution (based on the Cl/Na ratio), and the observation that  $NL_B < NL_{\text{Si}} < NL_{\text{Na}}$  indicates more sodalite than glass has dissolved.

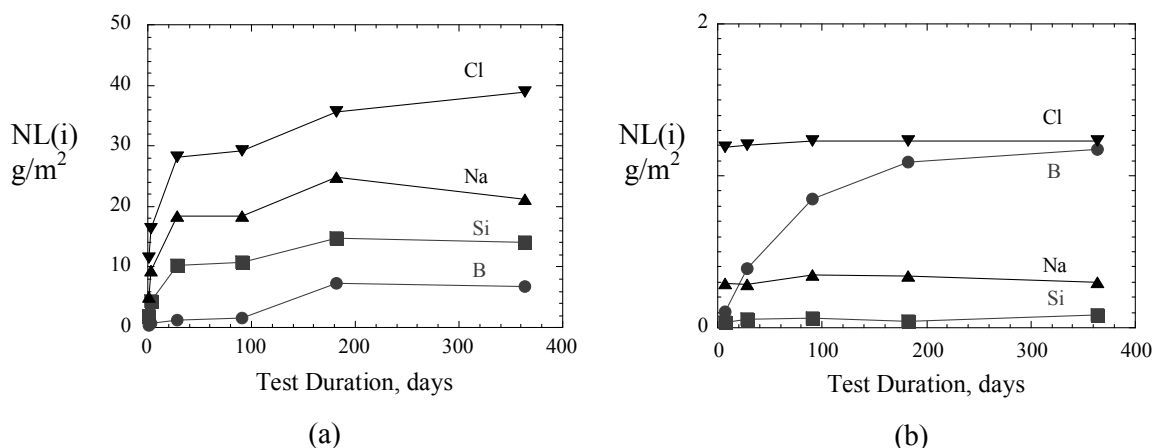


Figure 4.3. Solution results from (a) ASTM C1220 tests and (b) ASTM C1285 tests conducted in demineralized water at 90°C.

### 4.3 Performance of Metallic Waste Forms

Metallic waste forms are composites formulated to incorporate and immobilize radionuclides within several chemically durable intermetallic, alloy solid solution, and (possibly) oxide phases. Radionuclides are released upon oxidation reactions occurring at the alloy surfaces and dissolve according to solubility limits of the oxides that are formed. The degradation model for metallic waste forms includes terms representing (1) the oxidation rate of the host phase, which depends on the solution Eh and temperature, (2) the attenuating effect of passivation, which depends on the chloride concentration in the solution contacting the waste form, and (3) the propensity of the radionuclide to dissolve, which depends on its oxidation state and the solution composition. Electrode kinetic theory provides the scientific basis for modeling the electrochemical effects of environmental variables (primarily the temperature, Eh, pH, and  $\text{Cl}^-$ ) on the corrosion of each alloy that are combined with the chemical effects controlling the release of each oxidized radionuclide species to calculate the fractional release rate of each radionuclide (Ebert and Kolman, 2013).

The conceptual degradation model includes terms representing the fractional release rates of specific radionuclides for three processes including the bare surface oxidation rate, which depends on several environmental variables; attenuation of the bare surface oxidation rate by passivation, which develops as corrosion progresses and is poisoned by dissolved chloride (and other halides); and the solubility of the oxidized radionuclide (Ebert, 2014). An electrochemical test procedure was developed to determine the dependencies of these terms on key environmental factors and measure model parameter values for a range of alloy and solution compositions. The procedure tracks the corrosion current under potentiostatic conditions for about a month and is interrupted periodically so that the electrochemical characteristics of the evolving surface (e.g., daily) and the release of radionuclides into solution (e.g., weekly) can be measured. This is sufficient time for a stable surface layer to form and corrosion to attain a steady state rate.

The key issue for waste form performance is the long-term stability of the steady-state rate, whether it is controlled by active or passive corrosion behavior, and the long-term stability of the passivation layer. Although several corrosion tests developed for glass and ceramic waste forms have been applied to metallic waste forms in the past, consideration of the corrosion mechanism indicates the importance of oxidation reactions and the electrochemical effects on the corrosion rate that are not taken into account or controlled in those test methods. The recommended approach is to utilize electrochemical theory to provide confidence in the long-term predictions of a source term model and to parameterize the model based on empirical measurements made in electrochemically well-controlled systems. As discussed in the

previous section, the test specimens of multi-phase alloys must provide representative volumes to upscale the laboratory test results for use in field-scale calculations. This requires measurements with several specimens to provide a statistical distribution of parameter values.

#### **4.4 Experimental Approach**

The analyses in Section 4.2 illustrate the approach being taken to characterize the degradation behavior of other multi-phase waste forms composed of glass and ceramic phases, including the U-SAP, ZIT, and Pb-tellurite glass waste forms. The general approach is summarized below.

