Partitioning of Fission Products and Waste Salt Minimization during Pyroprocess

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KAERI

Backgrounds

❖ **Next generation nuclear fuel cycles**

- Reduction of environmental hazard by selectively recovering a long-lived nuclide and transmuting it
- Minimization of the waste volume to be eventually disposed of

❖ **Basic strategy for partitioning**

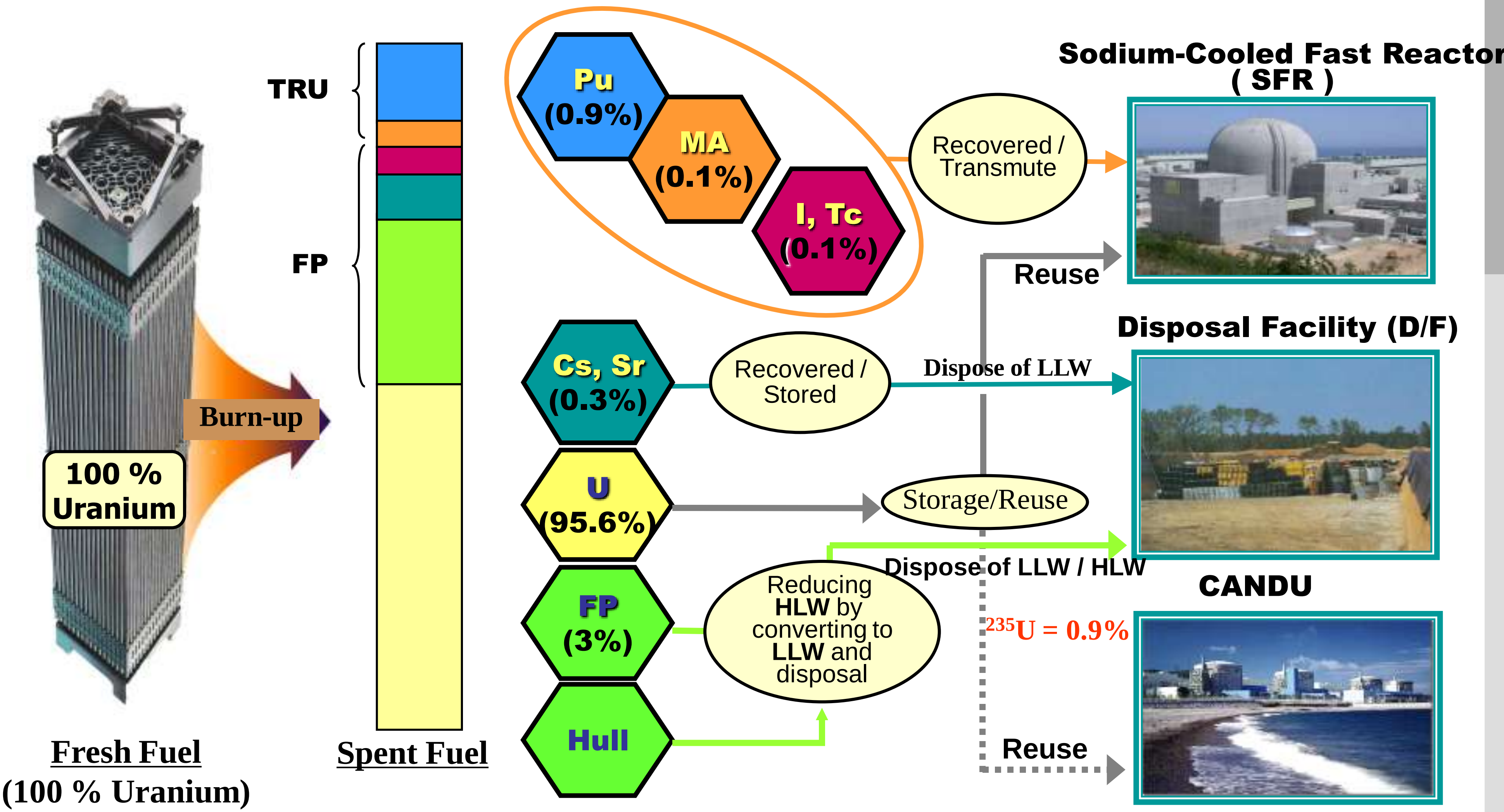
- Classify and optimize waste streams arising when treating spent fuel
- Minimize waste volumes resulting from each waste stream

Little information on a strategy for waste minimization in pyroprocess

❖ **Strategy for optimization of waste streams and waste minimization**

- Pyro-partitioning of fission products being performed in KAERI
- Strategy requested for optimizing waste streams and minimizing waste amounts
- Reduction of **HLW** generating from each waste stream
  -Converting **HLW** to **LLW** through an increase of **DF** or **SF**
- Candidate wasteforms for consolidation of waste salts from a pyroprocess

