ORP-52101 -VA
Revision 0

Iron-Phosphate Glasses for Immobilization of Radioactive Technetium

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

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Iron-Phosphate Glasses for Immobilization of Radioactive Technetium

Abstract 12216

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Outline

- **Introduction**
  - Concern on Technetium (Tc)-99
  - Proposed waste-forms for Tc-99
  - Iron-phosphate glasses
- **Objectives**
- **Experimental Procedures**
- **Morphology, structure characterization**
  Chemical analysis
- **Summary**

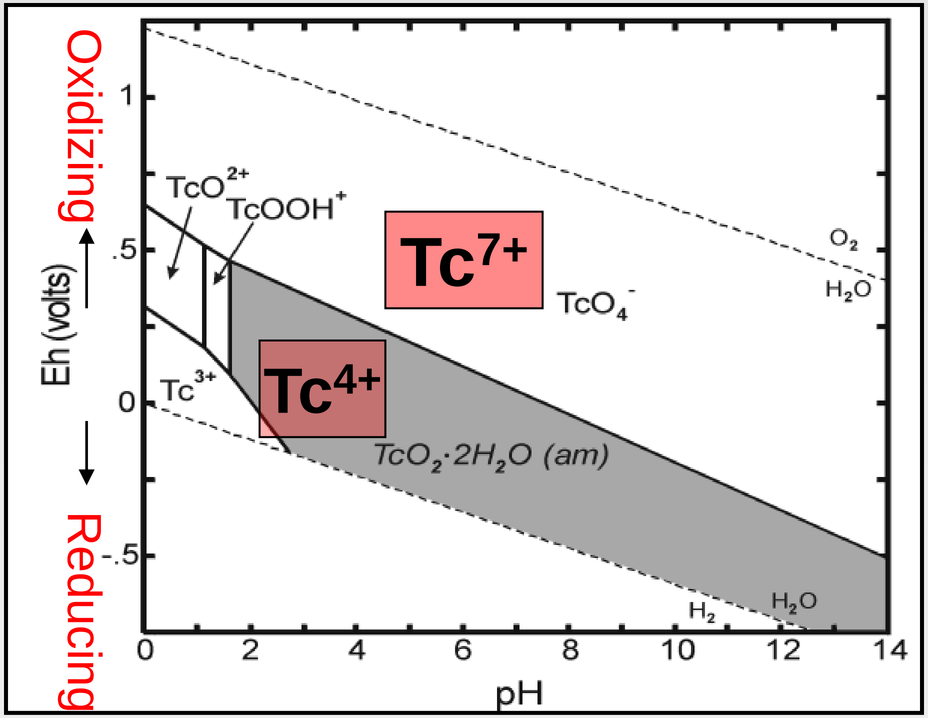
Concerns on Tc-99

Tc-99

Long half-life:
2.1×10^5 y.

High yield:
~6 %.

Dominant oxidation state: (TcO_4^-)

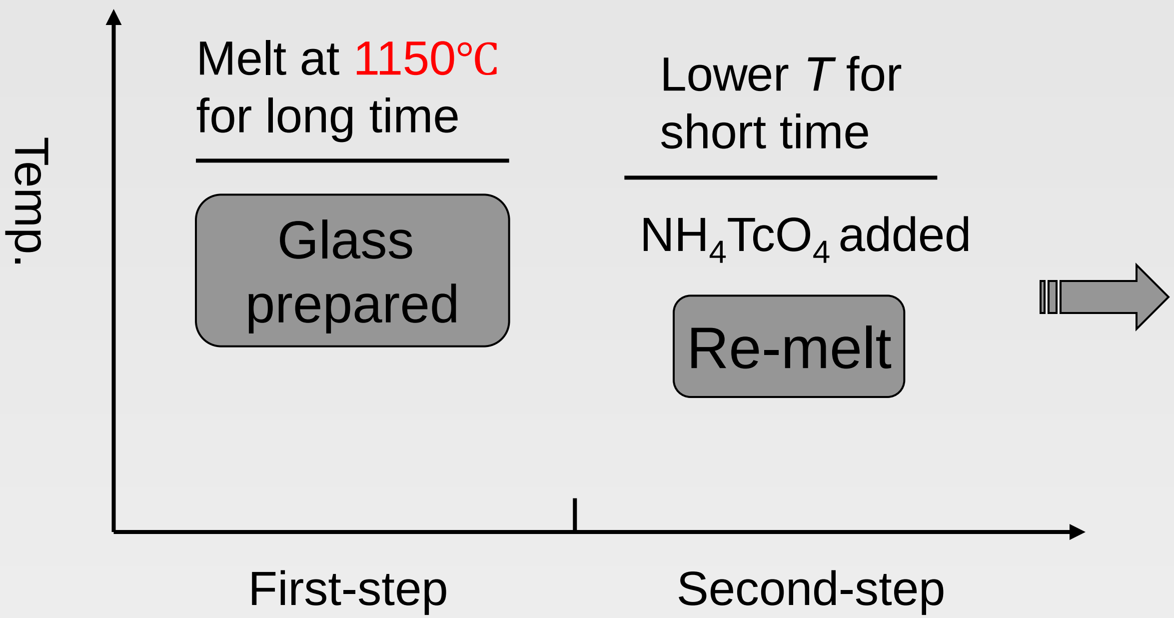


Eh-pH diagram for Tc species

TcO_4^-:
1) High solubility in water and acids; 2) High mobility;
3) Easy transport through the environment (cannot be adsorbed on sediments).

Proposed waste-forms for Tc

Vitrification of Tc using borosilicate glasses



1) >90 % Tc-99 volatilized.
2) ~0.003 wt% Tc-99 retained in defense glasses.

High volatilization

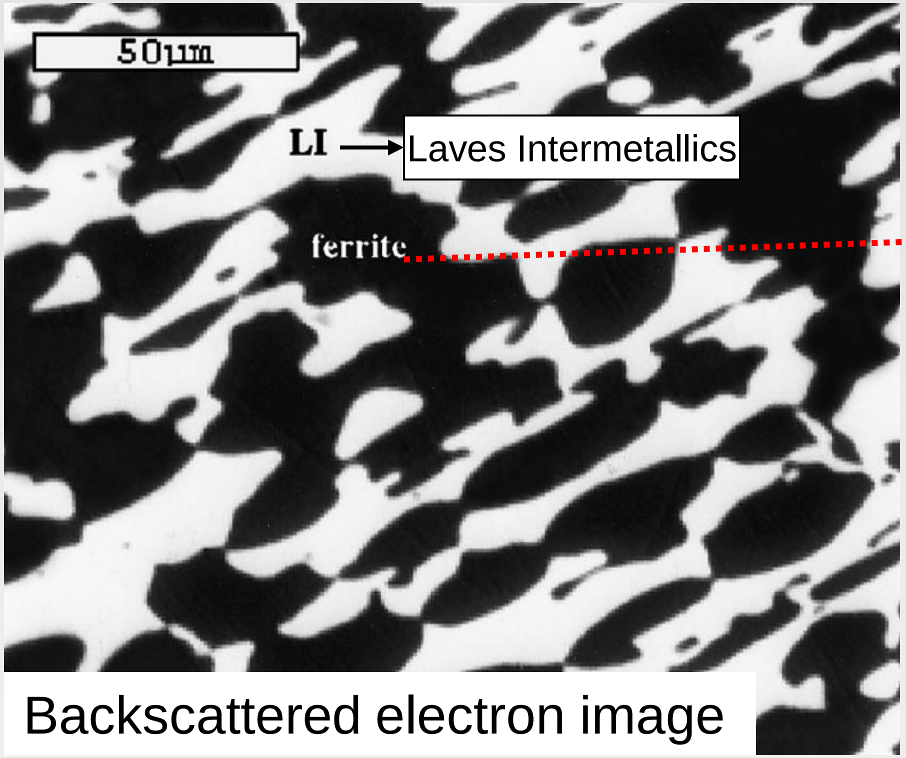
Low loading

Borosilicate glasses were not effective.