1. Measure compositions of host phases comprising the waste form including the distribution of radionuclides and the relative amounts of each phase in the waste form.
2. Conduct long-term PCT to generate solutions representing extensive corrosion and dissolution of the host phases. Use these solution compositions to formulate synthetic solutions to mitigate dissolution of selected phases for use in ASTM C1308 tests.
3. Conduct ASTM C1308 tests using several synthetic solutions to highlight and measure dissolution behavior of each constituent phase separately. Conduct tests at various exchange frequencies to discern degradation kinetics for important phases.
4. Conduct long-term ASTM C1220 tests in demineralized water to characterize degradation in solution-dominated system (solution and surface analyses). Use results from ASTM C1308 tests to interpret solution and solids analyses based on behaviors of separate phases.
5. Develop conceptual model for degradation behavior of composite waste form based on dissolution behaviors of important phases reacting in a common solution.

## 5. INTEGRATED RECYCLE TEST – WASTE STUDIES

The waste streams and their treatment processes are important aspects of evaluating the performance of pyroprocessing. There might be two approach concepts, (1) minimization of final waste volume by all means with appropriate performance and (2) optimizing waste treatment process for minimize highly radioactive secondary wastes. Waste treatment operations such as concentration, separation, or recycle would require disposing a smaller volume of waste than direct disposal. In general, processes with more unit operations are more difficult and generate more secondary wastes in a highly radioactive environment. Each treatment process has to be economically favorable by reducing the amount of waste for disposal and the footprint of a repository system.

Direct immobilization technologies such as compaction or melting of metal hardware waste, ceramic waste form (CWF) for LiCl-KCl waste, and alloy waste form for anode sludge waste from metal fuel ER process are well-defined by reliable investigation and data. Other technologies related with separation of FPs, recycle/reuse of recovered materials or LiCl waste immobilization have the potential to minimize the highly radioactive waste, though much work remains to be done. The status and remaining challenges for waste treatment technologies being developed to minimize final waste were described in Chapters 3 and 4. Some of these technologies will be demonstrated with actual fuel in the JFCS framework and the data will be used to evaluate the economic benefits.

### 5.1 Integrated Recycle Test

The Joint Fuel Cycle Study (JFCS) is a technical collaboration between the U.S. Department of Energy and the ROK Ministry of Science, ICT, and Future Planning, and Ministry of Knowledge Economy with three primary focuses:

- Definition and evaluation of fuel cycle options relevant to the Republic of Korea, including analysis and comparison of economics and relative benefits for each option (e.g., dry cask storage versus recycling)
- Joint investigation and demonstration of long-term safeguards and security technologies for fuel cycle options (e.g., used fuel transportation and storage)
- Evaluation of the technical, economic, and nonproliferation acceptability of electrochemical recycling of used fuel, with operations requiring potentially sensitive materials performed in U.S. facilities.

This is a 10-yr collaborative project that began in April 2011 and is divided into three technical phases with durations of approximately 2, 5 and 3 yrs with the time line for each phase shown in Figure 5.1.



Figure 5.1. Timeline for the three phase periods of the JFCS.

The JFCS organizational structure includes representatives from both countries and a steering committee that reviews, on an annual basis, the progress of the collaborative effort and approves work scope. The steering committee oversees the technical coordination committee that coordinates, integrates, and guides the execution of the approved work scope. The technical coordination committee oversees the three technical working groups: the Fuel Cycle Alternatives, Electrochemical Recycling, and Safeguards and Security. Each technical working group consists of joint, inter-disciplinary teams of technical experts who perform collaborative research and development activities.

The electrochemical recycling working group has three primary areas of research for the evaluation of the technical, economic, and non-proliferation acceptability of electrochemical recycling. These areas of research are:

- Laboratory-Scale Feasibility Study (LSFS)
  - A near-term study of the technical feasibility of electrochemical recycling that concluded at the end of Phase I
- Integrated Recycling Test (IRT)
  - A longer running evaluation of electrochemical recycling, focused on understanding the mass balances and reliability of integrated recycling
  - A test bed for Safeguards and Security evaluations
- Critical Gap Research and Development (CGR&D)
  - Research and development of identified technical gaps that may be critical to judging technical and/or economic feasibility at the end of the collaboration period.

The laboratory-scale feasibility study (LSFS) was started in 2011 and concluded in 2013 and is referred to as Phase I of the IRT. The purpose of the LSFS was to demonstrate each of the unit operations to be performed during the integrated recycle test at the gram-scale of material.

The integrated recycle test (IRT) was initiated in 2014 and is currently in the equipment design, testing, and hot cell installation phase. Commercial used nuclear fuel (UNF) operations are to begin early in 2015 with treatment later in the year. The overall IRT operation process is shown in Figure 5.2.

The IRT demonstration is focused mainly to provide data necessary to evaluate the performance of electrochemical pyroprocessing operations for the recovery of U and TRU. Key operations determining processing performance include (1) fuel recovery in head-end process, (2) oxide reduction efficiency and salt distillation performance in the OR process, (3) current efficiency, U recovery, and salt distillation performance in the ER process, (4) U/TRU recovery and Cd distillation performance in the U/TRU ER process, (5) residual U/TRU recovery and RE removal in drawdown process, and 6) fuel slug casting, fuel rodlet fabrication, effect of RE content in metal fuel produced with recovered U/TRU and irradiation performance. From such various works including a series of operation parameter tests, the performance and engineering factors related with the electrolytic process and U and U/TRU ingot fabrication will be successfully evaluated.