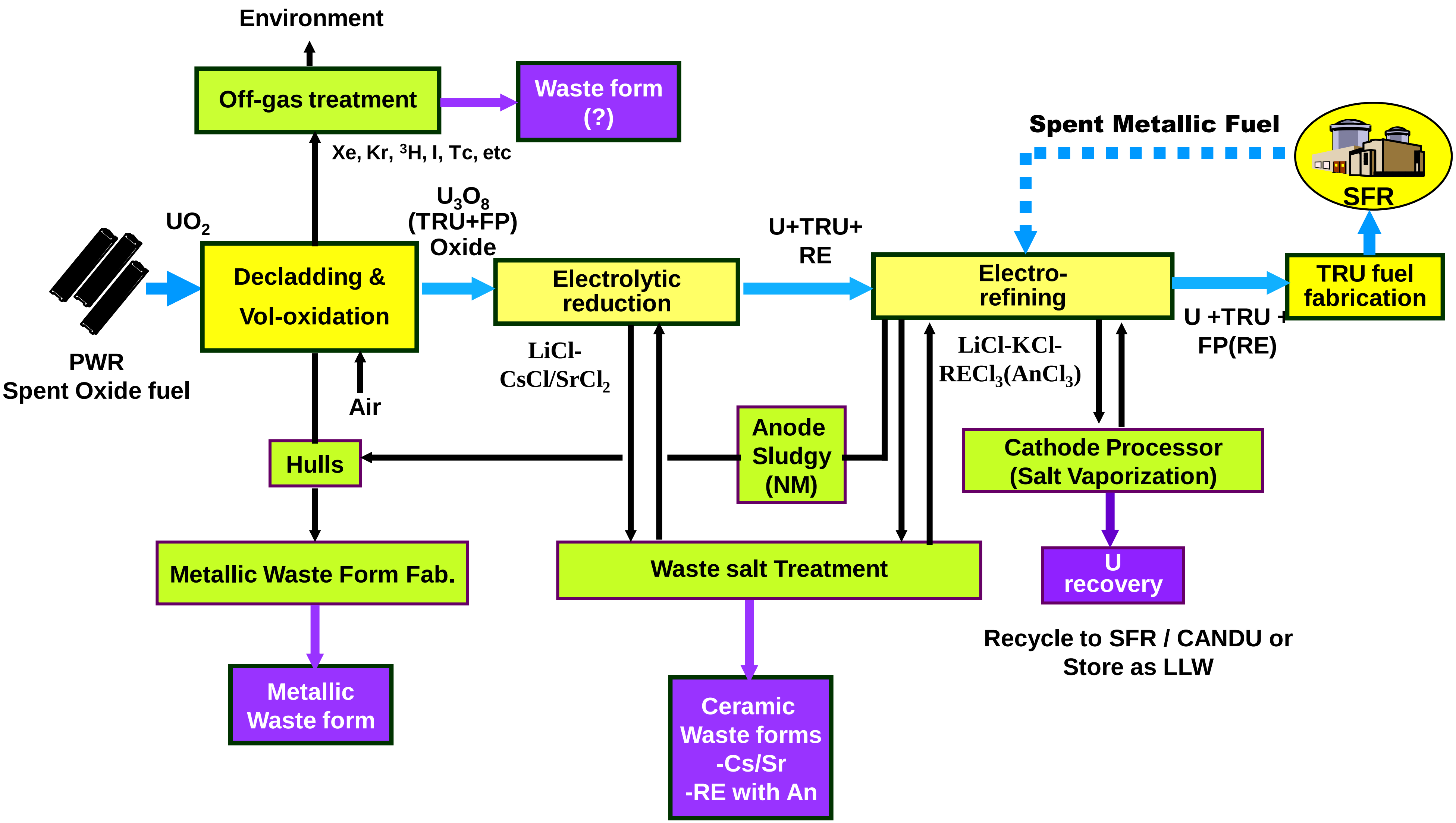
A Strategy for Efficient Management of Spent Fuel in Korea



FP: Rare earth, Noble metal, Volatile / Semi-volatile Fission Products
KAERI's waste management strategy: directed to minimize HLW amounts