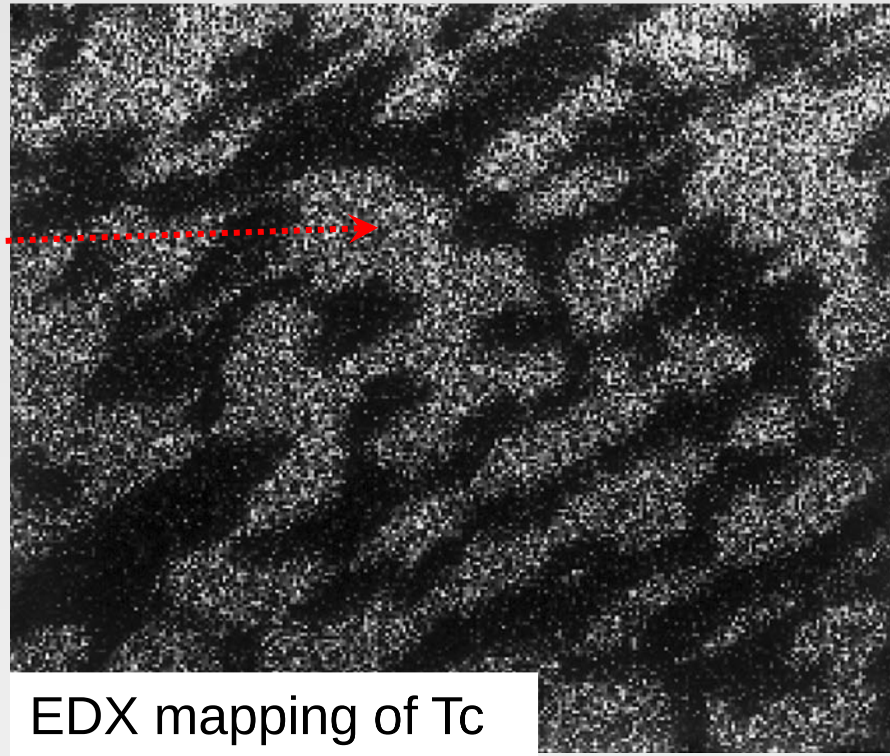
W. L. Ebert *et al.*, Material Research Society Meeting, Boston, MA, (1995).

Proposed waste-forms for Tc

Metallic alloys



Backscattered electron image


EDX mapping of Tc

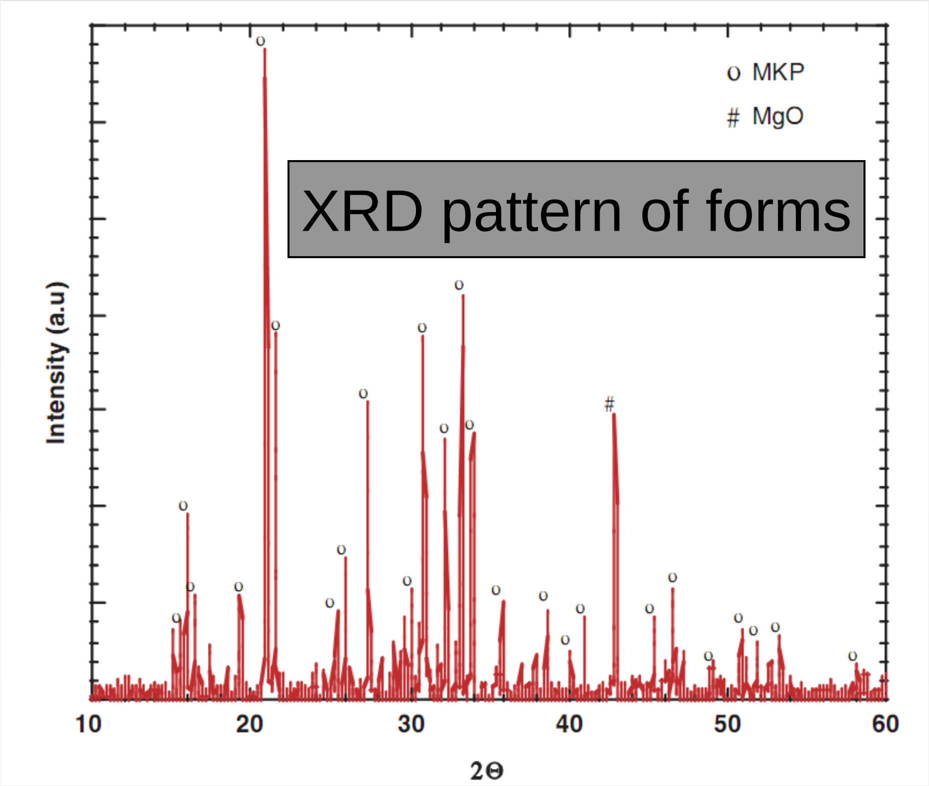
1) Stainless steel-15Zr (wt%) as the matrix;
2) High *T* (~1600 ℃) under argon atmosphere (Tc metal as source);
3) Tc goes into ferrite phase (Max. Tc loading: <2 wt%).

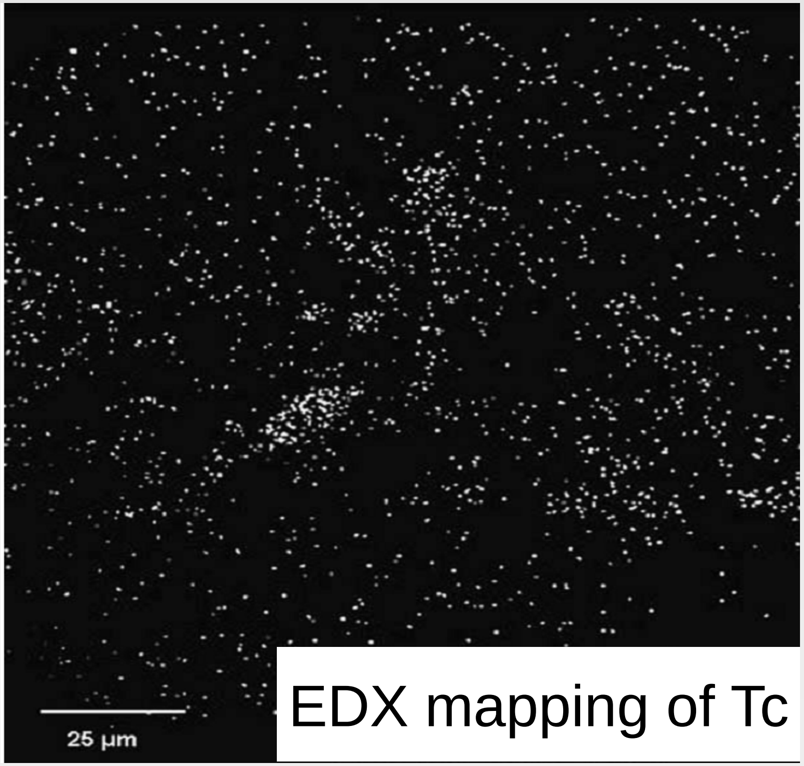
D. D. Keiser Jr *et al.*, J. Nucl. Mater., 277 (2000) 333.

Proposed waste-forms for Tc

Chemically bonded ceramic forms

Low temperature (<150 ℃)





1) $MgO+KH_2PO_4+5H_2O=MgKPO_4{\cdot}6H_2O$;

2) Max. Tc loading: ~900 ppm.

