Atoms for Next Generation

Immobilization of LiCl radioactive waste salt from Pyro-chemical process using U-SAP waste form

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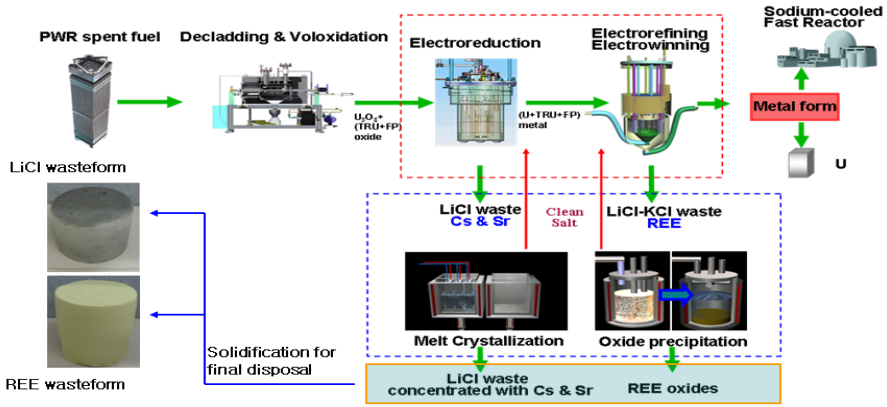
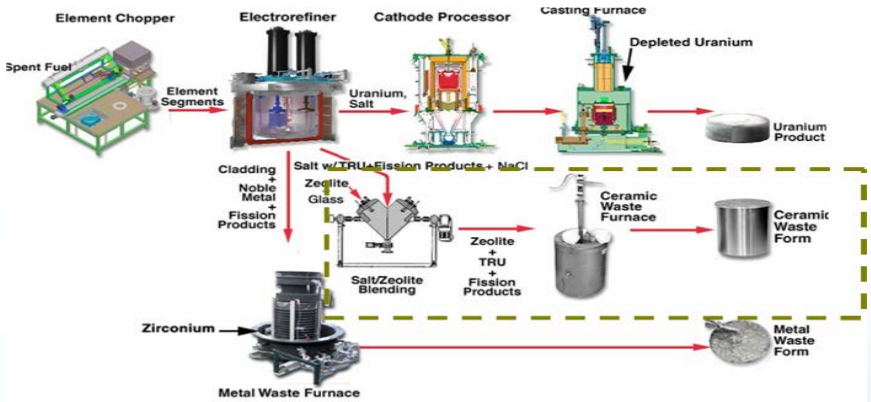
KAERI Korea Atomic Energy Research Institute

Generation of Radioactive Waste Salt from a Pyro-chemical Process in Korea

PWR Spent Fuel Treatment



SFR Spent Fuel Treatment



Off-gas, decladding materials

Sodium-cooled fast reactor

TRU fuel fabrication

PWR spent fuel → Pre-treatment process → Electrolytic reduction → Electrorefining → Electrowinning