A Flow Diagram of Pyroprocess being Developed by KAERI

Optimizing waste streams and evaluating a strategy for minimization of wastes

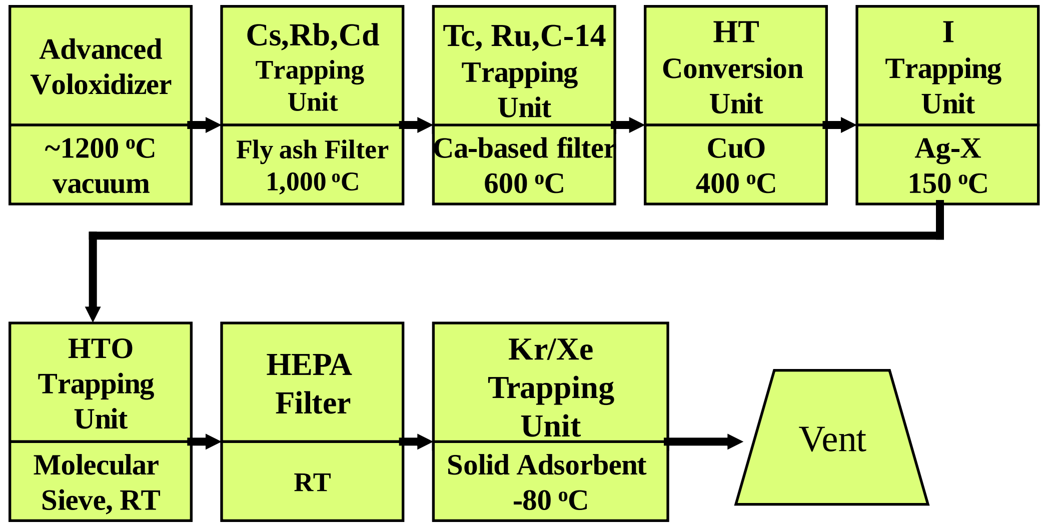


Fission Products Release with Voloxidation Conditions

Nuclides	Standard voloxidation (500°C)	Advanced voloxidation* (1200°C)	Remarks
Kr / Xe	<30%	100%	
H	100%	100%	
I	<10%	100%	I-129: long-lived nuclide
Tc	<1%	92%	Tc-99: long-lived nuclide
C	<10%	100%	C-14: long-lived nuclide
Cs	<1%	98%	Highly radioactive, high decay heat nuclide
Ru	<1%	98%	Noble metal
Mo	<1%	62%	Noble metal
Rh	<1%	83%	Noble metal
Rb	<1%	96%	

* INL hot experimental data in I-NERI program of INL-KAERI

Flow sheet for capturing fission gases



Advantages

- ✓ Minimize influence of fission products on the down-stream process conditions
- ✓ Recover and store fission products separately

Challenges

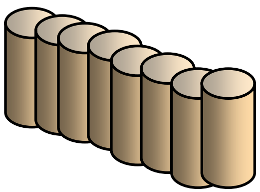
- ✓ DF > 10^4 to minimize the impact to the environment
  Further development of trapping technologies and conditions
- ✓ Optimization of waste forms for consolidation of several absorbents
- ✓ Minimization of waste amounts issued from capturing fission gases

Treatment of Hull

Objective:

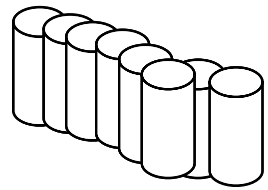
- Experimentally recover higher than 99% fissile material during air-voloxidation process
- Look for a promising way enabling a conversion of hull to LLW
- Strip residual fissile materials from the contaminated hull
- Classify the hull as LLW → Challenge !!

Promising technology (Rinsing Mechanism)



Hull contaminated with actinide

→ LiCl + KCl $ZrCl_4$ →



→ Fabrication of metallic Waste (Zr - 8SS[1)]) → LLW

LiCl + KCl
$AnCl_3$, $RECl_3$,
CsCl, $SrCl_2$
NMO+ZrO_2

→ Regeneration of Salt

Actinides	Rare earth and I/II groups	Noble metals
$4UO_2 + 3ZrCl_4 + Zr = 4UCl_3 + 4ZrO_2$ $4PuO_2 + 3ZrCl_4 + Zr = 4PuCl_3 + 4ZrO_2$ $4AmO_2 + 3ZrCl_4 + Zr = 4AmCl_3 + 4ZrO_2$	$RE_2O_3 + ZrCl_4 = RECl_3 + ZrO_2$ $Cs_2O + ZrCl_4 = CsCl + ZrO_2$ $SrO + ZrCl_4 = SrCl_2 + ZrO_2$	➢ Not chlorinated ➢ Co-precipitated with ZrO_2

1) Steven M. Frank, et al., "Immobilization of Technetium and other Fission Products from Processed Spent Nuclear Fuel into a Metallic Waste Form", 2008 IPRC, Aug 24-27, 2008 Jeju Island, Korea