D. Singh *et al.*, J. Nucl. Mater., 348, (2006) 272.

Proposed waste-forms for Tc

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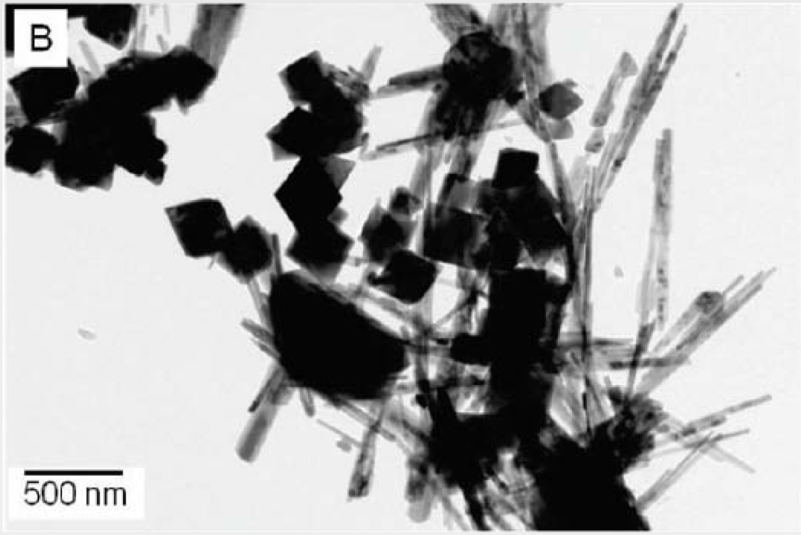
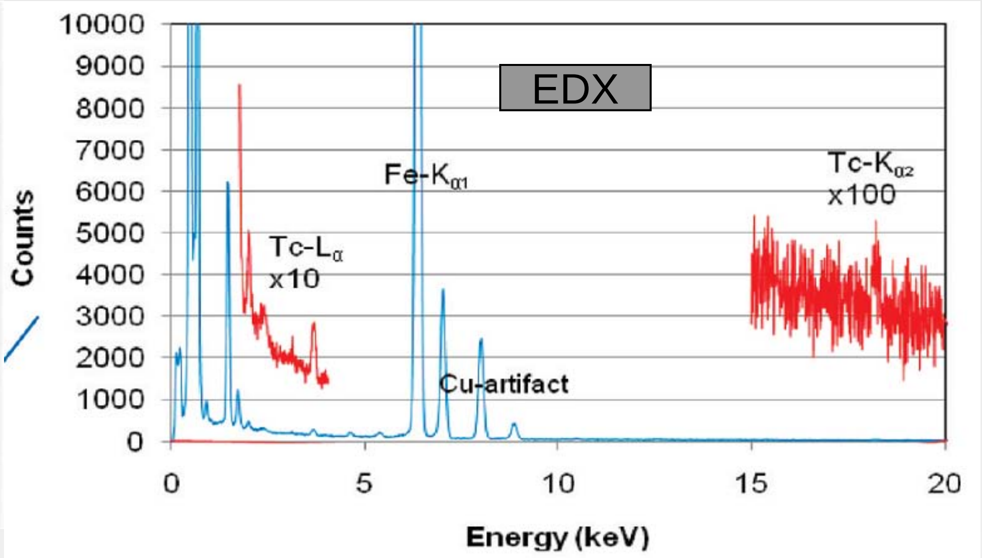
Iron-containing minerals

$$Tc(VII)O_4^- + 3Fe^{2+} + (n+7)H_2O =$$
$$Tc(IV)O_2 \cdot nH_2O_{(s)} + 3Fe(OH)_{3(s)} + 5H^+$$

T. Peretyazhko *et al.*, Environ. Sci. Technol. 42 (2008) 5499.





1)Tc (IV) enters into Fe(II)-goethite (or magnetite) structure;

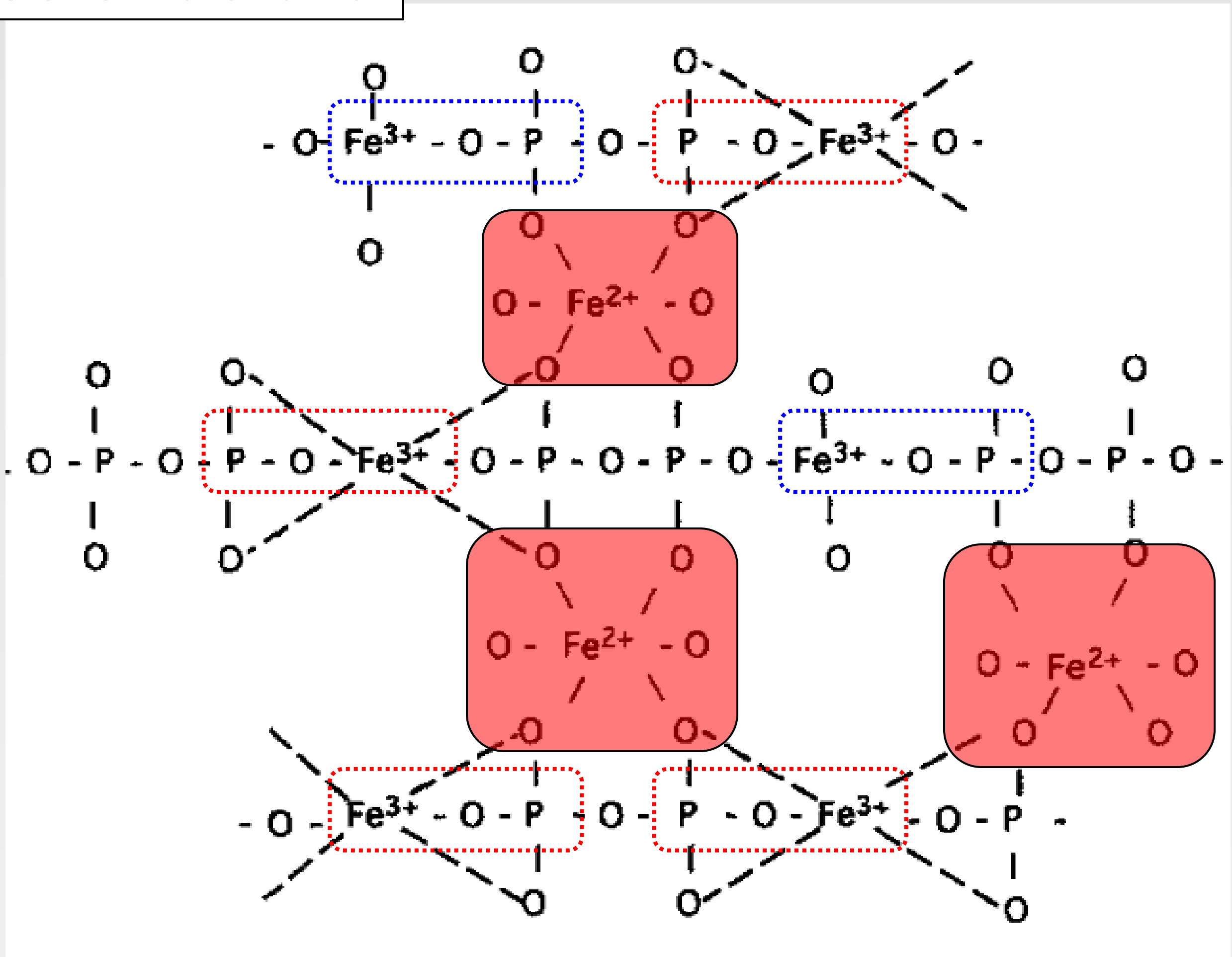
2) Low Tc release;

3) Max. Tc loading: **<1000 ppm**.