1. LiCl waste

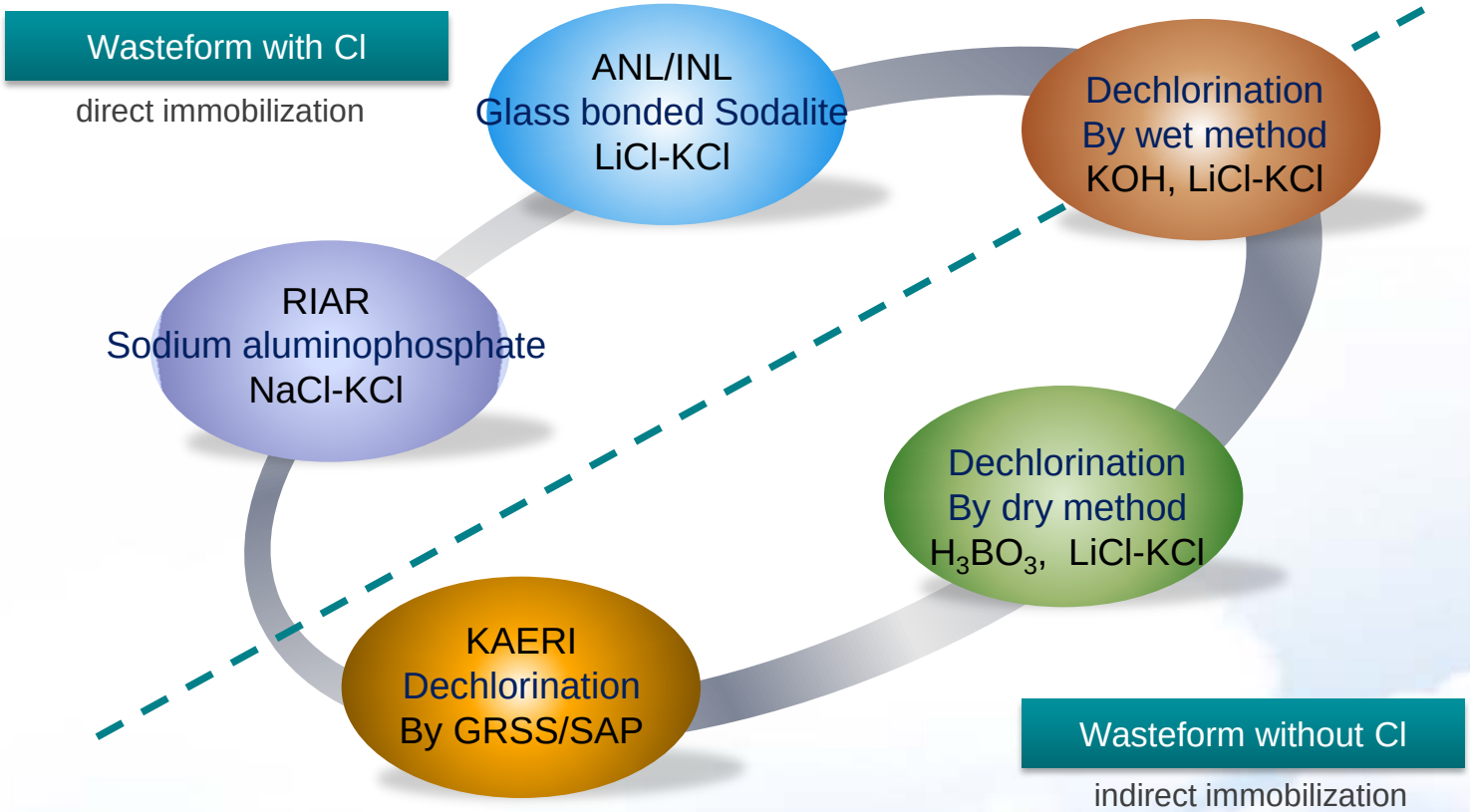
2. LiCl-KCl waste

oxide fuel process waste

3. LiCl-KCl waste

metal fuel cycle waste

Immobilization Technologies for Waste Salt



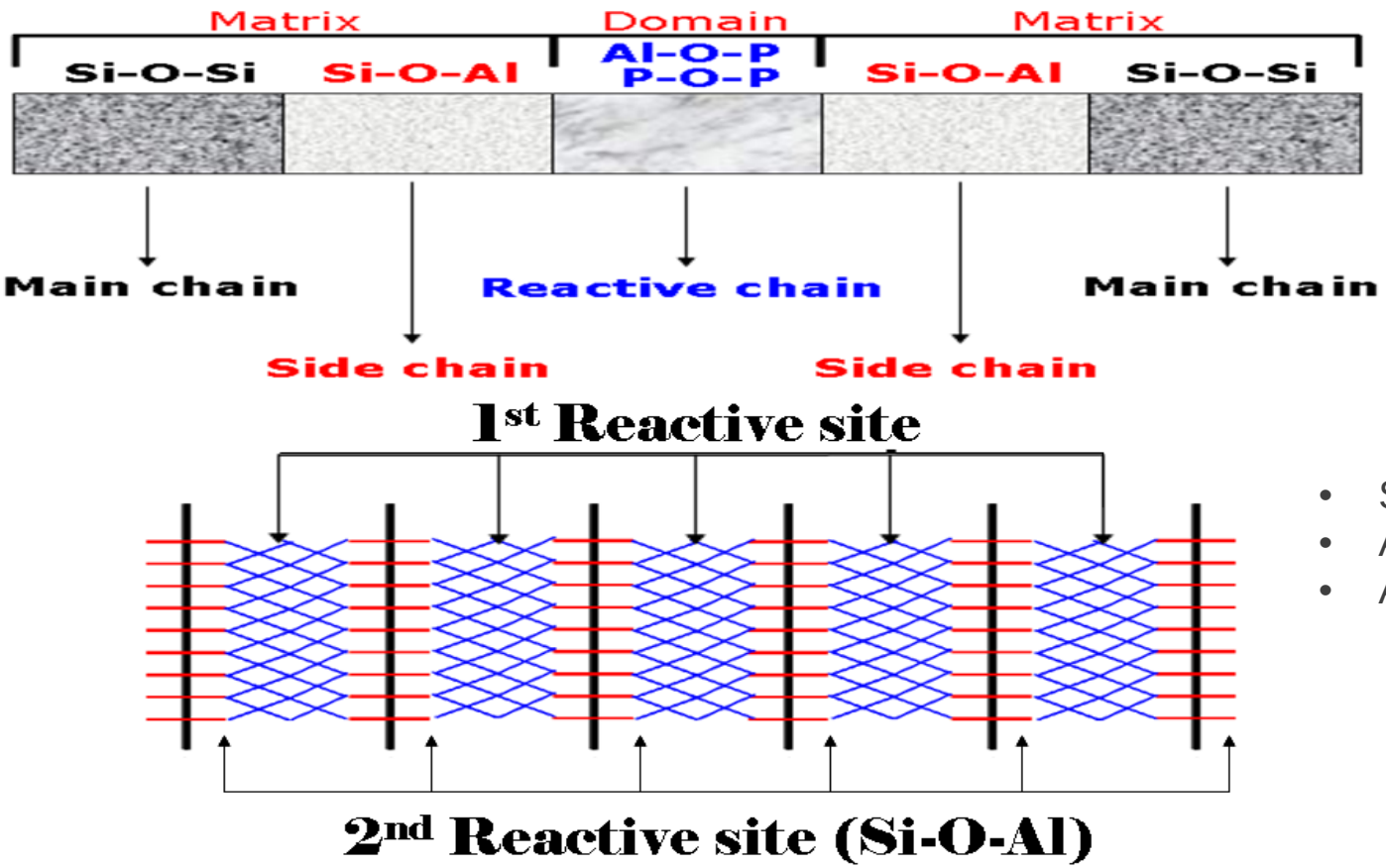
- ✓ Chloride Waste: Very volatile, low compatibility with silicate glass

  $NaPO_3$-Al_2O_3-AlF_3 (NaCl-KCl), $Na_6M_2(AlO_4)_6(SiO4)_6Cl_2$ (LiCl-KCl)

- ✓ De-Chlorination Approach: Remove Cl-induced problems

Conceptual Structure of SAP (SiO_2-Al_2O_3-P_2O_5)

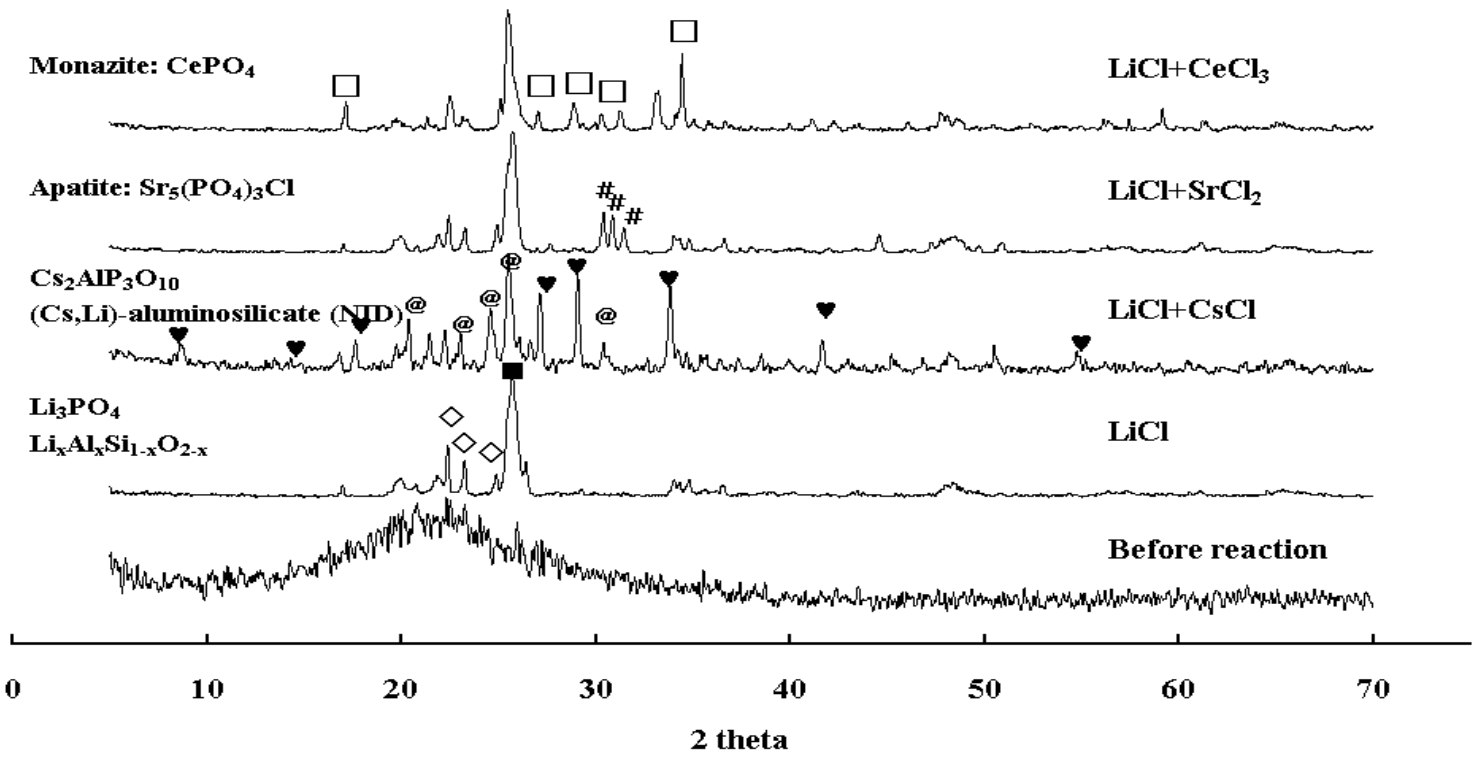
Sequential bond: -Si-O-Al-O-P-O-P-O-Al-O-Si