Waste Salt Treatment Technologies

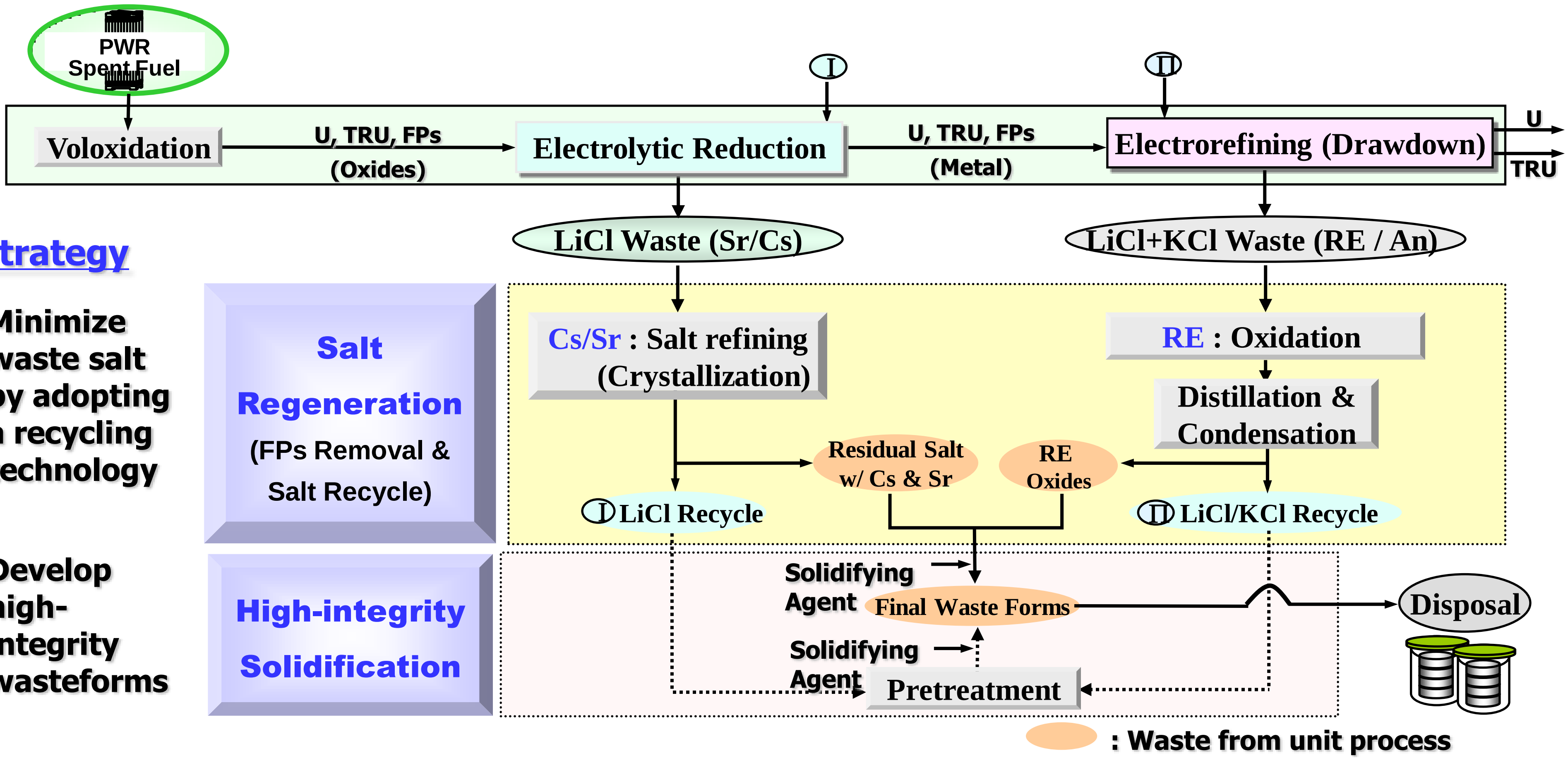
❖ **Developing technologies to recycle waste salts to process units, not by releasing to repository**

-Salt cooling technologies: Czochlarski, Zone freezing, Layer crystallization

-Precipitation technology: oxidation-precipitation using air

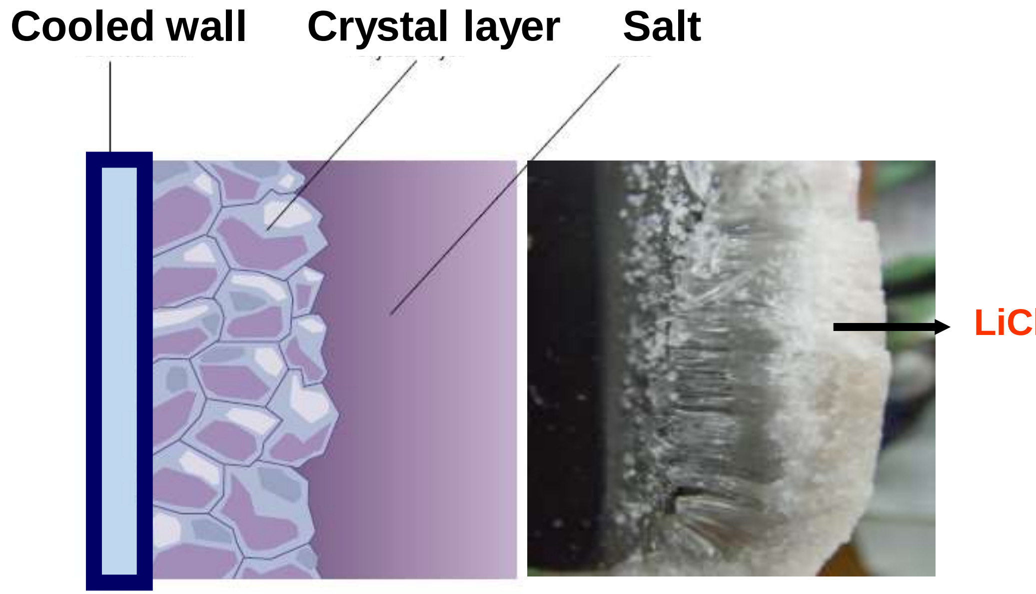
Strategy

- **Minimize waste salt by adopting a recycling technology**
- **Develop high-integrity wasteforms**



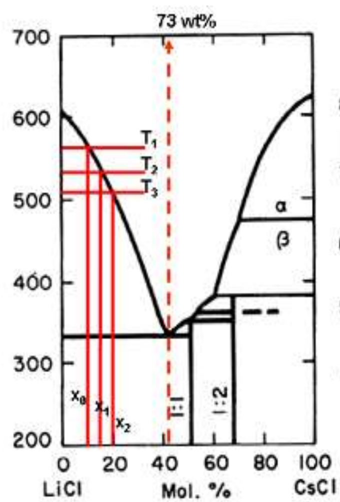
Recovery of Purified LiCl Salt from a Waste Salt

