Development of Pyro-Waste Treatment Process Technology

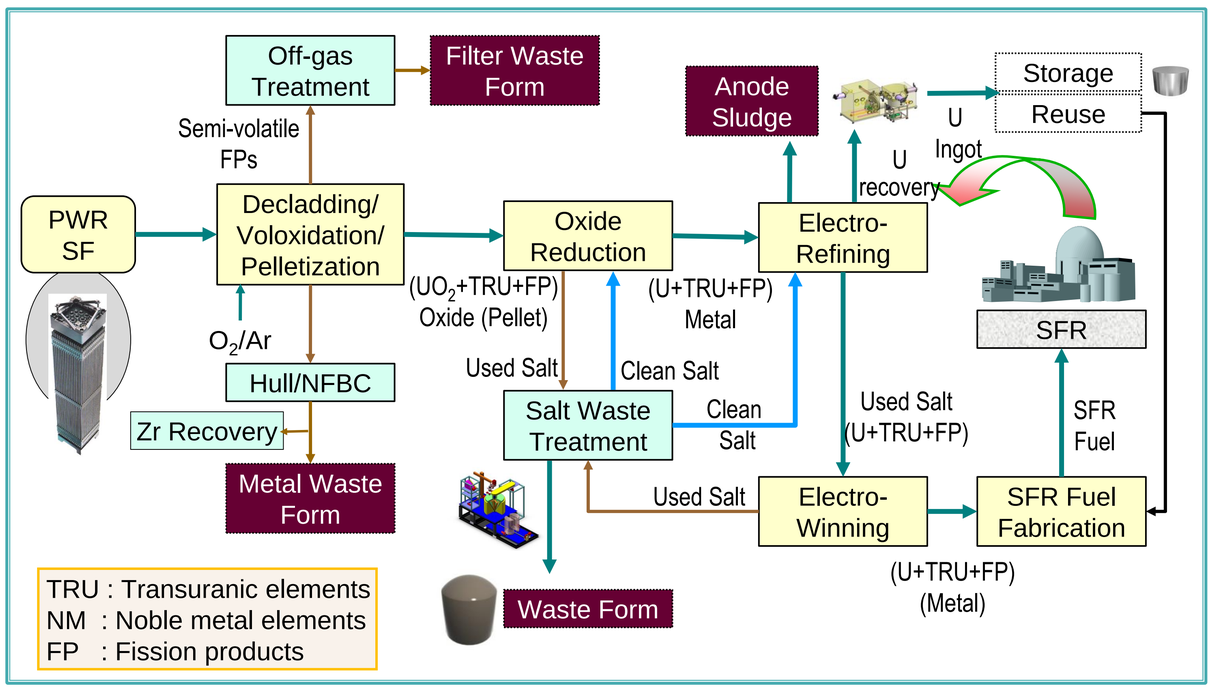
Geun-Il Park*, In-Tae Kim , Hwan-Seo Park, Jin-Mok Hur

Korea Atomic Energy Research Institute 989-111 Daedeok-daero, Yuseong, Daejeon, 34057, Republic of Korea, * ; ngipark@kaeri.re.kr

Background

❑ Pyroprocessing Technology

Electrochemical recycling technology to recover the valuable resources (U, TRU, etc.) from spent nuclear fuels in molten salt media at 500~650°C



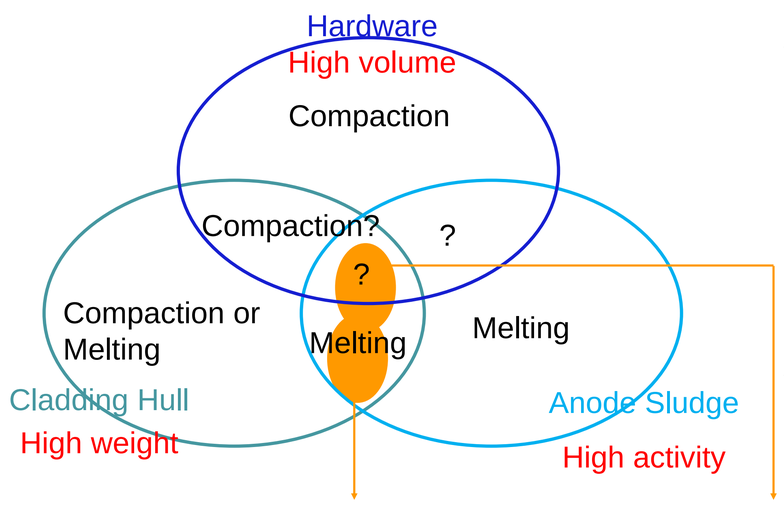
Objectives of Pyro-waste Treatment Tech.