The critical gap research and development (CGR&D) phase of the project was initiated in 2011 and is expected to continue through Phase III of the JFCS to fill specific knowledge gaps that may jeopardize the success of the IRT.



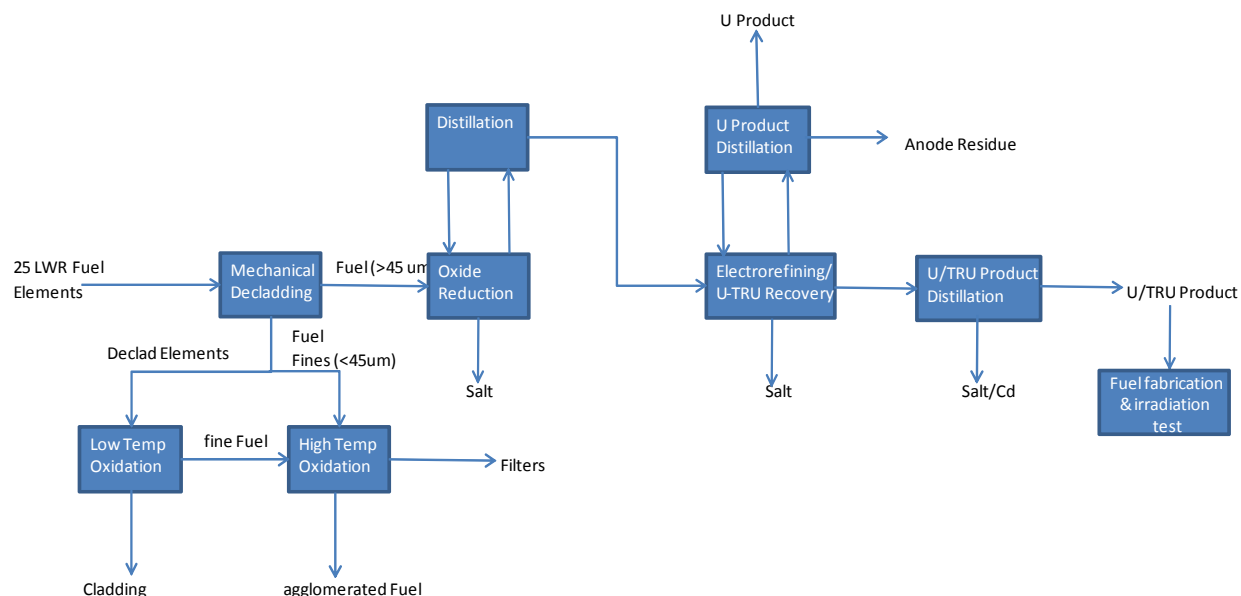


Figure 5.2. IRT flow of pyroprocessing LWR oxide fuel.

In the IRT experiments, about 25 fuel pins (~50 kg U in metal basis) will be treated following the tentative flow diagram in Figure 5.2. For successful test to recover U/TRU by using technologies suggested by U.S. and Korea, a plan composing of four campaigns has been established with the following objectives.

- **First campaign** to acquire initial U/TRU product using primary IRT unit operations with limited variations in conditions: about 17 batches (estimate)
- **Second and third campaigns** to acquire U/TRU product using graphite cathodes in ER process and processing data under various operation conditions in OR/ER processes
- **Fourth campaign** to investigate and perform the drawdown operation to recover remaining U/TRU in ER salt.

Two head-end thermal treatments of the oxide fuel will be performed to a limited extent. The first will involve low-temperature processing to assist in the recovery of fuel attached to cladding hulls. The second, high-temperature process will treat both the fuel recovered from the low-temperature process, and a portion of the fine fuel particles collected from mechanical decladding of the fuel. The high-temperature treatment of the two fuel fractions will remove semi-volatile FPs from the fuel to be trapped in a series of inorganic filters.

## 5.2 IRT Phase III Waste Stream Treatment

The waste streams generated from IRT demonstration will be somewhat different from the waste streams in the KAERI processing flowsheet in that the waste salt, anode sludge, and off-gas, will have different compositions and abundances that may affect the applicability of the KAERI waste treatment technologies to the IRT wastes. The main difference between the planned IRT demonstration and the KAERI process is the head-end process with or without high temperature processing. High-temperature treatment of fuel will remove cesium, technetium and iodine that are otherwise destined to be in the LiCl salt and anode sludge waste streams when a high temperature process is not applied. It is well known that iodine or tellurium in LiCl salt might corrode the platinum anode significantly as the reduction process goes on. The composition of uranium oxide in the anode sludge would be also dependent on the ER operating conditions, such as cut-off voltage and deposition time of uranium. This is because rare earth

oxides react with uranium metal to produce uranium oxide in the anode basket. Also, the amount of noble metals in the anode sludge depends on the amount of fuel treated in the ER process. It makes the composition of anode sludge variable, and changing the immobilization matrix composition or method in case of a high content of uranium oxides.