W. Um *et al.*, Environ. Sci. Technol. 45 (2011) 4904

Iron-phosphate glasses

Fe-P glass structure

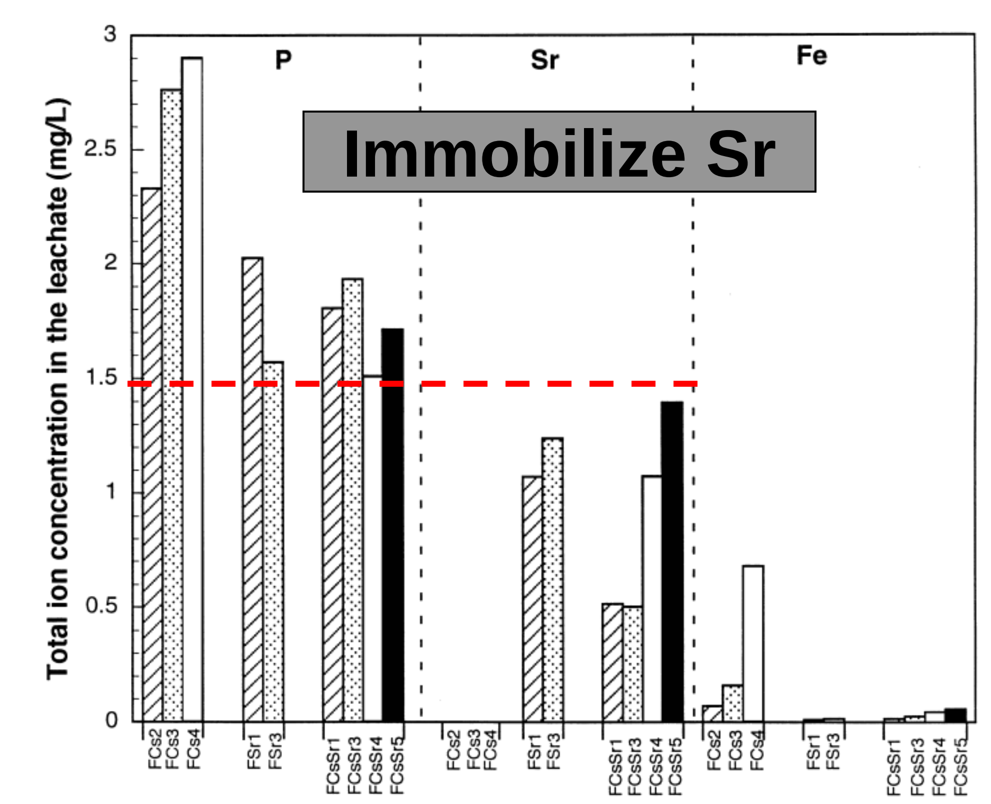


1) Low melting *T*: ~900-1100 ℃; 2) High waste loading;
3) Chemically durable P-O-Fe bonds in glass structure.

X. Yu *et al.*, *J. Non-Cryst. Solids* 215, (1997) 21.

Iron-phosphate glasses

Fe-P glasses as waste-forms



PCT at 90℃ for 7 days

Satisfy DOE regulation.

M. G. Mesko *et al.*, *Waste Manage.* 20, (2000) 271.

Other volatile elements

Immobilize low-activity wastes

	S	Cs	Re*
Contents in glasses (wt%)	~1.8	~0.12	~0.03

*:Re as a surrogate for Tc-99.

D. E. Day *et al.*, US DOE Report, June 30, 2011.

The content of Re in Fe-P glasses was very low, and release of Re was unavailable.

2. Objectives

Investigate the vitrification of Tc into Fe-P glasses.

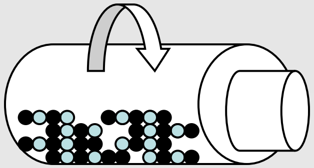
Increase the incorporation of Tc into Fe-P glasses.

Examine the chemical durability of Tc-containing Fe-P glasses.

3. Experimental Procedures

Glass frits prepared

- Nominal composition (in mol %): $42P_2O_5$-$25Na_2O$-$5Al_2O_3$-$10CaF_2$-$18Fe_3O_4$
- Mixing glass powders (~15 g).
- Melting at 1050 ℃ for 30 min.
- Casting and milling prepared glasses.



Re-melt to include Re*

Adding $KReO_4$ (wt%)				
1.5	2	3	4	6

- Mixing mixtures (~6.5 g), and re-melting at 1000 ℃ for 10 min.

*: Re as a surrogate for Tc-99

Characterization

- XRF, XRD, OM, ICP-MS etc.

4. Results & Discussion

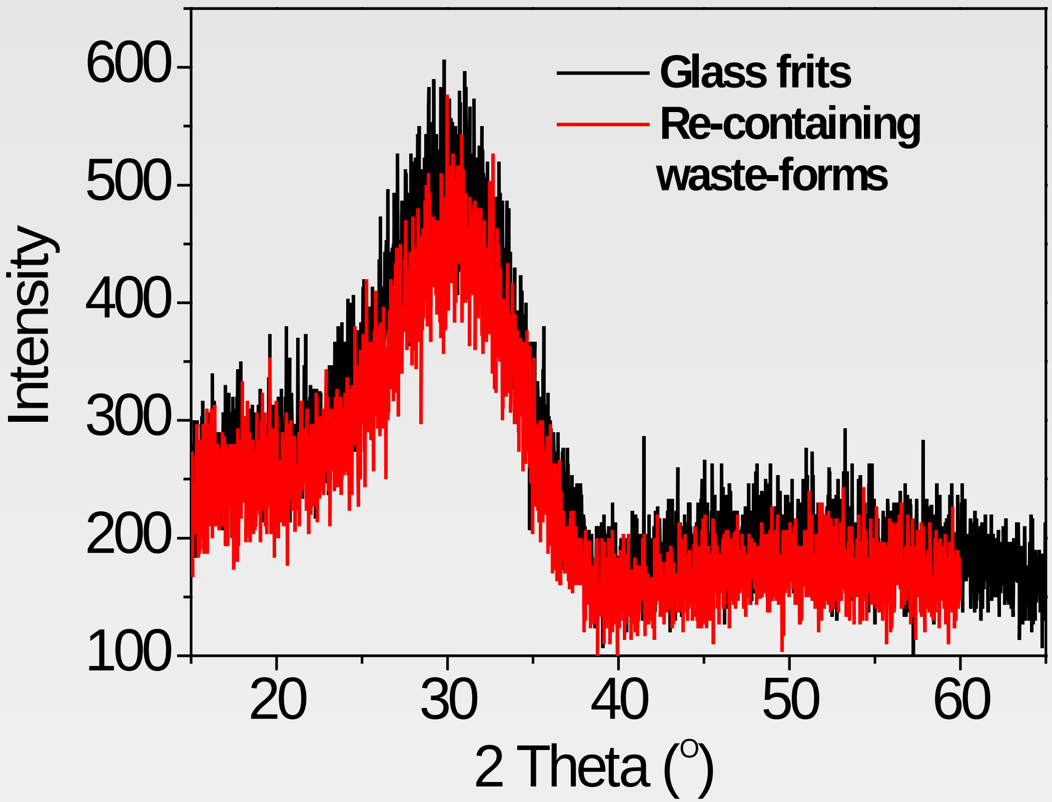
Batch and analyzed (XRF) composition of glass frits

Oxide (wt%)	Glass frits	
	Batch	XRF*
P_2O_5	45.5	47.0
Na_2O	11.8	12.2
Fe_3O_4	31.8	30.8
Al_2O_3	3.9	4.6
CaO	4.3	4.2
F	2.7	0.5
Total	100.0	99.3

*:Average values.

Satisfactory agreement.