- ❑ ***Minimization of highly radioactive waste***
- ❑ ***Integrated management of waste forms for final disposal***
- ❑ ***Optimization of waste treatment process***

Category	Waste	Main Characteristics	Approach concept
Gaseous waste	Filters	▪ Fly-ash : Cs trapping ▪ Ca filter : Tc trapping ▪ Ag filter : I-129 trapping ▪ Etc : Fission gases trapping	▪Selective trapping (High decay-heat & Long-lived FPs)
Metal waste	Hull NFBC Noble Metal	▪ Hull : FPs. TRU penetration ▪ NFBC : Activation (Nb-94, etc.) ▪ Noble Metal : Anode sludge	▪Zr recovery & FPs/TRU separation ▪Compaction/Melting
Salt Waste	LiCl LiCl-KCl	▪ LiCl : Sr, Ba, Cs(minor) ▪ LiCl-KCl : RE, TRU (minor)	▪FPs separation and ▪Recycling of purified salts

NFBC : Non-Fuel Bearing Component

Pyro Metal Waste Treatment



Based on Spent Fuel 30 t-HM

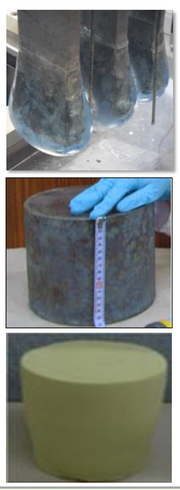
Metal Waste	Weight (kg)	Material	
Hardware (NFBC)	3,110	Zirlo	1330.2
		SS304	1281.3
		Inconel	466.5
		Zry-4	32.1
			3110.1
Cladding Hulls	7,362	Zirlo	
Anode Sludge	602	NM, Zr, metal oxide, etc.	
Total	11,074		

<Metal waste from pyro-process>

- ❑ **ZIRLO-Additive metal-NM alloy for MWF**
  - KAERI researched on Zr-Cr-Si-NM alloy
  - Representative composition: Zr-22Cr-4Si-8NM
  - Good corrosion resistance & Leaching property
  - High fraction of additive alloy element (over 20 wt.% Cr & Si)
- ❑ **ZIRLO-Inconel718-SS304-NM alloy for MWF**
  - MWF fabrication using all metal wastes from pyro-process
  - Hardware + Cladding Hull + Anode Sludge + (additive metal)
  - Additive metal for improving corrosion resistance and decreasing melting temperature

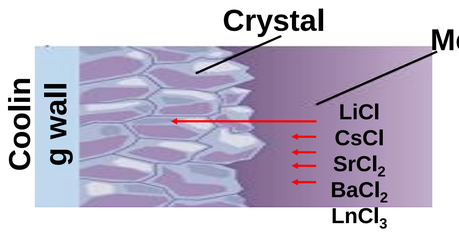
Overview of Waste Salts Treatment

- ❑ **Two kinds of waste salts from KAERI Pyroprocessing**
  - ***LiCl waste generated from OR(Oxide Reduction) process***
    - Main radionuclides : Cs, Sr(Ba)
    - Separation: Melt crystallization (recovery of pure LiCl)
    - Solidification: SAP method by de-chlorination of residual waste salt
  - ***LiCl-KCl waste generated from ER/EW process***
    - Main radionuclides: Ln and minor quantity of Ac
    - Separation: selective precipitation & distillation
    - Solidification: Ln/Ac to monazite and encapsulation by inert matrix
      - The matrix material depends on the precipitation method



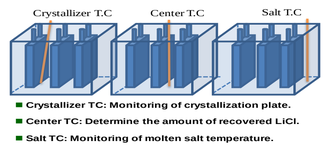
LiCl Waste Purification : Crystallization

- ■ **Layer Melt Crystallization by using phase equilibrium**
  - **Performance of Lab-scale(~3kg) Crystallizer**
    - *Recovery of pure LiCl and concentration of FPs*
    - *FPs 90% separation efficiency, 90% LiCl recovery*



Process concept

LiCl crystallized on the cold plate



TC points for monitoring

  - **Operation test for Eng-scale(~20kg) Crystallizer**
    - *Control & monitoring of temperature: Heat flux & end point*
    - *Lowering concentration for high separation of FPs ➲ Make-up process*
    - *High concentration (> 10% of FPs) : Sweating process ➲ Setup of operation condition*

LiCl-KCl Waste Purification : Precipitation/Dist.