The amount of waste salt generated during pyroprocessing is one of main factors to determine the waste volume. KAERI's criteria for releasing the salt from the electrolytic process are based on the concentration of heat-generating FPs in LiCl salt and the limiting concentration of TRU in LiCl-KCl salt. However, the waste salt from IRT demonstration is expected to be released after treating 50 kg uranium. The FPs concentration in salt will be much lower than a normal operation in pyroprocessing, meaning that the salt can continue to be used as the electrolyte.

Considering these differences between IRT processing and KAERI processing, there are some limits on the evaluation of final waste from the pyroprocessing of used oxide fuel based on IRT waste demonstration alone. The realistic purpose of IRT waste demonstration is to evaluate the potential to minimize final waste volume or feasibility of using the treatment technologies in a hot cell environment.

A series of assumptions provided initial input values to calculate the mass-balance for the waste-stream processing flowsheet. The quantities and compositions of the process streams expressed in the flowsheet are the expected values at the completion of fuel dissolution and TRU removal (Phase II of the IRT) based on the following assumptions:

- Commercial, pressurized water reactor (PWR) oxide fuel: 50 kg (4.5 mass%  $^{235}\text{U}$ , 55,000 MWD/MTU, 10-yr cooling)
- Oxide reduction (OR) salt: 20 kg-LiCl
- Electrorefiner (ER) salt: 10 kg-LiCl/KCl eutectic
- Ideal pyroprocessing: 100% separation efficiency
- No high temperature treatment in head-end process
- Fission products (FPs) in LiCl salt: Cs, Rb, Sr, Ba, Eu, I, Te
- Fission products in LiCl/KCl salt: lanthanoid element FPs, actinides (after Ln/An separation process, <100 ppm)
- Noble metal fission products (Tc): retained in in universal basket.

In the proposed IRT process, commercial oxide fuel is mechanically removed from cladding and ground to small particle size ( $\sim 150\ \mu\text{m}$ ). The fuel is loaded into the universal basket and electrolysis is performed in the oxide reduction (OR) vessel. The basket is removed and OR salt distilled off the reduced fuel and the basket is transferred to the electrorefiner (ER) where the fuel is dissolved. After fuel dissolution, the universal basket is removed, ER salt is distilled off, and the basket is reloaded with new fuel for processing in the OR vessel to repeat the process. The distilled salts with fission products are returned to the appropriate OR or ER vessel. It is expected that 20 to 25 OR/ER cycles will be required to treat all 50 kg of used fuel.

For the waste-stream flowsheet assumptions listed above, no off-gas or elevated temperature treatment is performed and all fission products enter salt or metallic waste streams. Group I and II element fission products (i.e., Rb, Cs, Sr, and Ba) accumulate in the OR salt along with iodine, europium and tellurium fission products. The lanthanoid (or rare earth) element fission products and residual actinides accumulate in the ER salt. The noble metal fission products (Mo, Tc, Ru, Rh, Pd, etc.), which are present as the epsilon phases in used oxide fuel, remain in the universal basket and cumulate in the particle trap at the bottom of the basket. Another waste stream containing alloying agents such as Sn, Fe, and Mo may be generated during Zircaloy cladding recycle. A depiction of the “basic” waste stream process expected during Phase II of the IRT along with proposed waste forms is shown in Figure 5.3.

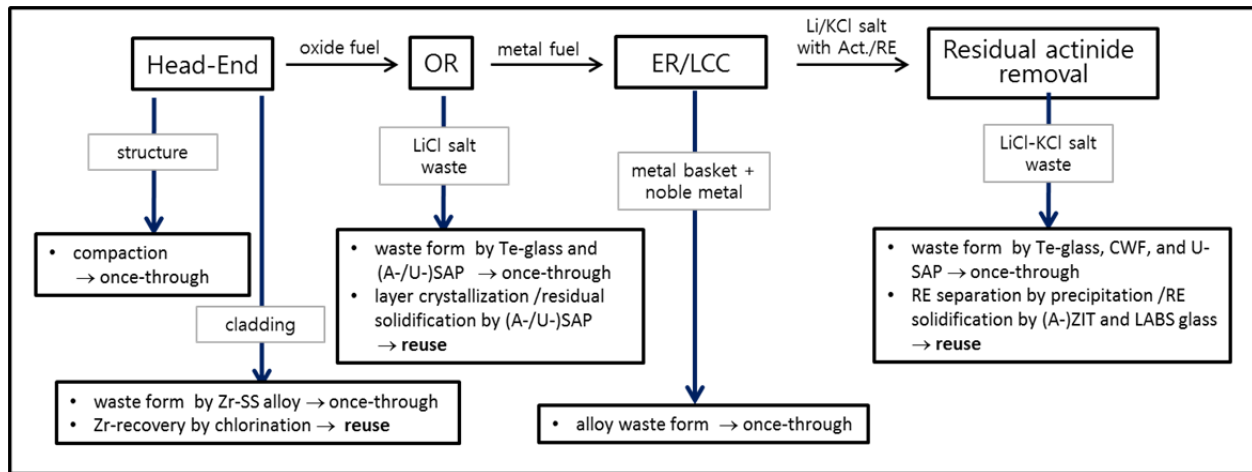


Figure 5.3. “Basic” process stream description for the IRT with waste streams and waste forms proposed for Phase III of the IRT.