- Silicate
- Aluminosilicate
- Aluminophosphate or phosphate

- Sol-gel process using TEOS, H_3PO_4 and $AlCl_3$ in $EtOH/H_2O$

Reaction products of SAP with Metal chlorides at 650℃



$LiCl + SAP \rightarrow Li_xAl_xSi_{1-x}O_{2-x} + Li_3PO_4 + Cl_2$

$LiCl + CsCl + SAP \rightarrow$ (Li, Cs)-aluminosilicate + Li_3PO_4 + $Cs_2AlP_3O_{10}$ + Cl_2

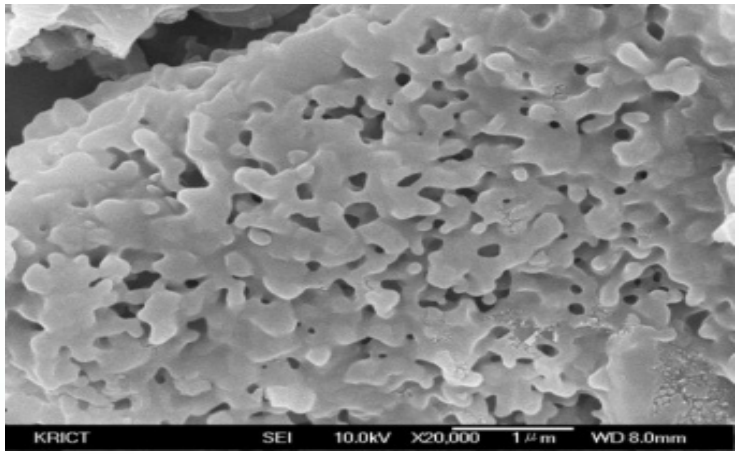
$LiCl + SrCl_2 + SAP \rightarrow Li_xAl_xSi_{1-x}O_{2-x} + Li_3PO_4 + Sr_5(PO4)_3Cl$(apatite) + Cl_2

$LiCl + CeCl_3 + SAP \rightarrow Li_xAl_xSi_{1-x}O_{2-x} + Li_3PO_4 + CePO_4$(monazite) + Cl_2

Reaction of SAP with LiCl-KCl

❖ De-Chlorination behavior of SAP

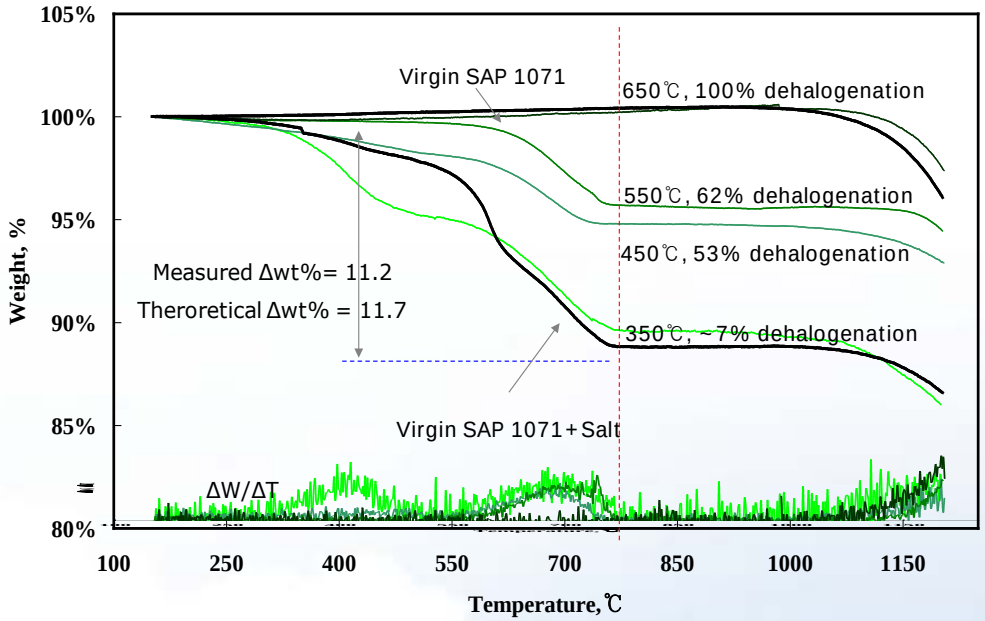
Image of SAP

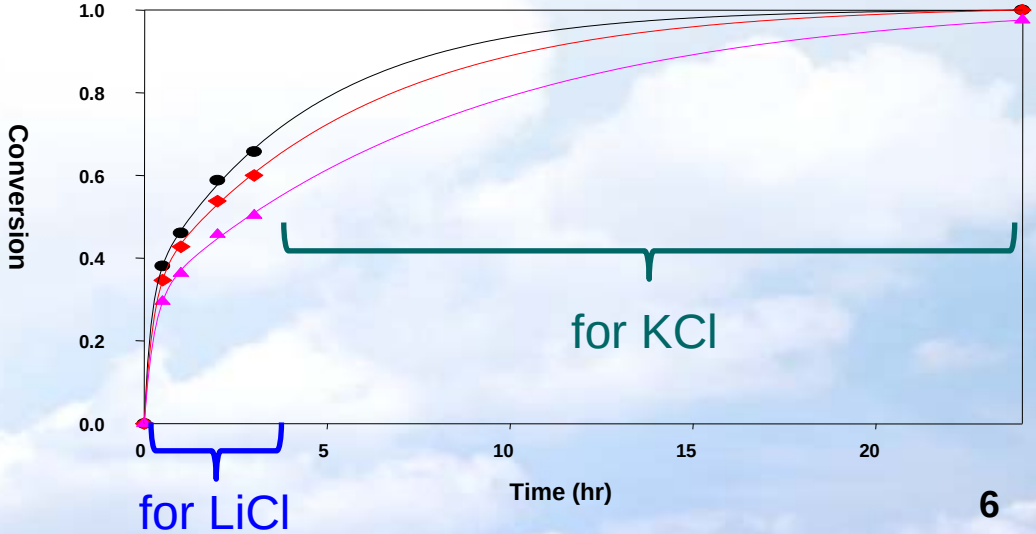


- Product: thermally stable
  - eliminated waste volatility

- Reaction time at 650℃: ~24hr
  LiCl in waste: fast reaction in 5hrs
  KCl in waste: slow reaction in 18hrs