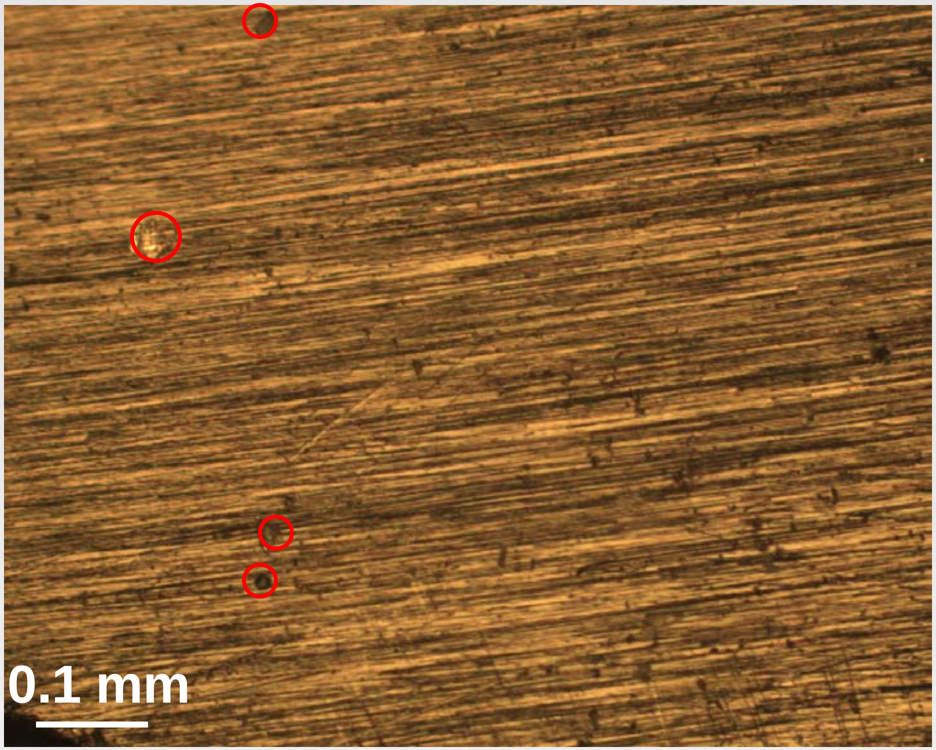
XRD patterns of glass frits and Re-containing waste forms



Crystals were not detectable with XRD.

Glass with 1.5 $KReO_4$ addition

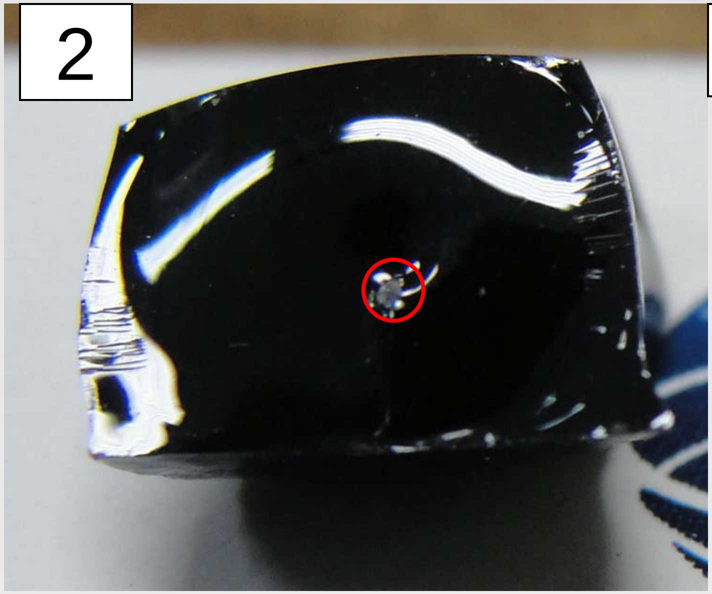
Photo

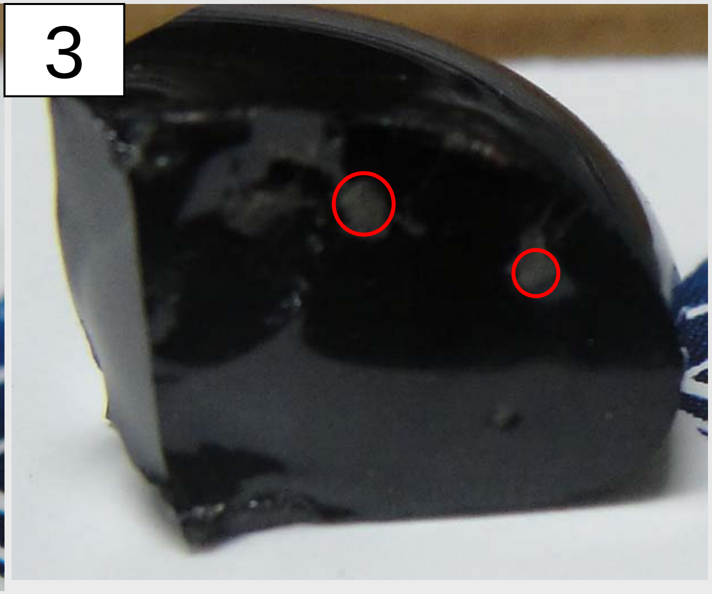


Optical Microscope

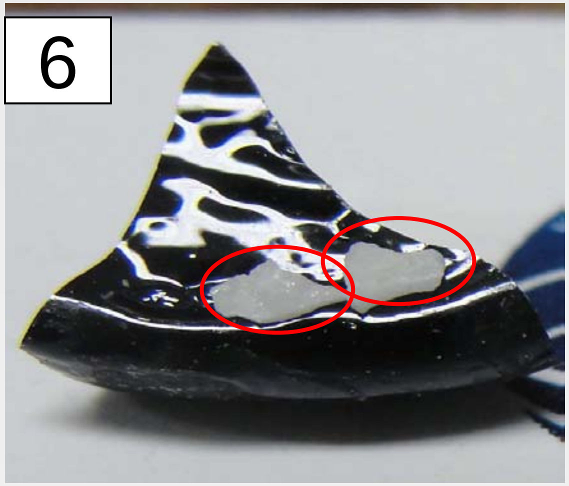
Tiny crystals containing, but less than 2 wt%.

Different $KReO_4$ addition





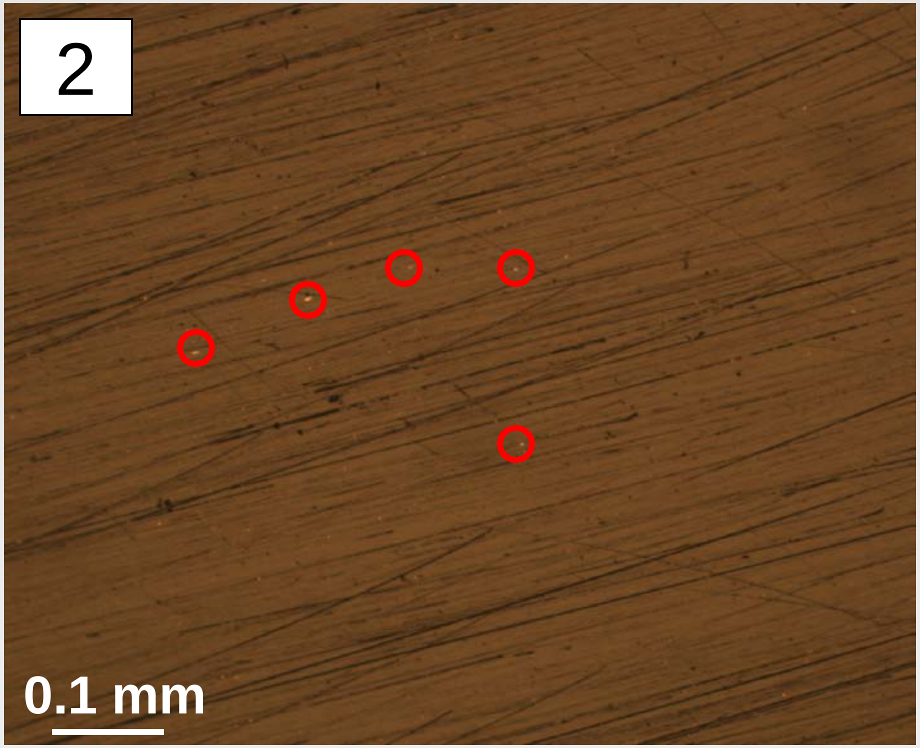
Visible gray crystals, less than 5 wt%.