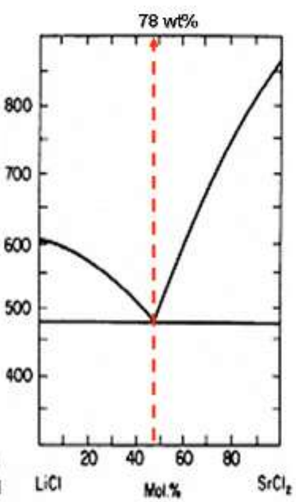
Czochlarski



Layer Crystallization

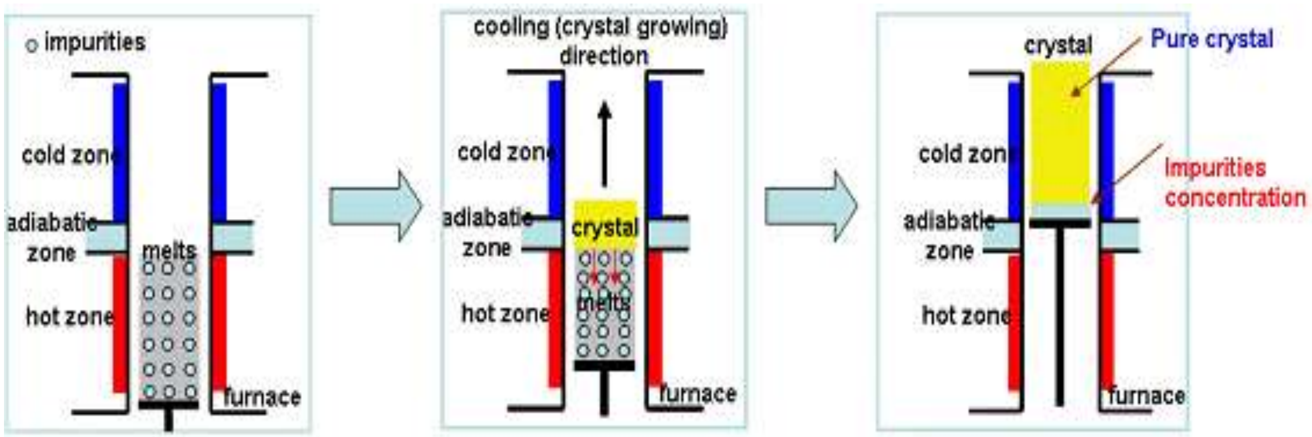
Zone Freezing

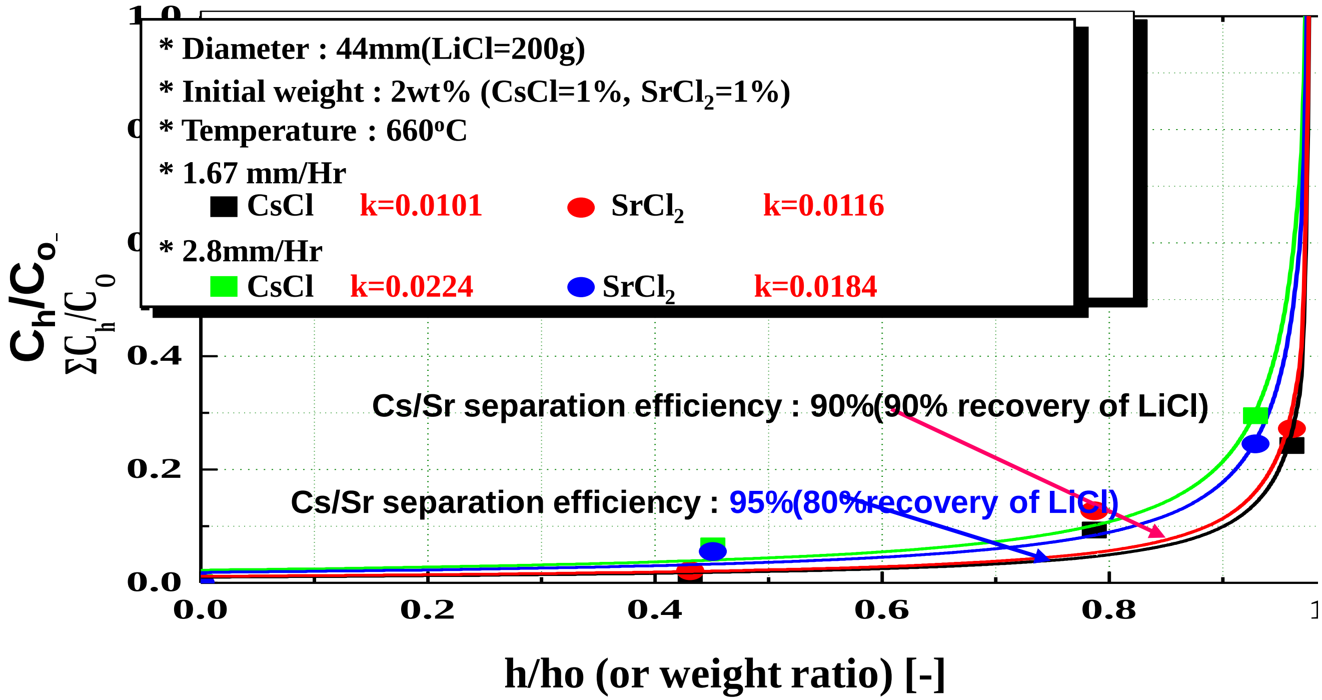


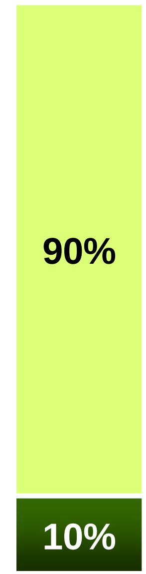


- To concentrate Cs and Sr to eutectic point by cooling method
- To theoretically recover 99wt% of LiCl from a waste salt
- To evaluate and select which technology is more preferable and effective for scale-up and practical use.

Zone Freezing Technology for Recovery of LiCl Salt







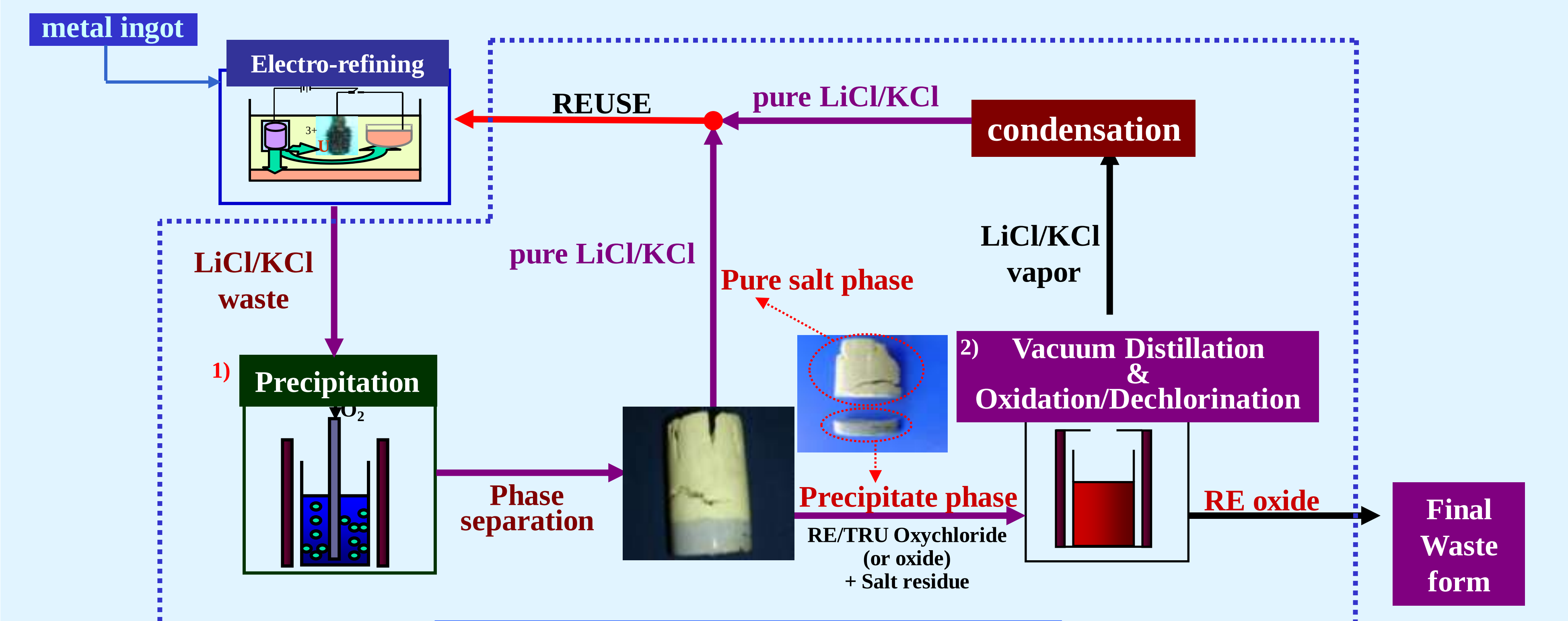
Experimentally recycle 90% of LiCl (contaminated with a small amount of impurity)

Fabricated to a final wasteform (contaminated with 90% of initial impurity amount)

LiCl-KCl Waste Salt Recycle

Possible to recycle all most of eutectic salts to electrorefiner and to minimize waste salt to be disposed of

- REE are precipitated as oxide or oxychloride forms



1) $RECl_3 + 0.5O_2 \rightarrow REOCl + Cl_2$

or $RECl_3 + O_2 \rightarrow REO_2 + 1.5Cl_2$

2) $REOCl + 0.25O_2 \rightarrow 0.5RE_2O_3 + 0.5Cl_2$

Wasteforms

Waste LiCl from Electro-reduction

Waste LiCl-KCl from Electro-refining

Recycle of clean salt

Melt Crystallization

Oxide precipitation

Concentrated residual salt

Oxide precipitates

Cs & Sr

REE

Solidification

Candidate wasteform for consolidation of waste salt [LiCl residual salt]

