

Iron-Phosphate Glass for Immobilization of Radioactive Technetium

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

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K. Xu
POSTECH

J. Choi
POSTECH

W. Um,
POSTECH

A. A. Kruger
Department of Energy - Office of River Protection

J. Heo
POSTECH

P. R. Hrma
Pacific Northwest National Laboratory

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Iron-Phosphate Glass for Immobilization of Radioactive Technetium - 12216

Kai Xu^{*}, Jong Heo^{*,**}, Wooyong Um^{**,***}, Pavel Hrna^{**,***} and Jong Kwon Choi^{**}

^{*}Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790784, Republic of Korea

^{**}Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790784, Republic of Korea

^{***}Pacific Northwest National Laboratory (PNNL), P.O. Box 999, Richland, Washington 99354

ABSTRACT

Technetium-99 (Tc-99) can bring a serious environmental threat because of its high fission yield, long half-life, and high solubility and mobility in the ground water. The present work investigated the immobilization of Tc-99 (surrogated by Re) by heat-treating mixtures of an iron-phosphate glass with 1.5 to 6 wt. % $KReO_4$ at $\sim 1000^\circ C$. The Re retention in the glass was as high as ~ 1.2 wt. % while the loss of Re by evaporation during melting was $\sim 50\%$. Re was uniformly distributed within the glass. The normalized Re release by the 7-day Product Consistency Test was ~ 0.39 g/m², comparable with that in phosphate-bonded ceramics and borosilicate glasses. These results suggest that iron-phosphate glass can provide a good matrix for immobilizing Tc-99.

INTRODUCTION

Technetium (Tc) is artificially generated as a fission product during the irradiation of U-235 for commercial power production and Pu-239 for nuclear weapons. The most abundant Tc isotope in the wastes, Tc-99, is an environmentally dangerous radionuclide that has been classified as high-level wastes by the US Department of Energy because it has a high fission yield ($\sim 6\%$), long half-life (2.1×10^5 years) and high mobility in oxidizing subsurface conditions [1, 2]. The total annual Tc-99 production is 8-10 ton, and two thirds of them are contained in irradiated nuclear fuel while the rest is removed by fuel processing and kept as Tc (VII) compounds [3]. The pertechnetate, $Tc(VII)O_4^-$, is highly soluble in ground water, does not adsorb onto sediments, and thus easily transports through geologic systems [2]. Due to the significant increases in radioactive waste throughput, immobilizing Tc-99 into a stable waste form becomes an urgent eco-problem.

Several waste forms have been proposed to immobilize Tc-99 including metallic alloys [4], titanates with the spinel structure [5], phosphate-bonded ceramics [6] and recently developed Fe(II)-goethite [7]. Although each of these waste forms has its own merit and was proved to be a promising candidate, none has yet been produced on the industrial-scale. One of the main

reasons was the high volatilization of Tc-99 during synthesis process of metallic alloys and titanates at temperatures above 1300°C. In addition, the complex chemical preparation procedures, the high cost and a low Tc-99 loading (hundreds of ppm) may appear problematic for large-scale processing of the phosphate-bonded ceramics and Fe(II)-goethite.

High-level wastes have been immobilized into a glass in USA, France, Russia, Germany and Japan as an effective and cost-efficient disposal form using well-established technologies. Immobilization of Tc-99 using borosilicate (BS) glasses [8] showed that >90 % of added Tc volatilized and only ~0.003 wt. % of Tc remained in those glasses. Day *et al.* [9] developed iron-phosphate (FeP) glass as an alternative type of glass waste form. While FeP glasses with their strong P-O-Fe bonds [10] possess chemical durability equivalent to BS glasses, they have a lower viscosity than BS glasses, and their lower melting temperature (~950 – 1050°C) and shorter melting time allow reducing volatilization losses during Tc-99 encapsulation.

Recently, Day *et al.* [11] investigated the retention of volatile components (S, Cs and Re, a surrogate for Tc-99) in a FeP glass. The losses of Re varied from ~30% to 70% depending on the melting temperature and time. Because Day *et al.* [11] focused on the vitrification of low-activity wastes, the Re content in FeP glass was low (~0.03 wt. %). Therefore, the aim of the present work is to investigate the incorporation of high additions of Re in an FeP glass as a secondary waste form.