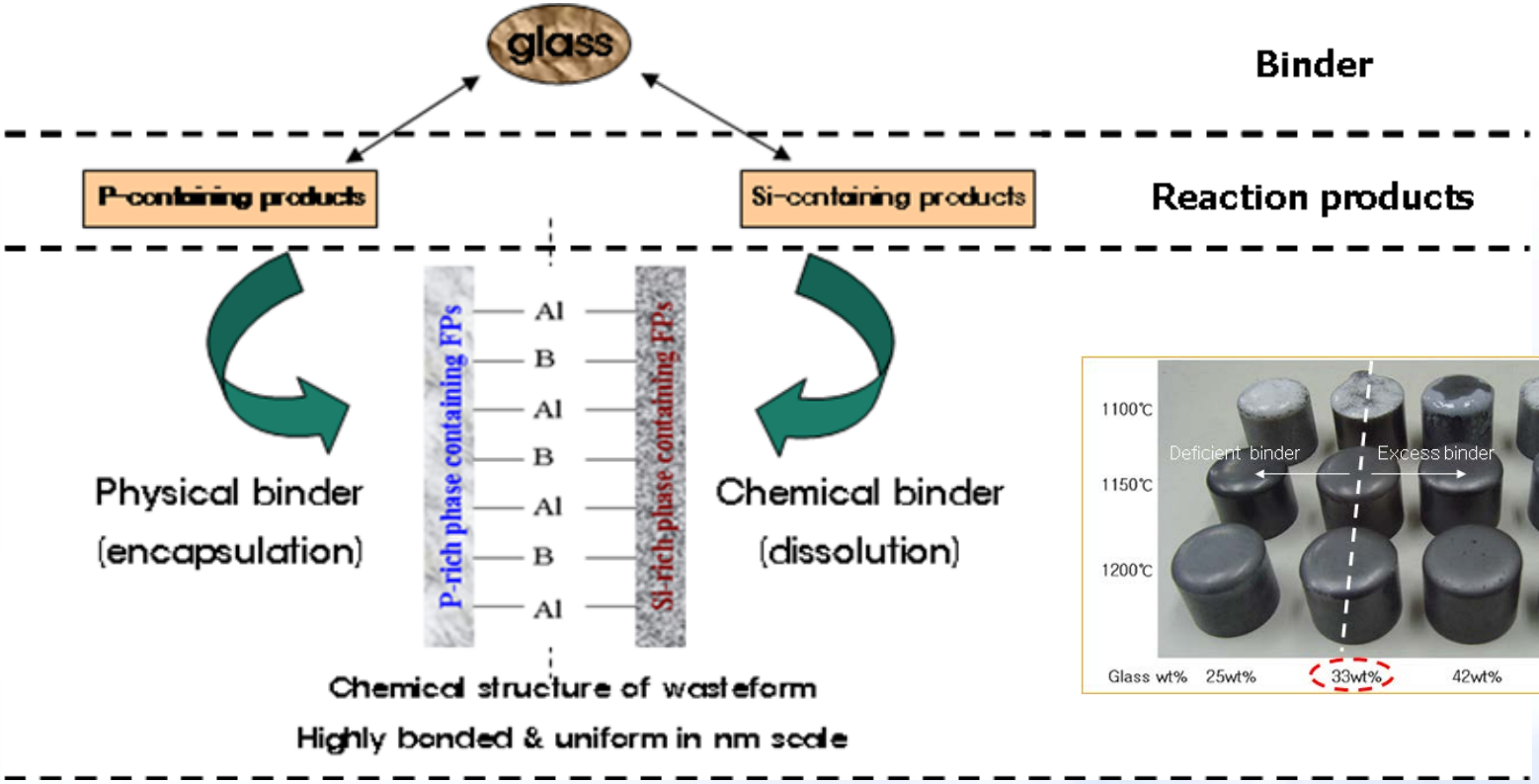
TGA





Consolidation of Reaction Products

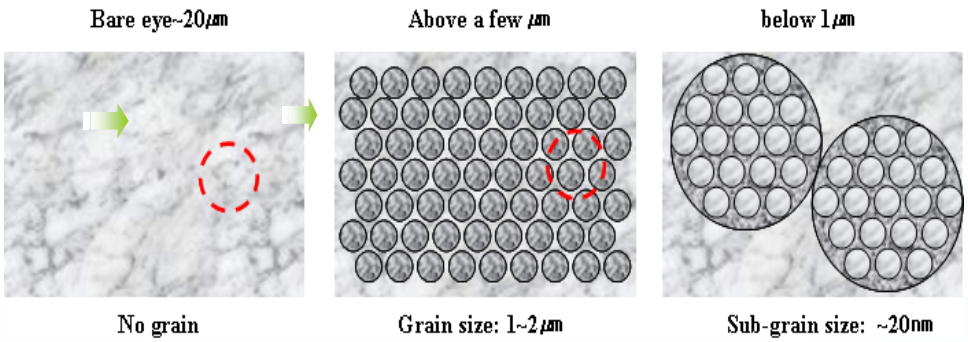
Function of binder & Chemical structure

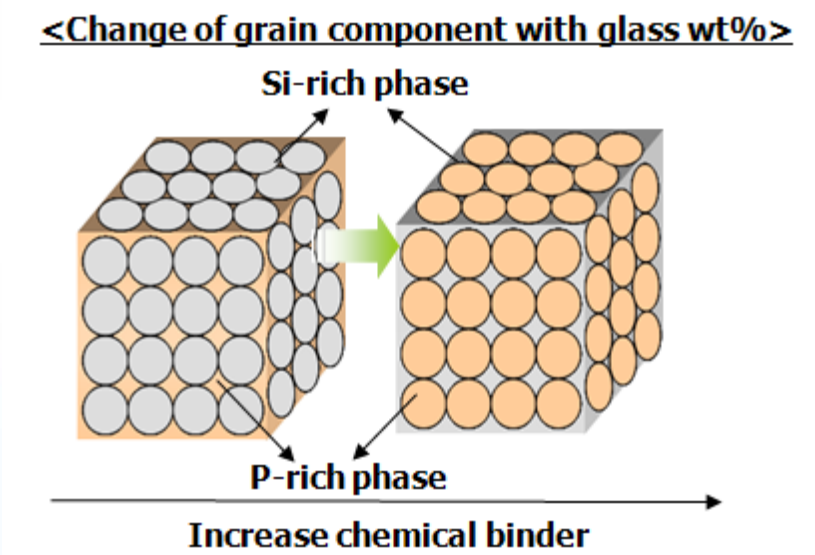


- The given glass has a physical or chemical binding ability for each reaction products
- Intermediate element, Al or B, chemically connects the two different phases