The waste stream, mass-balance flowsheet is an Excel based spread sheet that calculates final (end of Phase II) fission-product compositions in the various waste streams as shown as the group fission products in the various waste streams in Figure 5.4. Estimated waste form volumes with assumed waste loadings are also calculated and indicated on the flowsheet. This waste stream flowsheet was used to determine waste treatment options being evaluated for use in Phase III of the IRT.

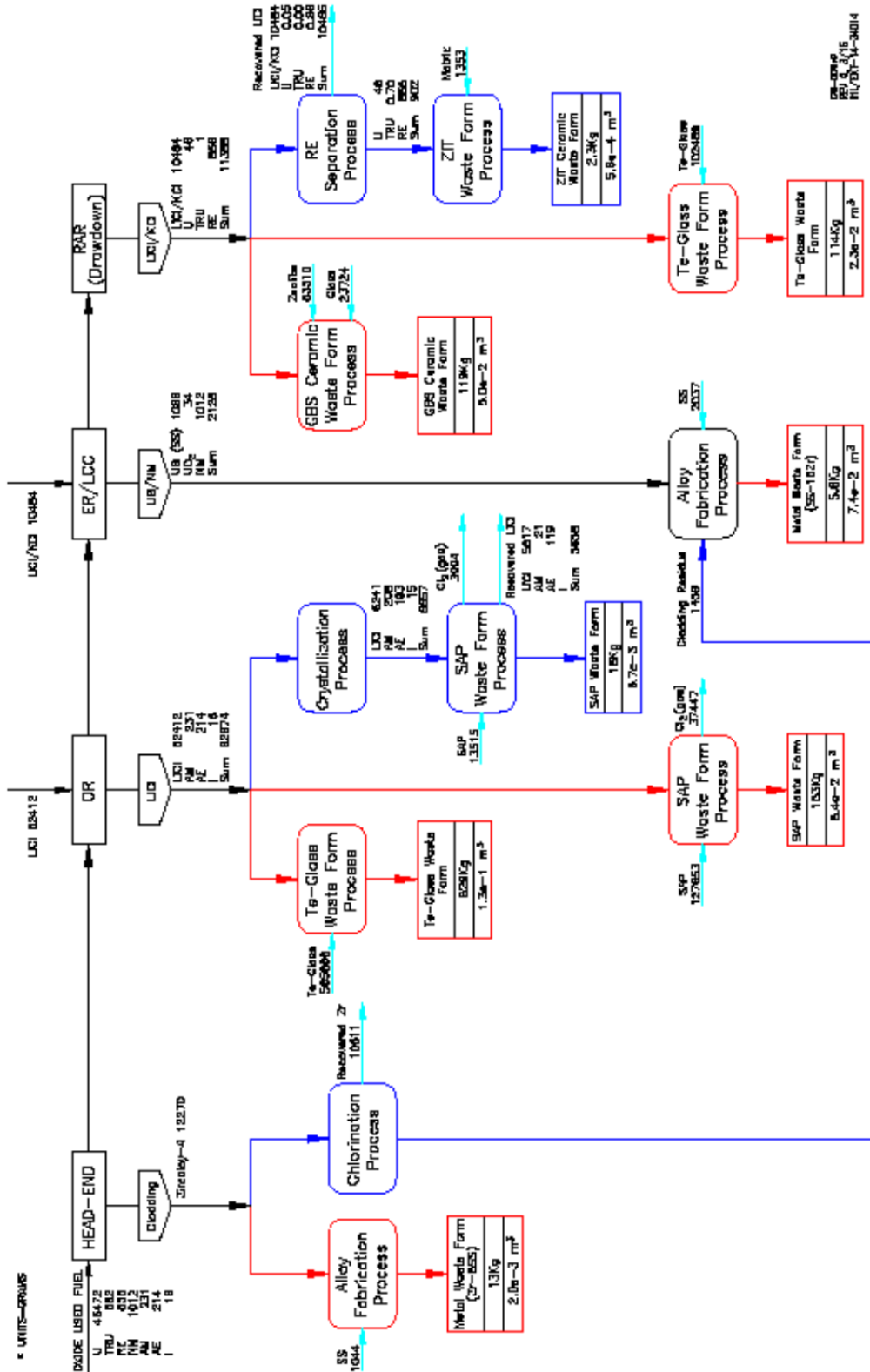


Figure 5.4. Waste steam flowsheet and proposed waste forms for Phase III of the IRT (red: once-through, blue: recycle).