EXPERIMENTAL METHOD

The base FeP glass composition used in this work was developed by Day *et al.* [12]. Table I lists the nominal glass composition and batch materials. It is known that Fe₃O₄ can improve the chemical durability and CaF₂ was added to increase the glass formation tendency [12]. KReO₄ was used as the source of Re (a non-radioactive surrogate for Tc-99). The melting and boiling points of KReO₄ are 550°C and 1370°C, respectively, while KTcO₄ melts at 540°C and decomposes at 1000°C. The FeP glass was prepared by heating ~15 g batches in alumina crucibles at 1050°C for 30 min under the ambient atmosphere. The molten glass was poured onto a clean brass plate and then crushed into fine powders. Approximately 6 g mixtures of the glass powders with 1.5, 2, 4 and 6 wt. % KReO₄ were melted again at 1000°C for 10 min, and then poured onto brass molds. Crystalline phases in the samples were identified with X-ray diffraction (XRD). The retention of Re was determined with the inductively coupled plasma atomic emission spectrometry (ICP-AES). The chemical uniformity was checked with the scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

The chemical durability of the samples was evaluated with the 90°C 7-day Product Consistency Test (PCT)-ASTM C 1285-02. The elements in the solution were analyzed with ICP-AES. The normalized Re release, L (g/m²) was calculated by the formula:

$$L = \frac{C_i}{f_i(A/V)} \quad (\text{Eq. 1})$$

where C_i is the Re concentration ($\mu\text{g/ml}$ or g/m^3) in the solution, V is the solution volume (ml), f_i is the Re fraction in glass, and A is the specimen surface area (m^2). The A/V ratio is 2000 m^{-1} .

Table I. Nominal Glass Composition and Batch Materials.

Component	Nominal Composition		Batch Materials
	mol. %	wt. %	
P ₂ O ₅	42	46	NH ₄ H ₂ PO ₄ , Na ₃ PO ₄
Na ₂ O	25	12	Na ₃ PO ₄
Al ₂ O ₃	5	4	Al(OH) ₃
Fe ₃ O ₄	18	32	Fe ₃ O ₄
CaF ₂	10	6	CaF ₂
Total	100	100	

RESULTS AND DISCUSSION

All samples with different contents of KReO₄ were completely fused within 10 min at 1000°C.

X-Ray Diffraction Patterns

The sample with 1.5 wt. % of KReO₄ addition contained tiny crystals visible in optical microscope (Fig. 1a) but not detectable with XRD (Fig. 1b). Other samples contained ~10 wt. % of crystals in the form of spherical inclusions that could be mechanically separated from crushed specimens by tweezers. Fig. 2 shows their XRD patterns. The main crystalline phase was Fe₂Na₃(PO₄)₃ in samples with less than 4 wt. % of KReO₄ added, whereas NaReO₄ and KReO₄ crystals were identified in samples with further addition of KReO₄. Table II summarizes sample appearances and crystalline phases settling down.

Inductively Coupled Plasma Atomic Emission Spectrometry Analysis

The amorphous phases were mechanically separated from the waste forms with 4 and 6 wt. % of KReO₄ added for ICP-AES analysis. The waste forms including both amorphous and crystalline phases were measured for Re retention analysis when KReO₄ additions were 1.5 and 2 wt. %, respectively. Total amount of Re retained in waste forms after melting and their volatilization are shown in Table III. The Re retention was as high as ~1.2 wt. % in the sample with ~4 wt. % KReO₄ added; thus, approximately half of the elemental Re was encapsulated in the FeP glass. The main mechanism for this half of Re retention in FeP glass results from low melting

temperature and short melting time [11].