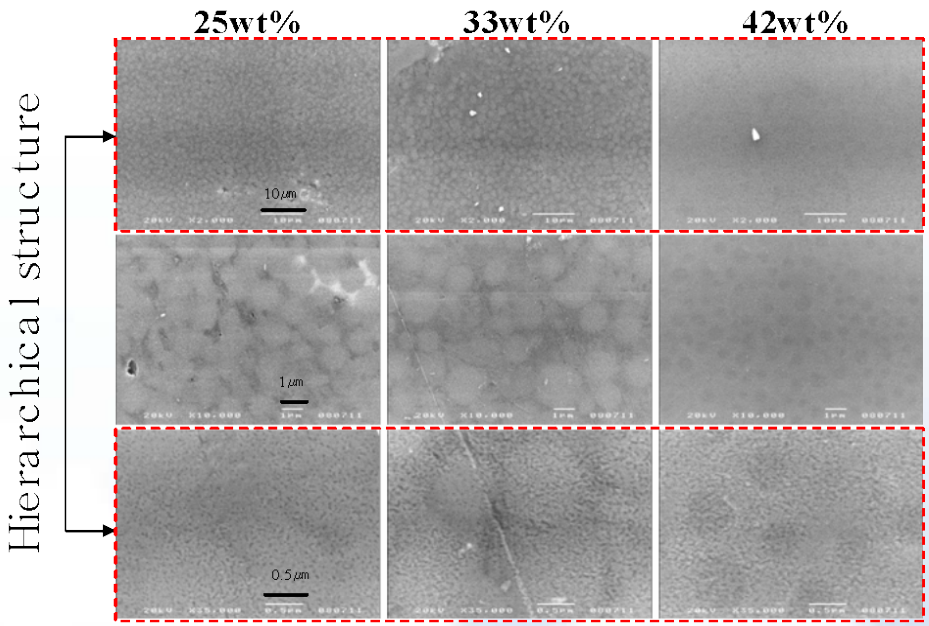
Microstructure of Consolidated Forms

Homogeneity with view scale





SEM-BSE

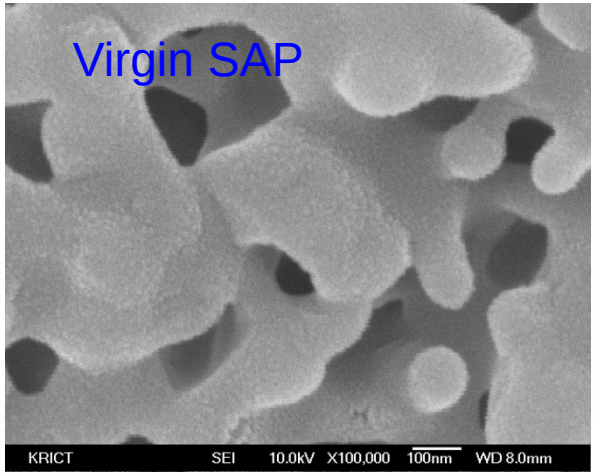


White : Si-rich phase
Dark : P-rich phase
Al is uniformly distributed
(element mapping)

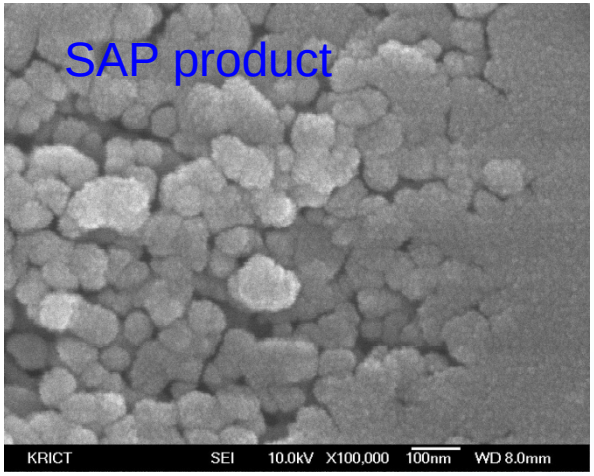
matrix : P-rich → Si rich
Grain size : decreased

Conservation of Original Morphology

❖ Morphology of the wasteform



Scale bar 100nm



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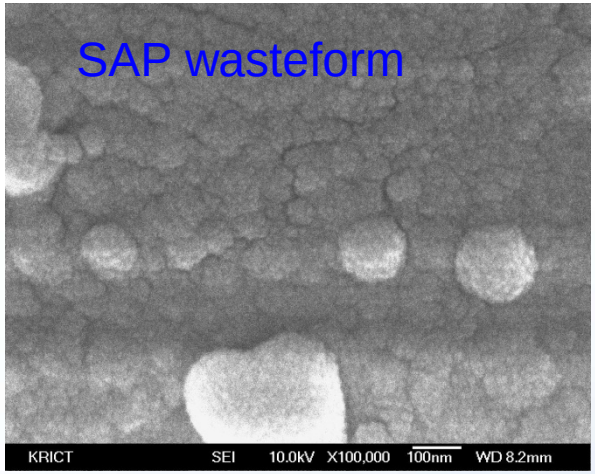
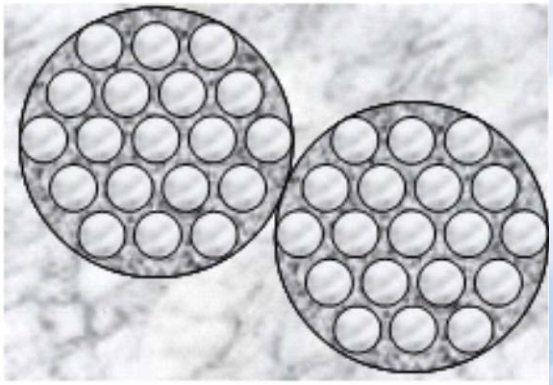


Scale bar 100nm



Sub-grain: about 10nm

- ✓ "domain-matrix structure" below μm scale
- ✓ glassy wasteform composing of silicate & phosphates