### 5.3 IRT Phase III Waste Form Selection

The IRT waste demonstration provides an opportunity to evaluate the treatment methods for waste minimization discussed in Section 0, including the technical compatibility with a hot cell environment and compare optional waste forms available for some of the waste streams identified in Figure 5.3. Considering that the state of waste streams will depend on the fuel treatment process options that are used, the efficiency of the process, and waste treatment method, the waste stream flow sheet described in Figure 5.3 provides tentative compositions and flow based on the some proper assumptions. The main activities to minimize waste volumes are Zr recovery and electrolyte recycling and the simplest path is the direct immobilization or solidification of the waste streams. The optional waste forms have some advantages and disadvantages for immobilization of specific residual wastes.

First, three separation technologies for waste salt purification need to be performed: melt crystallization, selective distillation, and selective precipitation. Waste salt treatment is the main issue for pyroprocessing. The efficiency of salt purification on the recycling salt for minimizing final waste volume depends on the composition or concentration of FPs in the salt, which is affected by the fuel pre-treatment options and the efficiencies of the electrolytic processes. Therefore, the amount of final waste depends on the separation or concentration schemes for LiCl and LiCl-KCl wastes. In order to find the best way to lower the final waste volume, distribution data for FPs and TRU in each separation process with actual fuel are necessary.

Second, Zr recovery process as an alternative technology to direct disposal for minimizing metal waste is necessary to be performed to evaluate whether it has the potential to adequately separate pure zirconium from the cladding hulls or not. For this, it is required to collect data to determine the Zr recovery yield and the distributions of FPs and TRU in the product.

Third, it is necessary to evaluate some waste treatment methods using surrogates or by using results in the literature. Treatment of hardware from used nuclear fuel assemblies is not an issue in the IRT waste demonstration. There are many reliable data and methods related with disassembly parts for evaluation. Off-gas capturing processes or equipment for fuel pretreatment or OR/ER processes during the IRT works can be used to evaluate the ability to capture or prevent the volatile gases from distributing into the hot cell. The captured off-gas waste and capture media is not appropriate to perform the immobilization tests because they will not have representative amounts of volatile radionuclides in the waste. The filters from OR/ER process is considered as a secondary waste, not a main waste in a pyroprocessing. The filter waste from the off-gas system during the high temperature process has not had a matured immobilization method up to now, even though some methods are suggested. Therefore, evaluation of some wastes is desirable to use data from surrogate tests or literature until the suggested technologies will have matured in near future.

Implementations of the waste treatments for each waste stream suggested in Figure 5.3 would have limitations due to the state of IRT waste and the results may not be support the final selection of a treatment method. However, the IRT waste demonstration will provide some results to evaluate the compatibility of waste treatment technology with specific wastes from a pyroprocessing. This enables the researchers to estimate the characteristics of final waste such as volume, activity, heat generation, etc.

Waste forms will be recommended for use in the Phase III demonstration based on confidence that they (1) can be successfully produced with the waste streams that are generated during the demonstration and consistently produced in practice, and (2) can be demonstrated to perform acceptably in a disposal system based on an understanding of the degradation process and the ability to measure and model it. Work done to-date has addressed the production of potential waste forms with specific waste streams and provided a good understanding of the corrosion behaviors of some waste forms. The objective of the Phase IIB waste form studies is to supplement the available testing and modeling results to provide confidence that those waste forms can (after further testing and modeling) be shown to meet performance requirements for waste disposal. That will be done by showing how test responses are related to the

conceptual degradation models that are the basis for the performance models. The Phase IIB results will provide a basis to identify tests that can be used to evaluate the performance of each waste form that is recommended to be made in Phase III. This will include a conceptual model of waste form degradation by which the performance is evaluated, test methods used to quantify a measure of the performance, and a threshold to evaluate the adequacy of the measured performance.

The waste forms identified in the flowsheet (Figure 5.4) have been developed to immobilize waste streams similar to those predicted to be generated the IRT demonstration. The two primary technical gaps impacting technical assessments of the suitability of each waste form for one or more waste stream are (1) the presently limited understanding of the degradation mechanism that is necessary to reliably predict long-term performance, and (2) adequate demonstration of the capacity to accommodate the waste stream at acceptable waste loadings. The current state of understanding and remaining information gaps being addressed in the on-going Phase II activities with each of the waste forms proposed for one or more waste stream (listed in parentheses) are summarized below.

### **5.3.1 Metallic Waste Form (Head End OP-1; ER OP-1; ER OP-2)**

**Waste streams.** Stainless steel or zirconium alloys as cladding or other assembly hardware, metallic fuel waste constituents, and mixed metal/oxide wastes from cladding recycle.

**Objectives/critical gaps.** Minimize amounts of steel used to alloy Zircaloy wastes and metallic fuel wastes. Demonstrate capacity to accommodate oxide-bearing waste streams from Zr recycle operations.

**Comments.** The fundamental degradation behavior of metallic waste forms has been measured with specially-designed electrochemical dissolution tests and a corrosion model is being developed under the auspices of the DOE FCRD program.

**Recommended activities.** Produce alloys with oxide-bearing surrogate waste streams to demonstrate feasible waste form compositions and with various amounts of steel and zirconium to optimize alloy composition for Zircaloy waste streams.