- ❑ **Selective Precipitation by using high reactivity of Ln in melt**
  - Chemical reaction using oxygen or phosphates followed by distillation
    - *FPs 99% separation efficiency, <98% LiCl-KCl recovery*
      - *- Oxygen sparging: Oxide & oxychloride : corrosion problem, no contamination*
      - *- Oxygen sparging + phosphate (hybrid) : variable amount of chemical forms*
      - *- Only Li(K)-Phosphate(well known method) : excess phosphate, milder condition*
    - *All the methods were tested and confirmed the performance for separation*
    - The best method depends on the feasibility of Eng-scale process
- ❑ **Distillation for separation of salt in the precipitation layer**
  - Recovery of pure LiCl-KCl salt by using volatility at a low pressure
  - Distillation for FPs separation by using phase equilibrium

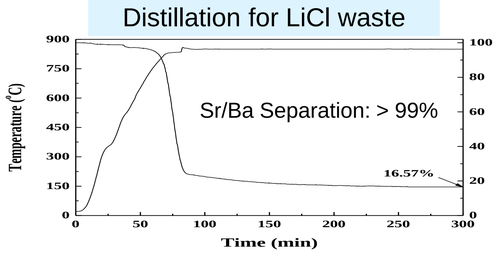
Recovered Salt

FPs Separation from Waste Salt (Cs/Sr/Ln)

- ❑ **Primary separation technology for FPs from Waste Salt**
  - *Combination of crystallization, distillation & precipitation*

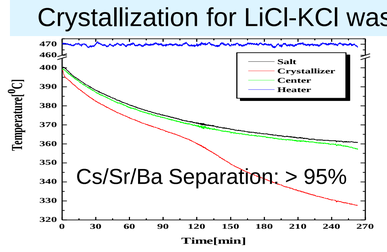
	Crystallization	Distillation	Precipitation
Mechanism	Liquid-Solid Phase equilibrium	Gas-Liquid Phase equilibrium	Chemical reaction
Temperature	360~650℃	~900℃	450℃~
Target metal	**Cs/Sr/Ln**	**Sr/Ln**	**Ln**

Distillation for LiCl waste



LiCl-$BaCl_2$-$SrCl_2$, 850℃ and 1 torr

Crystallization for LiCl-KCl waste

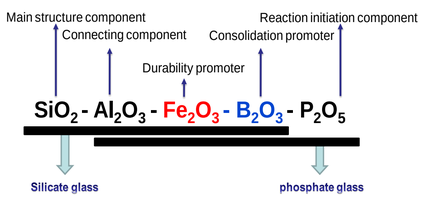


LiCl-KCl-CsCl-$BaCl_2$-$SrCl_2$, 360~400℃, FPs(1wt%)

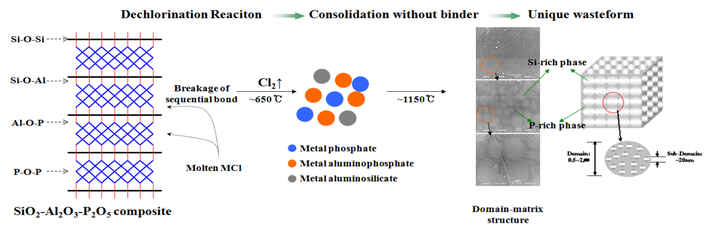
Solidification : Waste Salt & Ln Waste

- ❑ ***Waste Salt* : Dechlorination by using inorganic composite**
  - Removal of Cl-induced problems
    - *Metal chloride: Low solubility in conventional glass and high volatility*
    - *SAP: dechlorination agent, Li_2O-Li_2O_2: Chlorine gas capture & Re-use as MCl*

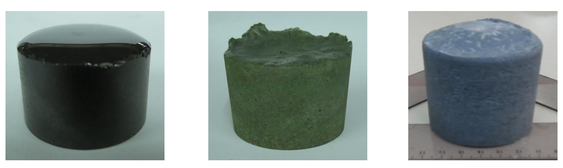
U-SAP composition



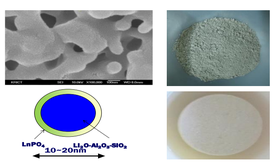
Treatment procedure



- ❑ ***Ln Waste* : Use of monazite as host phase of Ln & Consolidation**
  - Four kinds of matrixes according to purification methods
    - *Ln with low leaching rate (10-5~10-6g/m2day) for wasteform*
    - *Purpose: consolidation at milder condition & simple process*



[LABS glass for oxide] [LIPS/A-ZIT forms for LnPO4]



[Li-SAP: Li_2O-SiO_2--Al_2O_3–P_2O_5]

The engineering-scale salt purification process was performed to obtain the information on performance of eng-scale process. Also, a series of wasteforms related with pyro-waste from KEARI pyrorprocessing was fabricated by using some synthetic materials and specific Lab-scale equipment.

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