- Incorporation of Cl into a wasteform
  - Mineral-based wasteform
    sodalite, apatite, spodiosite, wadalite
  - phosphate-based glass
- Not incorporation of Cl [KAERI]
  - **SAP-based wasteform**
    [SAP: $xSiO_2$-yAl_2O_3-zP_2O_5]

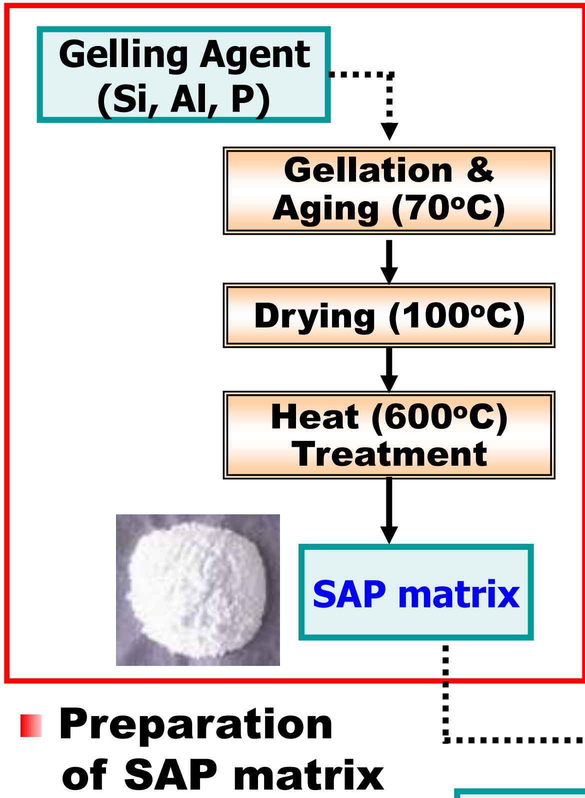
Candidate wasteform for REE / An oxides

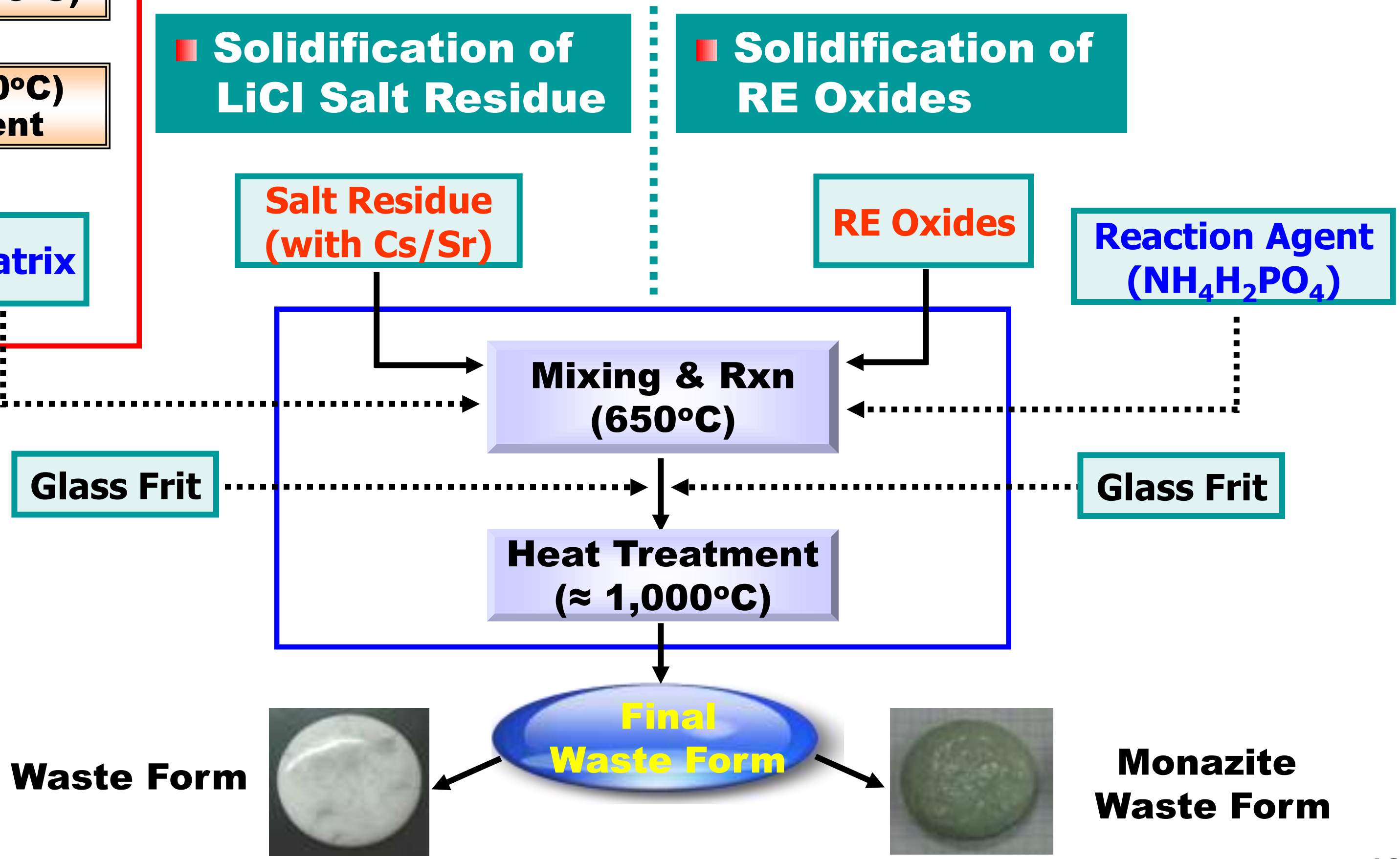
- BSG, SynRoc, Pyrochlore and etc
- **Monazite-based wasteform [KAERI]**
  - Reliable host matrix for α-radionuclide
  - Reasonable processing condition
  - Waste loading & Chemical durability
  - Radiation stability