### **5.3.2 Ceramic Waste Form (RAR OP-1)**

**Waste stream.** LiCl/KCl eutectic salt from ER with residual U, TRU, RE after drawdown

**Objectives/critical gap.** Maximize waste loading.

**Comments.** The degradation behavior of CWF materials has been sufficiently well characterized with standard laboratory dissolution tests. Additional tests are in progress under the auspices of the DOE FCRD program to demonstrate higher waste loadings can be attained.

**Recommended activities.** None.

### **5.3.3 SAP Waste Form (OR OP-2; OP-3-2)**

**Waste streams.** LiCl salt from OR with residual AM, AE, and I with and without salt purification step.

**Objectives/critical gaps.** Determine degradation mechanism and rate law. Maximize waste loading.

**Comments.** The fundamental degradation behavior of SAP waste forms has been measured with standard laboratory dissolution tests. Additional tests are needed to distinguish the behaviors of silicate-based and phosphate-based phases and understand the distributions and release kinetics of radionuclides.

**Recommended activities.** Produce materials with nominal OR salt compositions before and after salt purification step. Demonstrate capacity to retain surrogates for radionuclides using various dissolution tests following approach discussed in Section 4.4. Evaluate dissolution behaviors of silicate- and phosphate-based crystalline and amorphous phases as coupled through common solution, including effects of pH and solution feedback.

#### **5.3.4 Lead Tellurite Glass Waste Form (OR OP-1; OR OP-3-1; RAR OP-2)**

**Waste streams.** LiCl salt from OR with residual AM, AE, and I with and without salt purification step. LiCl/KCl eutectic salt from ER with residual U, TRU, RE after drawdown

**Objectives/critical gaps.** Determine degradation mechanism and rate law. Maximize waste loading.

**Recommended activities.** Produce glasses with ranges of surrogate OR and ER salt compositions and range of salt loadings. Demonstrate capacity to retain salt surrogates for radionuclides using various dissolution tests following approach discussed in Section 4.4. Evaluate role of glass matrix in retaining wastes and importance of dissolved Pb and Te on the continued dissolution rate of the glass matrix.

#### **5.3.5 ZIT Waste Form (RAR OP-3)**

**Waste stream.** LiCl/KCl eutectic salt from ER with residual U, TRU, RE after drawdown

**Objective/critical gap.** Determine degradation mechanism and rate law. Maximize waste loading.

**Recommended activities.** Produce representative materials for testing to characterize degradation behavior and measure contaminant release rates using various dissolution tests following approach discussed in Section 4.4.

## **6. SUMMARY OF WASTE STREAM TREATMENT AND WASTE FORM PRODUCTION IN THE IRT**

This document describes treatment strategies being evaluated for waste-streams that result from the pyroprocessing of used nuclear fuel. The development of these treatment options and waste forms comes primarily from research activities performed over the last several decades in the ROK and the U.S. The primary objectives of pyroprocessing waste-stream treatment and waste form development are:

- Minimization of waste volume for disposal.
- Development of technologies that enable the reuse of UNF components that would otherwise require waste treatment, storage, transportation, and disposal.
- Development of waste forms for long-lived radionuclides that have improved durability and provide higher confidence in performance under a range of potential disposal environments to reduce the reliance on engineered and natural barrier systems and thereby open new disposal options and reduce disposal costs.
- Development of waste forms and processes that will facilitate lower cost management through less expensive and less complex processing operations, lower storage and disposal costs, and greater flexibility for multiple disposal environments.

The focus of this report is on the waste-stream treatment processes for separation of fission products and subsequent waste form fabrication, detailed description of methods to determine important pyroprocessing waste form performance characteristics, advanced pyroprocessing waste form development, and waste treatment processes that have yet to be demonstrated in a hot cell environment with actual UNF. Another important component of this report is a description of the scientific basis and experimental strategy for the determination of the expected long-term performance of HLW forms in a geological repository, and how this testing strategy will be applied to candidate waste forms to be evaluated in the IRT. The multi-year IRT project will demonstrate the performance of electrochemical and pyroprocessing operations for the recovery of U and TRU from UNF. This will provide data to evaluate the performance and engineering factors related with the electrolytic process, U and U/TRU ingot fabrication, waste-stream treatment for fission product isolation and volume reduction, waste form fabrication and performance testing.

### **6.1 Waste-Stream Treatment Technology IRT Demonstration**

Due to specific facilities limitations, waste-stream treatment and waste form fabrication during the IRT demonstrations will not be completely representative of the ROK used fuel treatment process. Nevertheless, the IRT waste-stream treatment demonstration will provide important information needed to evaluate the compatibility of waste treatment technologies with specific waste forms. This will enable waste form characteristics pertinent to the ROK process to be estimated, such as volume, activity, heat generation, etc.

Both the ROK and the U.S. have active cladding recycle programs. Cladding treatment with zirconium recycle would allow for significant waste-stream volume reduction, but cladding residue waste streams will need to be addressed. During the IRT demonstration, a small quantity of irradiated cladding will be treated for Zr recycle. The recovered Zr will be analyzed for potential TRU content, and cladding residue will be mixed with other alloy components to generate an alloy waste form and the waste form performance evaluated.