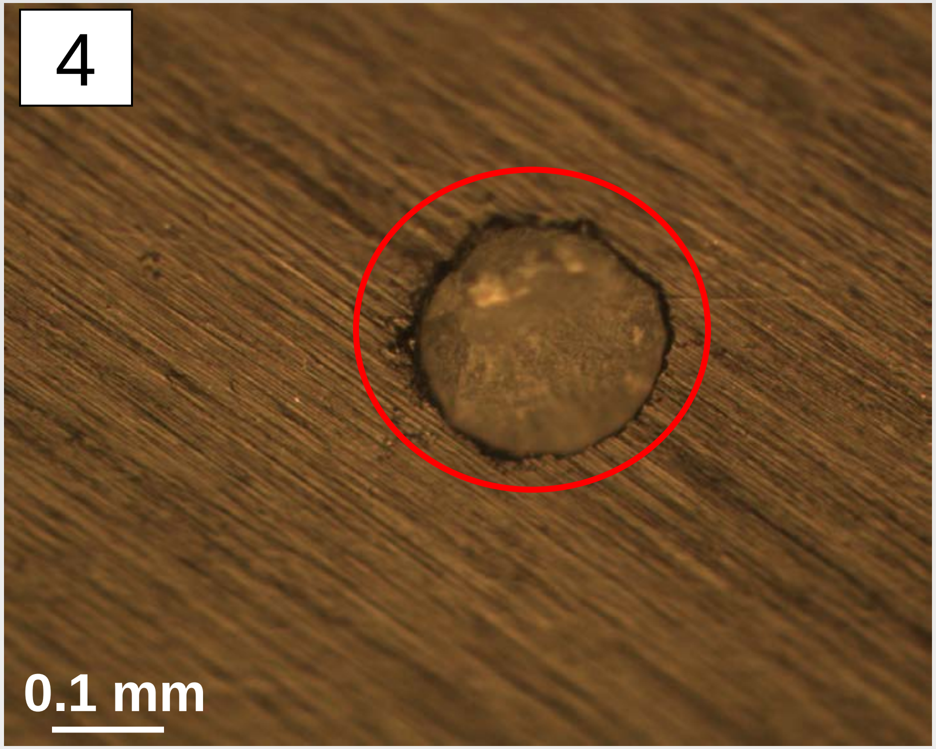


4: Visible gray and white crystals;
6: Isolated white crystals.

Photos

Different $KReO_4$ addition



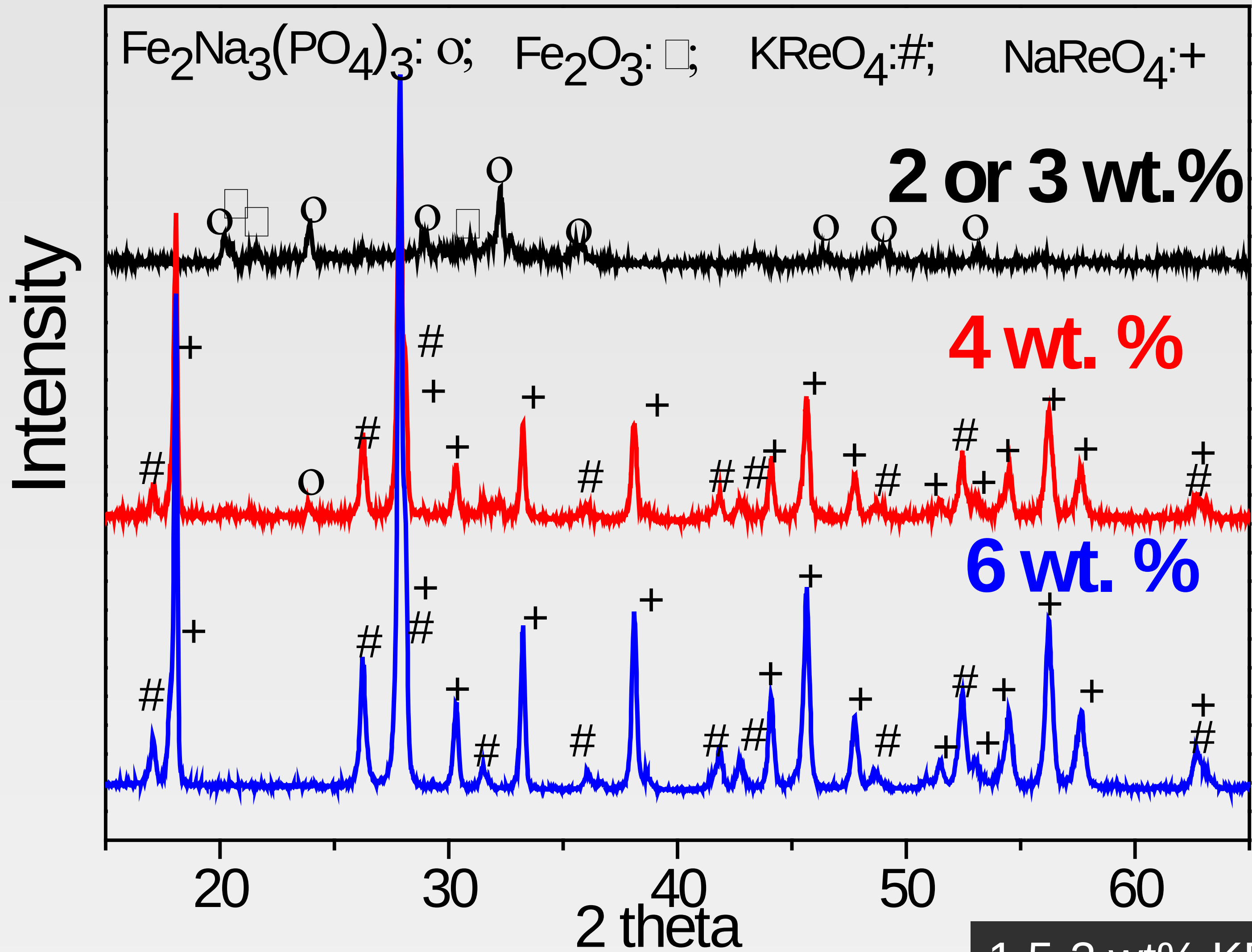


Optical microscopes

Crystal content: <5 wt%.

Tiny and small crystals exist in the glasses.