A Flowsheet for Wasteforms Fabrication

Fabrication of Final Ceramic Waste Forms

- Two different waste streams : LiCl salt residue and RE oxides
- Each waste can be treated by using the same solidification equipment, but at different processing conditions.





Chemical route and Qualification of Waste forms

❖ Chemical route for the immobilization of each waste

For LiCl waste

Salt waste + 2 SAP → $Li_xAl_xSi_{1-x}O_{2-x}$ + Li_3PO_4 + (Li, Cs)-aluminosilicate + $Cs_2AlP_3O_{10}$ + $Sr_5(PO_4)_3Cl$(apatite) + $CePO_4$(monazite) + amorphous phase (M_2O-Al_2O_3-P_2O_5) + Cl_2 (Vaporized as gas)

$x SiO_2$-$y Al_2O_3$-$z P_2O_5$

For REE oxide waste

$RE(An)_2O_3 + 2\ NH_4H_2PO_4 = 2\ RE(An)PO_4 + 2\ NH_3 + 3\ H_2O$

❖ Waste loading factor of waste forms

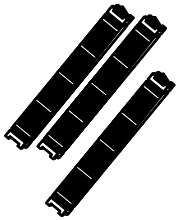
LiCl waste salt : SAP material : Glass frit = 1 : 2 :1 [waste loading : 25 wt%] for SAP
RE oxide : Chemical additive($NH_4H_2PO_4$) : Glass frit = 1 : 0.52 : 3.48 [waste loading: 20wt%] for Monazite

❖ Chemical durability of waste forms

PCT-7days, (unit : g/m^2)

	SAP for LiCl waste	Monazite for REE oxides	Conventional BSG	Sodalite for LiCl-KCl
Cs	~ 10^{-2}	-	~ 10^{-1}	~10^{-2}
Sr	~ 10^{-2}	-	~ 10^{-2}	~10^{-2}
RE	-	< 10^{-3}	< 10^{-3}	-

Partitioning-Waste Streams



Spent fuel

↓

Pyroprocess

Waste stream	Partitioning & Recovery	Potential Wasteform	Classification
Volatile / Semi-volatile species	Selective partitioning of FP's using substrates	Not determined	LLW
Hull Metal sludgy (NM)	Removal of residual actinides from metallic products	Alloy form with Zr and Fe (may include Tc and other noble metals)	HLW →LLW
Cs / Sr + LiCl salt	Recycling of LiCl to Electroreducer	Ceramic waste (SAP)	HLW(?)
Lanthanides + LiCl-KCl (with TRU)	Oxide precipitation & salt recycled to ER	Ceramic waste (Monazite)	HLW
U	Removal of actinides (contaminated with > 100 nCi-TRU/g) to store as LLW	Temporally stored as Metallic form	LLW
TRU	Recovery yield: > 99.9 %	Transmuted at ABR	

Conclusion

❖ **Classify into 4 waste streams**

-Volatile and semi-volatile species waste stream
-Metallic form waste stream
-Uranium metal waste stream
-Salt waste stream-ceramic composite wasteform

❖ **KAERI' strategy for waste minimization is focused on**

-Reduction of HLW by converting to LLW
☞Removal of actinide residual from hull
☞Removal of actinides from an electrorefinned uranium metal product
☞Increase of decontamination factor of actinide from waste LiCl salt
-Reduction of LLW: waste arising from voloxidation
☞Simplification of wasteforms applicable to several absorbents
☞Reduction of waste amounts

❖ **Comparison of wasteform volume with and without a salt recycle**

-Possible to reduce HLW amounts by 30 times
-Predictable to reduce HLW by 80 times if converting LiCl waste to LLW

❖ **Eng.-scale demonstration for waste salt recovery and wasteform fabrication**

-Establishment of Eng.-scale facility(10 t-HM/yr) for an inactive test by 2011 at KAERI

한국원자력연구원
Korea Atomic Energy Research Institute

Thank for your attention !!

Environmentally-Friendly Nuclear Energy for Next Generation

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