Head-end thermal processing of UNF allows for more efficient fuel/cladding separation and for the removal of volatile and semi-volatile fission products that can be trapped for waste form fabrication. Removal of the volatile and semi-volatile fission products improves operation of the fuel oxide reduction processes. A limited volume of fuel will undergo thermal processing during the IRT demonstration; the



majority of fuel will not be subjected to head-end thermal processing. This will result in a distribution of fission products in the IRT waste streams, particularly in the OR salt, that is different than that in KAERI's proposed process flow diagram for UNF treatment. This is one example of fission-product distribution variation between KAERI's process stream for UNF and what is expected in the IRT.

The specific operations for salt waste-stream treatment will include three separation processes for salt purification: melt crystallization, selective distillation, and selective precipitation. The distribution data for FPs and TRU in each separation process performed with actual UNF will be used to determine which process generates the smallest final waste volume. Melt crystallization processing of OR salt will purify a fraction of the LiCl salt used for fuel reduction that can be recycled to the OR vessel. The remaining fraction of OR salt with high concentrations of fission products will then be processed into optional candidate waste forms. Selective distillation processing of the ER salt containing mixtures of actinide chloride and rare earth fission-product chlorides will be performed to separate the RE chlorides for waste form fabrication. Finally, selective precipitation will be used to remove residual RE fission products and allow recycle of the purified ER salt. The precipitated RE fission products can be fabricated into a titanate mineral or glass waste form.

The final waste stream to be investigated during the IRT will be residual UDS from the electrorefining operation. It is anticipated that the UDS will contain the noble metal fission products in the fuel that are not reactive in either the OR or ER processes and oxides that formed during processing—primarily  $\text{UO}_2$ . This material will be collected for waste form fabrication after residual salt distillation.

## **6.2 Waste Form Fabrication and Testing IRT Demonstration**

Waste forms will be recommended for use in the Phase III demonstration based on confidence that they (1) can be successfully produced with the waste streams that will be generated during the demonstration and can be consistently produced in practice, and (2) can be demonstrated to perform acceptably in a disposal system based on an understanding of the degradation process and the ability to measure and model it. A significant portion of the Critical Gap R&D activities to be performed for the next several years will involve performance testing of candidate waste forms described in Section 0. Promising waste forms that have been evaluated during Phase II will be fabricated during Phase III of the IRT. The scientific basis for waste form performance involves an understanding of which processes control degradation under the relevant range of disposal conditions that is developed through laboratory tests to identify and quantify the dependencies of the key processes on environmental variables. The general hierarchy for testing is to first identify the host phases for key radionuclides and the likely release modes such as:

- Must the host phase dissolve or are radionuclides leached?
- Will the host phase equilibrate with the solution or continuously transform to alteration phases?
- Must the host phase and radionuclides be oxidized prior to release?
- Do the controlling processes change as the waste form surface and solution compositions evolve?

A conceptual model can be developed based on insights from these tests. The conceptual model identifies the processes to be represented by the analytical model for waste form degradation, in which oxidation, diffusion, and surface reactions are likely to be important, and depend on environmental variables. The CWF and MWF developed in support of EBR-II spent fuel treatment have undergone this testing regime and degradation and radionuclide release models have been developed based on that information (Ebert 2005).

The waste forms identified in Section 0 have been developed to immobilize waste streams similar to those predicted to be generated the IRT demonstration. The experimental testing for these advanced candidate waste forms is in the initial stages. The two primary technical gaps limiting technical assessments of the suitability of each waste form for immobilizing one or more waste stream are (1) the

presently limited understanding of the degradation mechanism needed to reliably predict long-term performance, and (2) adequate demonstration of the capacity to accommodate the waste stream at acceptable waste loadings.

The analyses described for the CWF in Section 4.2 illustrate the approach being taken to characterize the degradation behavior of the multi-phase U-SAP, ZIT, and Pb-tellurite glass waste forms. The general testing approach was summarized in Section 4.4 and specific test methods were given in Section 5.3.

Work done to date has addressed the production of potential waste forms with specific waste streams and provided a good understanding of the corrosion behaviors of some waste forms. The objective of the Phase IIB waste form studies is to supplement the available testing and modeling data bases to provide confidence that those waste forms can (after further testing and modeling) be shown to meet performance requirements for waste disposal. That will be done by showing how test responses are related to the conceptual degradation models that are the basis for the performance models. The Phase IIB results will provide the technical bases to identify tests that can be used to evaluate the performance of each waste form that is made in Phase III. This will include a conceptual model of waste form degradation by which the performance can be evaluated, test methods that can be used to quantify a measure of the performance, and a threshold to evaluate the adequacy of the measured performance. Waste forms will be recommended for use in the Phase III demonstration based on confidence that they (1) can be successfully produced with the waste streams that are generated during the demonstration by the various waste treatment processes and consistently produced in practice, and (2) can be demonstrated to perform acceptably in a disposal system based on an understanding of the degradation process and confidence in the ability to measure and model it for safety assessments of the disposal system.

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