Modification of Basic Material System

- Optimization of de-halogenation matrix:
  - Basic SAP: De-chlorination

    SiO_2-Al_2O_3-P_2O_5

  - Enhancement of reactivity by additives

    Basic SAP: SAP/salt=3
    M-SAP: SAP/salt=2

    SiO_2-Al_2O_3-Fe_2O_3-P_2O_5

  - Simple consolidation

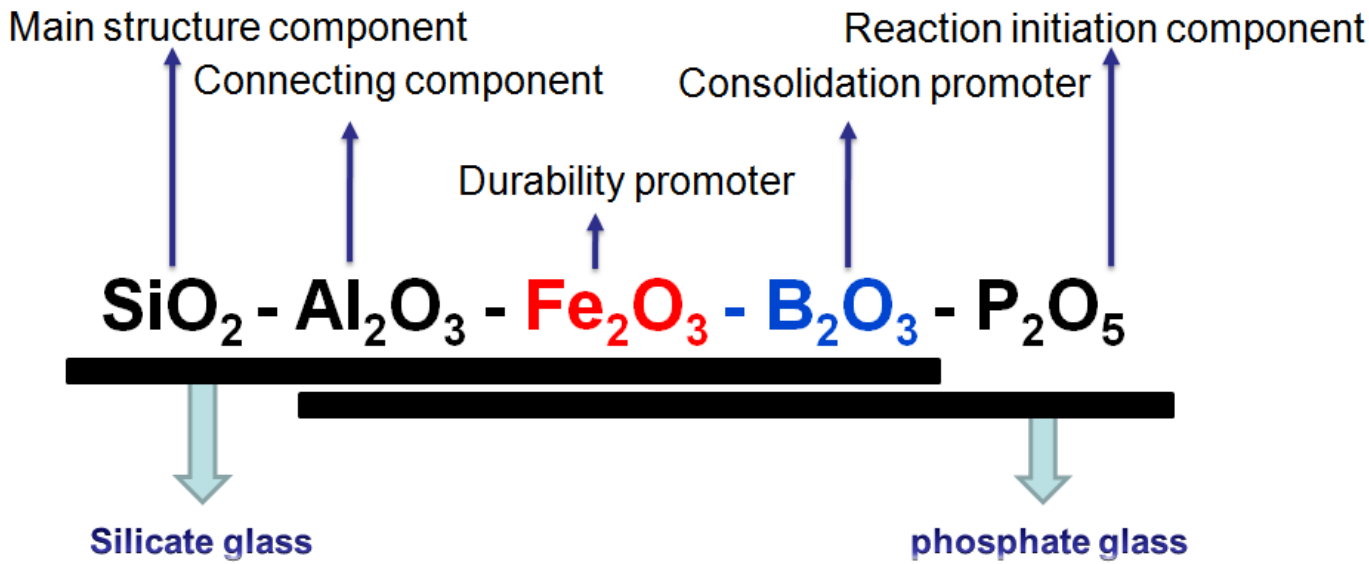
    SAPs: needs glass binder
    U-SAPs: NO glass binder

    SiO_2-Al_2O_3-Fe_2O_3-P_2O_5-B_2O_3

Composition of U-SAP

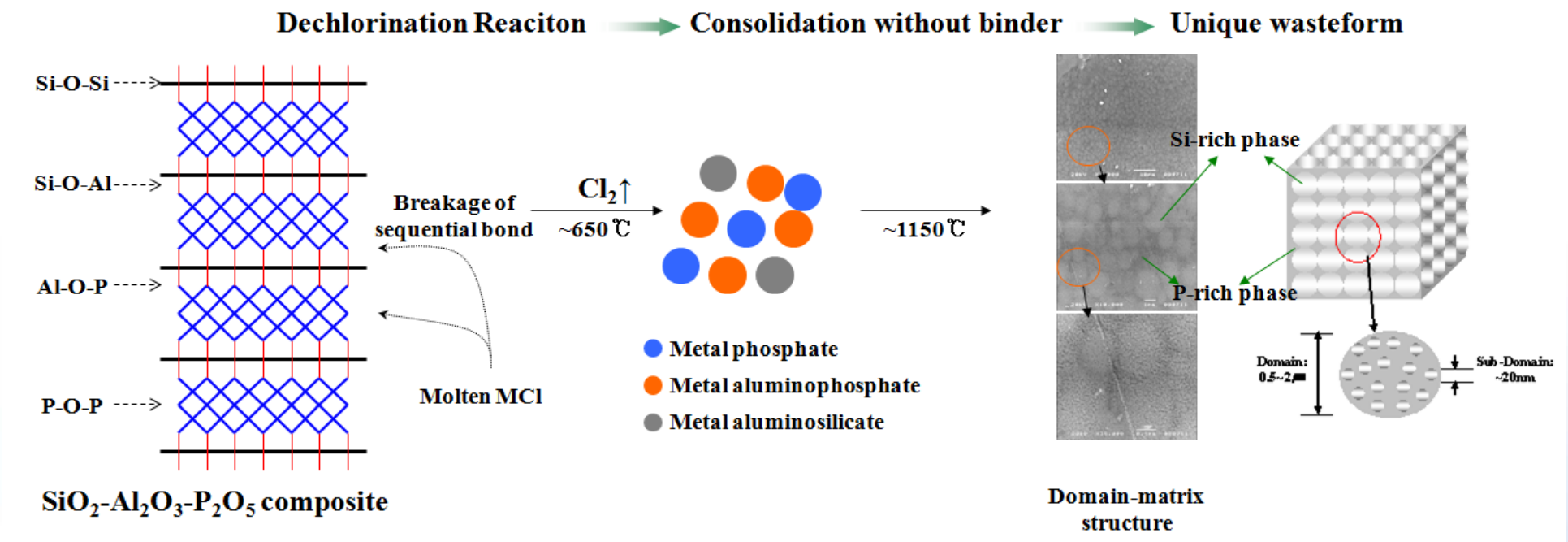
❖ De-halogenation Matrix for waste salt

Stabilization/ Solidification of metal chloride by one material



- ✓ MC: main component : 30~40wt%
- ✓ RIC: unstable material in molten salt→ reactive material (P_2O_5 best): 25~30wt%
- ✓ CC: reactive material to MC and RIC: 15~20wt%
- ✓ DP: Compatible with MC/RIC-rich phase, transition metal: 3~5wt%
- ✓ CP: Low melting point (B_2O_3 best): 5~10wt%