Crystal phases identification



$Fe_2Na_3PO_4$ +Fe_2O_3

$Fe_2Na_3PO_4$ +$KReO_4$+ $NaReO_4$

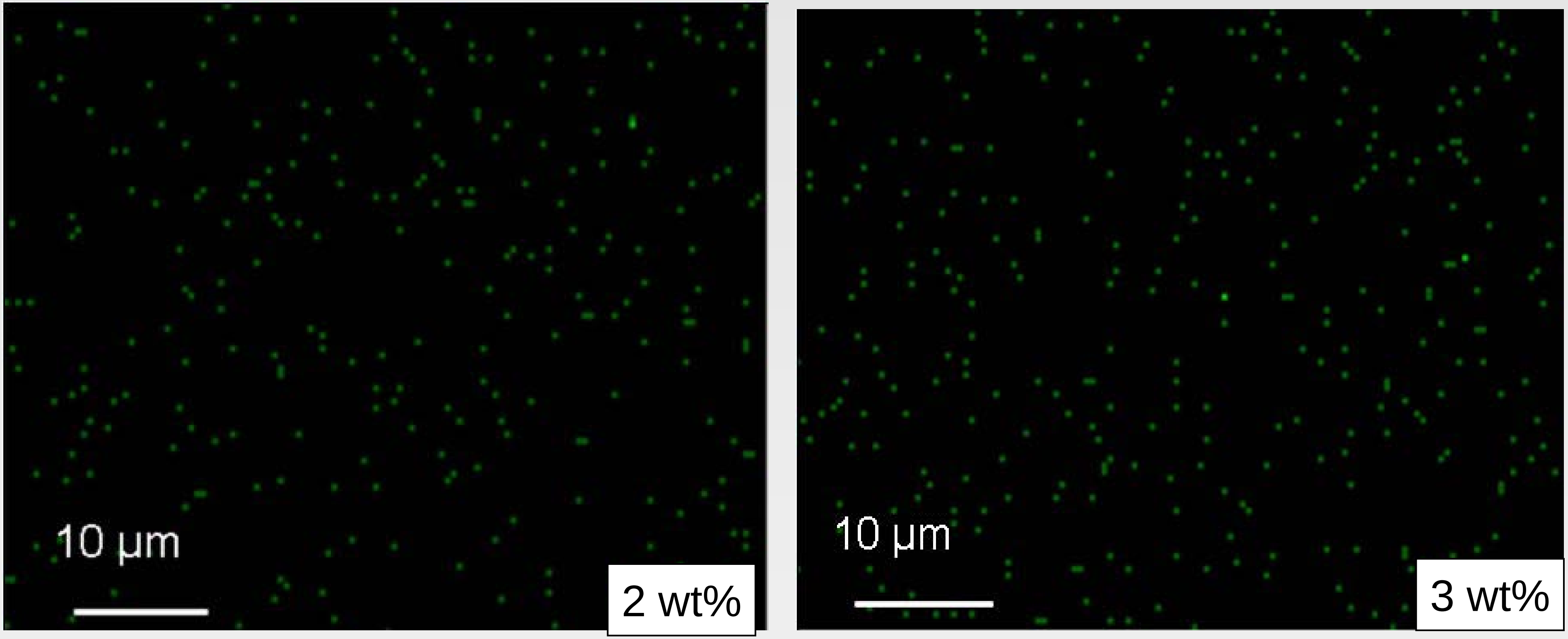
$KReO_4$+ $NaReO_4$

XRD patterns

1.5-3 wt% $KReO_4$ addition: OK;
≥4 KReO4: unacceptable.

Re distribution in glasses

EDX mapping of Re



Uniform distribution, no Re-rich phase.

Re content in Glasses

Analyzed (ICP-MS) Re retained in Fe-P glasses

$KReO_4$ (wt%)	Re addition (wt%)	Retained Re (wt%)	Retention (%)
1.5	0.97	0.50	52
2	1.29	0.65	50
3	1.93	0.88	46
4*	2.57	1.12	44
6*	3.86	1.13	29

*: Glasses separated with $KReO_4$

1) ~50 % of Re can be retained in glasses.
2) ~1 % Re loading in Fe-P glasses;

Re volatility in Fe-P glasses

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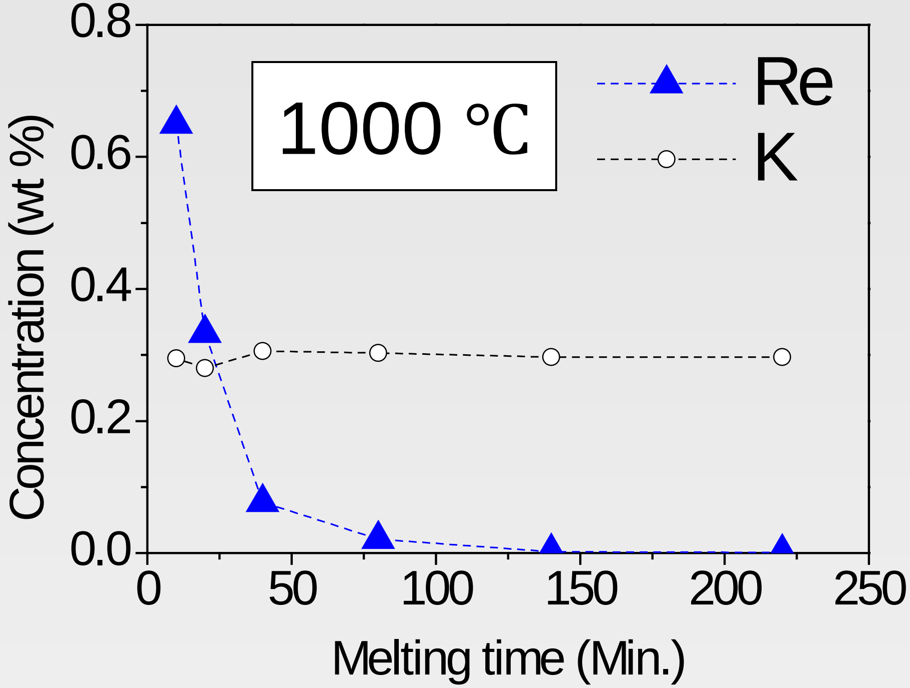
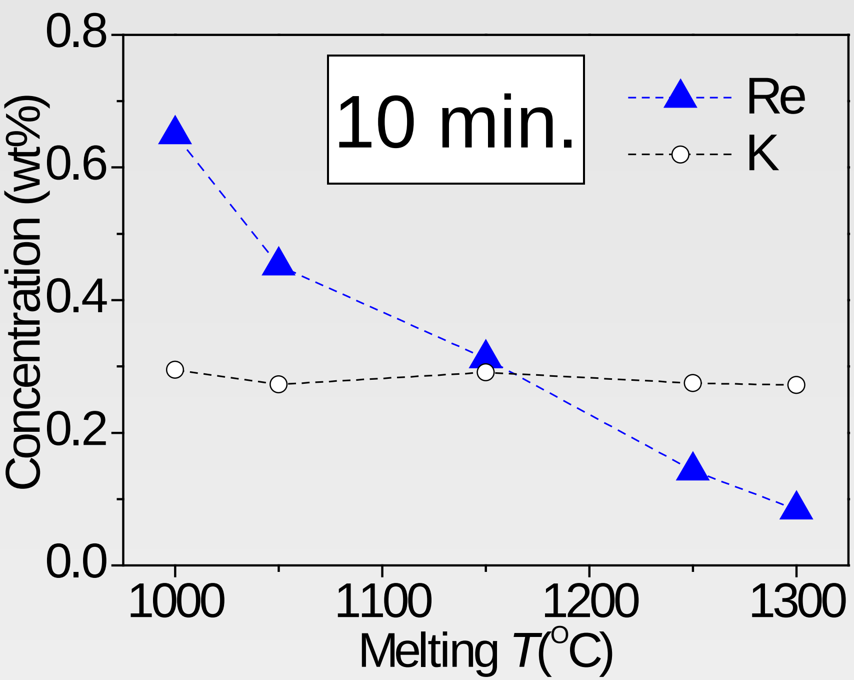
Re retention in glasses with 2 wt% $KReO_4$ addition.



Retention-melting time



Retention-melting *T*

1) Re retention decreased with increasing melting time or *T*.
2) Re volatility is sensitive with melting conditions.

Chemical durability test

Product consistency test (PCT)

Glass powders (-100 to + 200 mesh) →

Ultrasonically washing

1.5 g powder + 15 ml DIW in a Teflon vessel

At 90±2 ℃for 7, 14 or 21 days

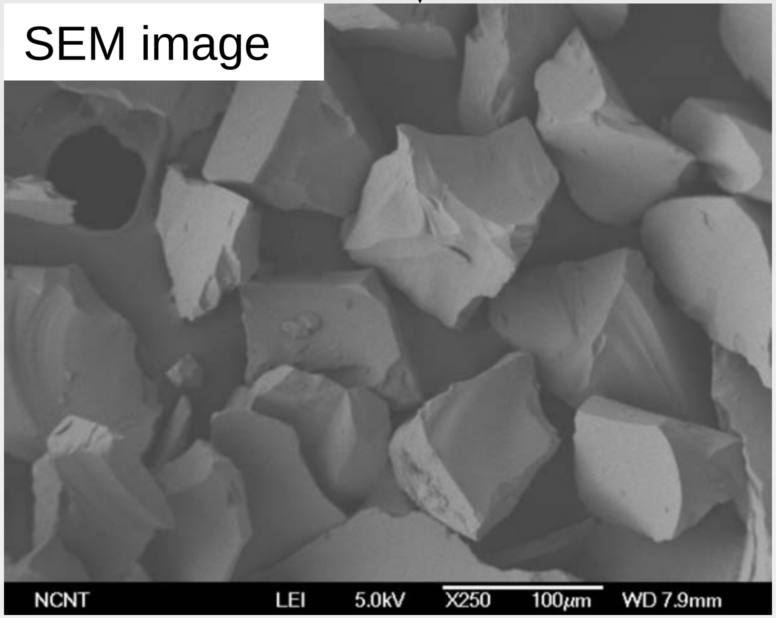
Leachate filtered with 0.45 μm syringe filter

Elemental analysis by ICP-MS

\+

Clean particles

SEM image



Normalized elemental mass release, r_i

$$r_i(\mathrm{g/m^2}) = \frac{C_i}{f_i(A/V)}$$

A/V: 1790 m^{-1} (ρ:~3.0g/cm^3)

Normalized results

r_i (g/cm^3) for different Re addition (PCT-7days)

$KReO_4$	r_{Re}	r_{Na}	r_P	r_{Fe}	r_{Al}	r_{Ca}
1.5	8.4×10^{-2}	0.15	4.3×10^{-2}	$<10^{-4}$	1.9×10^{-2}	1.5×10^{-3}
2	6.3×10^{-2}	0.19	3.8×10^{-2}	$<10^{-4}$	5.8×10^{-3}	3.7×10^{-3}
3	6.4×10^{-2}	0.17	5.1×10^{-2}	$<10^{-4}$	1.5×10^{-2}	2.8×10^{-3}
4	6.8×10^{-2}	0.19	5.8×10^{-2}	$<10^{-4}$	9.4×10^{-3}	3.7×10^{-3}

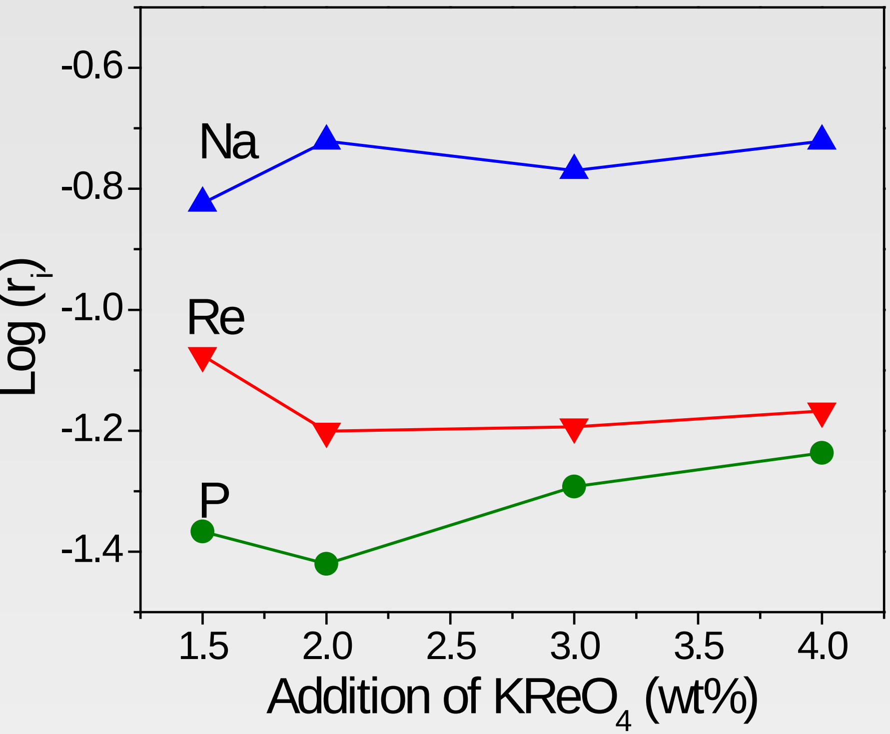
r_i (g/cm^3) for PCT-7, 14 and 21 days (2 wt% addition)

Days	r_{Re}	r_{Na}	r_P	r_{Fe}	r_{Al}	r_{Ca}
7	6.3×10^{-2}	0.19	3.8×10^{-2}	$\sim10^{-4}$	5.8×10^{-3}	3.7×10^{-3}
14	7.2×10^{-2}	0.23	4.6×10^{-2}	$\sim10^{-4}$	8.3×10^{-3}	3.7×10^{-3}
21	9.4×10^{-2}	0.27	5.5×10^{-2}	$\sim10^{-4}$	1.1×10^{-2}	3.9×10^{-3}

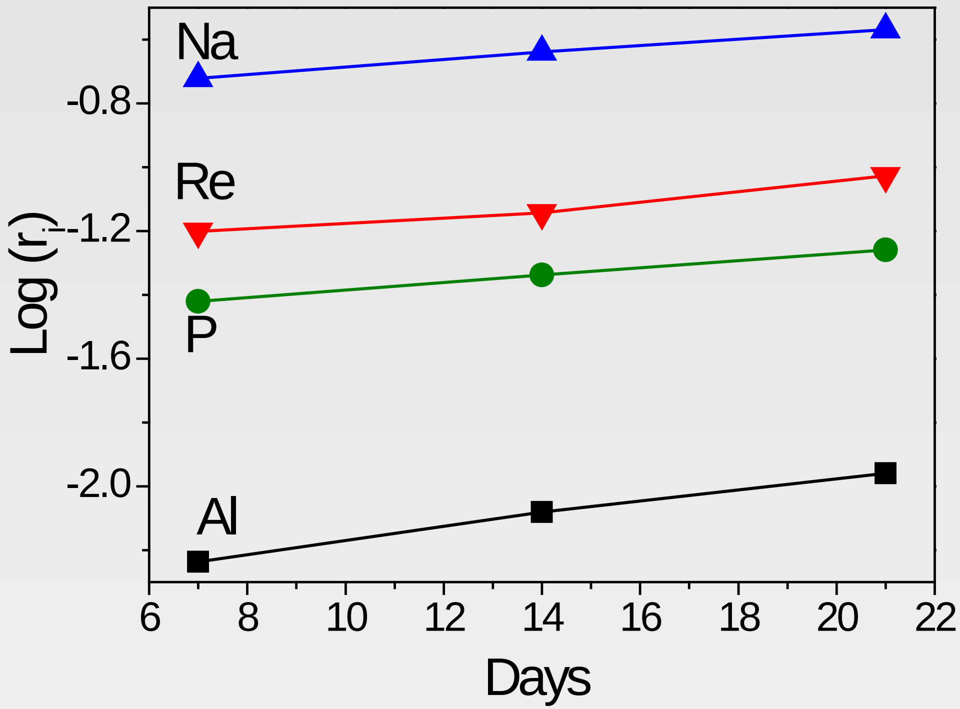
Normalized Re release was in the level of $\sim10^{-2}$.

Plot of r_i

Semi log plot of Re, Na and P releases.



Effect of Re addition
(7-day PCT)



Diff. PCT durations
(2 wt% addition)

Re addition hardly affects 7-day PCT.

Re congruently released with the glass matrix.

Comparison

Different waste-forms comparison

	Fe-P glass	BS glass	MKP ceramics	Fe-containing minerals	Metallic alloys
Tc (Re) release (g/m^2)	$\sim 10^{-2}$	$>10^{-2}$	$\sim 10^{-1}$	$\sim 10^{-3}$	$<10^{-2}$
Loading (ppm)	$\sim 1\times10^{4}$	~2000	~900	<1000	$<2\times10^{4}$
Retention (wt%)	~50	<10	>95	>95	No data (?)
Processing	Easy	Easy	Complex	Complex	Complex

Fe-P glasses is a promising candidate for immobilizing Tc-99

5. Summary

Fe-P glass of $42P_2O_5$-$25Na_2O$-$5Al_2O_3$-$10CaF_2$-$18Fe_3O_4$ (mol%) was investigated to immobilize Tc.

Two-step method was used to prepare Re-containing Fe-P glasses. (1050℃ for 30 min+1000℃ for 10 min.)

Re loading in Fe-P glass was as high as~1wt%, and its volatilization was as low as ~50%.

Normalized Re and other elements release of PCT-7 was satisfied DOE limitation.

Fe-P glass can be as a candidate for immobilizing Tc.

Supported by World Class University program through the National Research Foundation of Korea

Thanks for your attention and comments!

February 26 – March 1, 2012 ♦ Phoenix, Arizona