U-SAP process for chloride waste via de-chlorination

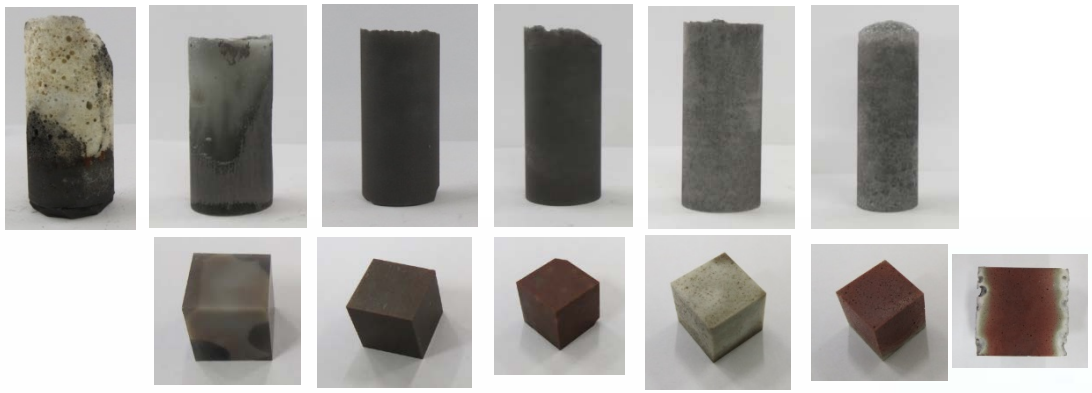


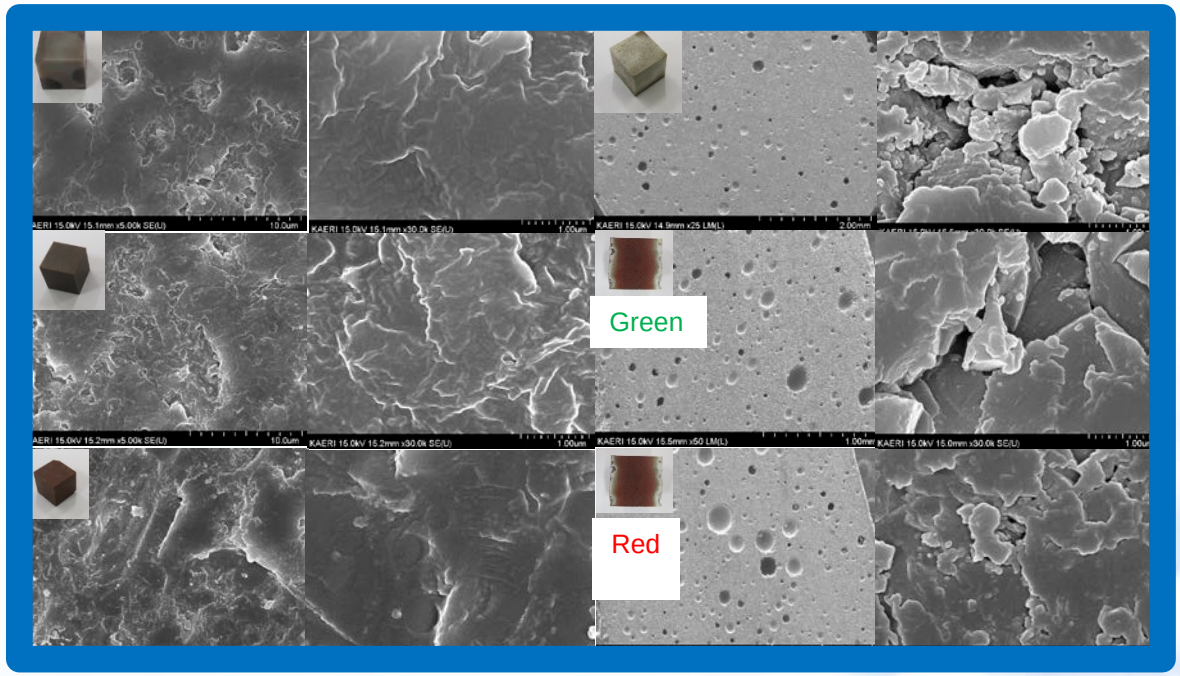
Wasteforms with varius salt/U-SAP ratios

U-SAP/salt ratio

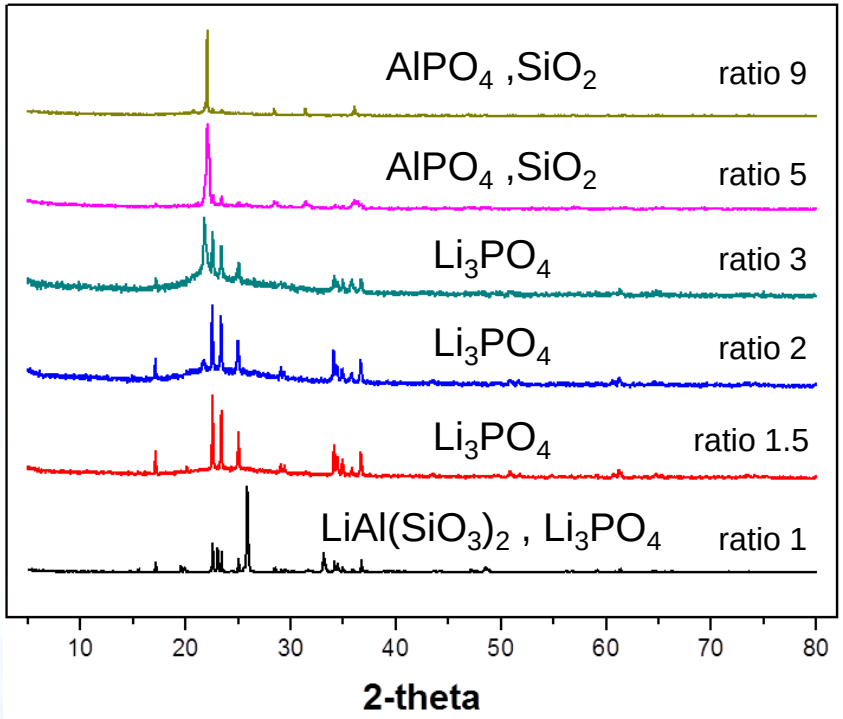
Salt : LiCl (CsCl 2wt%, $SrCl_2$ 3wt%, $BaCl_2$ 5wt%)

1 1.5 2 3 5 9



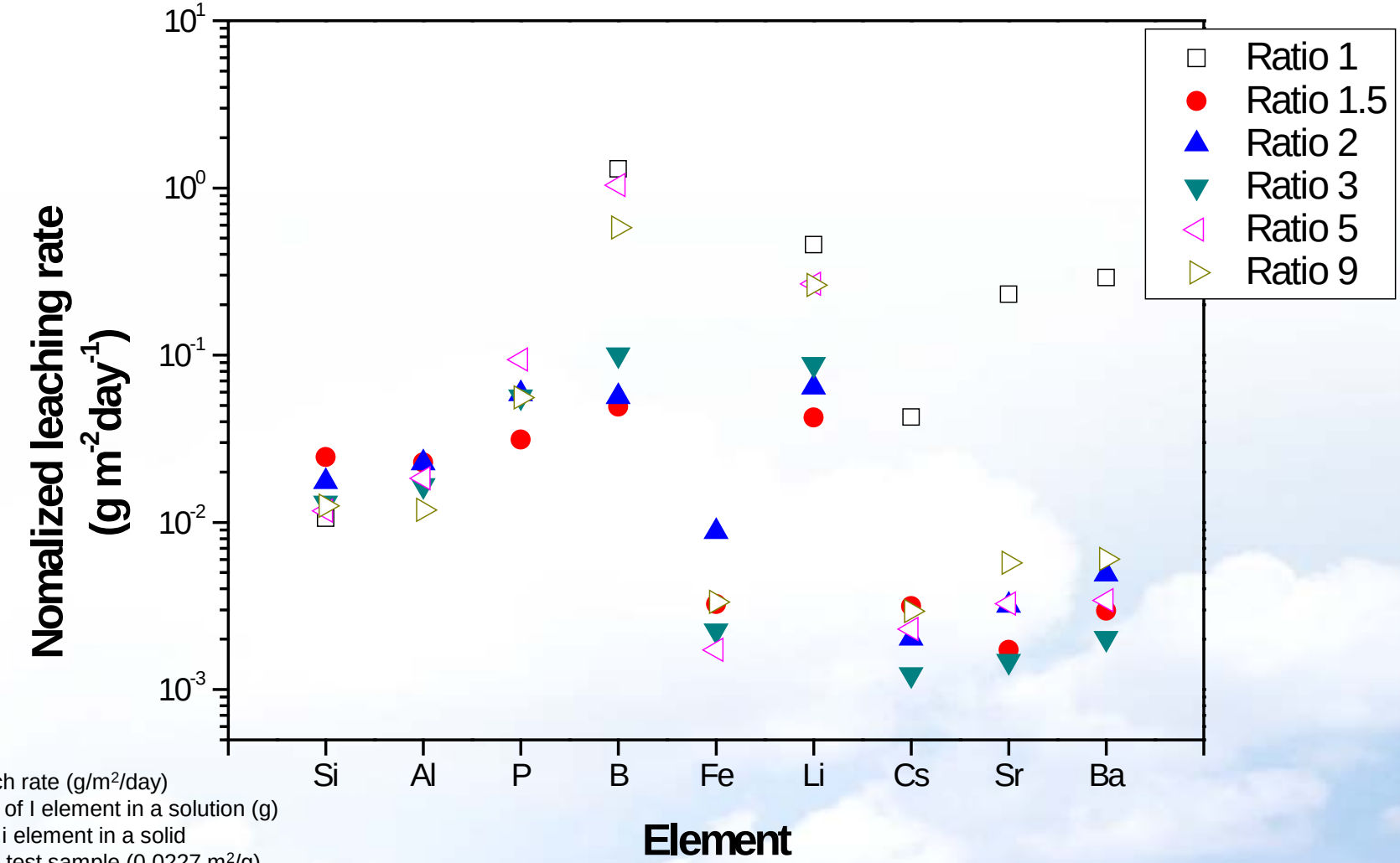


XRD results for U-SAP wastefroms



Chemical durability for U-SAPs wasteform: Normalized Mass Loss

U-SAPs wasteforms for LiCl waste: PCT-A test at 90℃ for 7days



$$LR_i = \frac{m_i}{f_i \cdot S \cdot t}$$

LR : normalized leach rate (g/m^2/day)
m_i : leached amount of I element in a solution (g)
f_i : weight fraction of i element in a solid
S : surface area of a test sample (0.0227 m^2/g)
t : test duration (day)

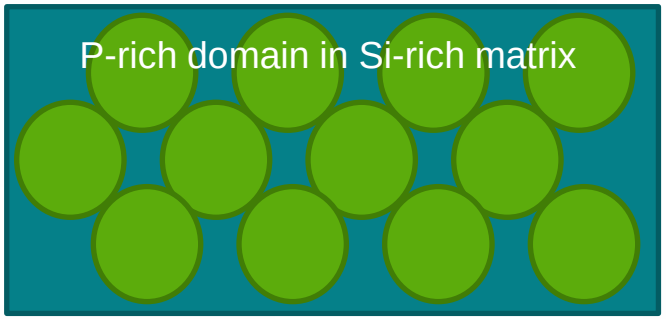
Physical properties of U-SAP wasteform

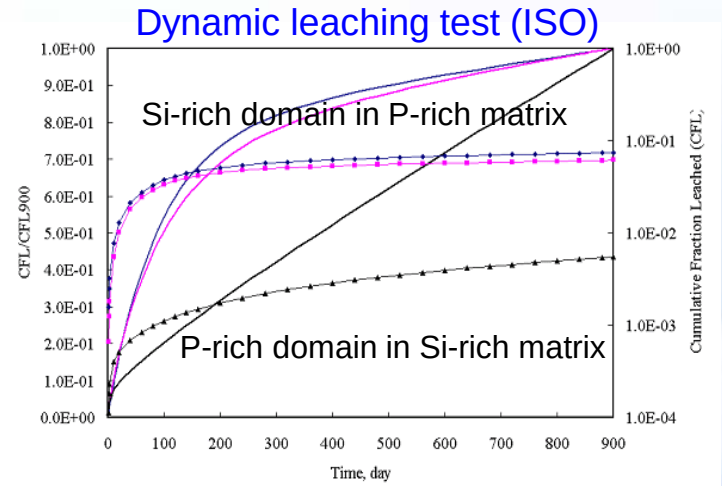
Density (ρ)	2.35~2.4 g/cm^3
Thermal Conductivity (k)	1.1~1.4 W/mK
Thermal Capacity (C_p)	0.96~1.07 J/gK
Glass Transition Temperature (Tg)	753~800 K (480~527℃)
Thermal expansion coefficient (TEC)	~3.0E-6 K^{-1}
Micro-hardess	486 ± 14.9 Hv (4.76 Gpa± 0.15)

Summary

- Metal chlorides is possible to apply a conventional vitrification process?
  - If no specific material system, the answer is NO!
    ex) $NaPO_3$-Al_2O_3-AlF_3 for NaCl-KCl(RIAR), Tellurite glass for LiCl-KCl(PNNL)

- De-chlorination by using U-SAP (SiO_2-Al_2O_3-Fe_2O_3-B_2O_3-P_2O_5) → glassy wasteform
  - A unique wasteform composing of silicate glass and phosphate glass
  - The incompatibility size: about tens of nm





- U-SAP wasteforms of ratio 1.5, 2, and 3 show better properties than other wasteforms.
  - Dense surface
  - Lower leaching property

Thank you

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