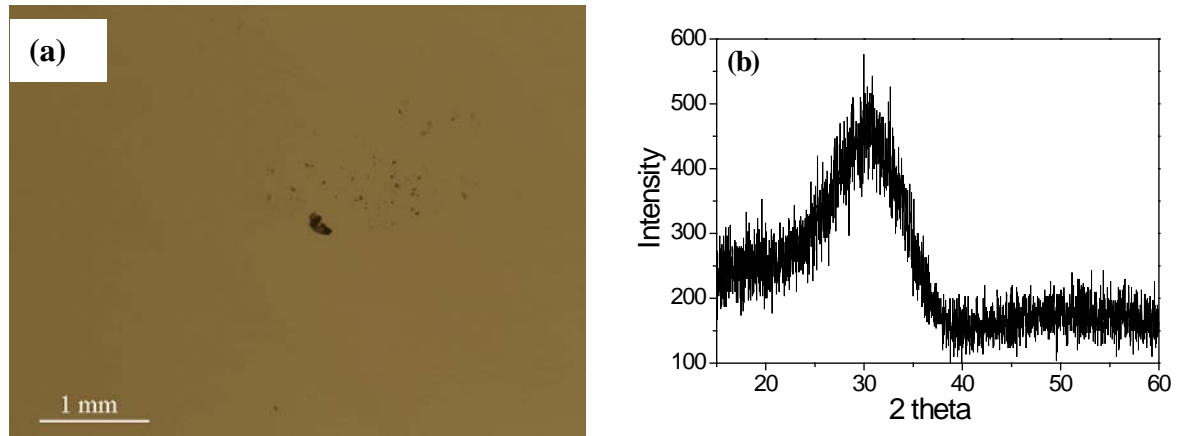


Fig. 1. (a) Optical microphotograph and (b) XRD pattern of glass sample with 1.5 wt. % KReO_4 addition.

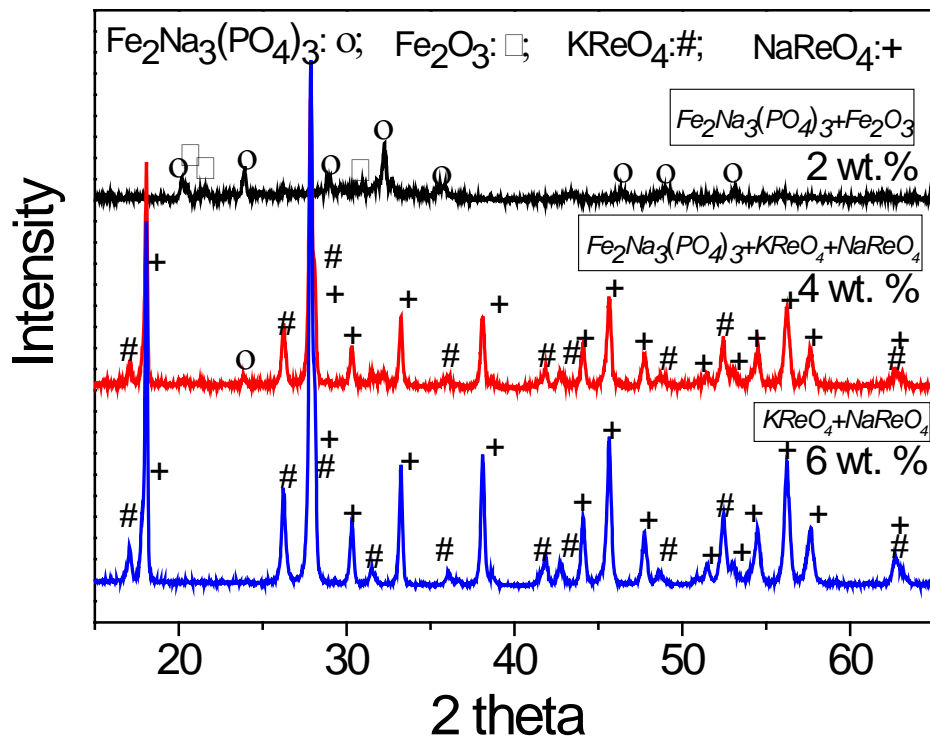


Fig. 2. XRD patterns of crystals in samples with 2, 4 and 6 wt. % KReO_4 addition.

Table II. Appearance of the Waste Forms and Crystalline Phases.

KReO ₄ (wt. %)	Appearance	Crystalline Phases
1.5 ^(a)	Black glasses with tiny crystals.	Fe ₂ Na ₃ (PO ₄) ₃ + Fe ₂ O ₃
2	Black glasses with gray crystals.	Fe ₂ Na ₃ (PO ₄) ₃ + Fe ₂ O ₃
4	Black glasses with gray and white crystals.	Fe ₂ Na ₃ (PO ₄) ₃ + NaReO ₄ + KReO ₄
6	Black glasses with isolated white crystals.	NaReO ₄ + KReO ₄

^(a) The tiny crystals are assumed to be Fe₂Na₃(PO₄)₃ + Fe₂O₃.

Table III. Retention of Re in Waste Forms and Their Volatilization.

KReO ₄ (wt. %)	Re addition (wt. %)	Retained Re (wt. %)	Volatilization (%)
1.5	0.965	0.474	51
2	1.287	0.603	53
4	2.574	1.190	54
6	3.862	1.130	71

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The glass with ~1.2 wt. % of Re retained was checked with SEM-EDX for compositional uniformity (Fig. 3). The EDX elemental mapping (Fig. 3b-f) shows that chemical elements, including Re, are distributed uniformly in the glass. The concentration of Re in glass form was ~1.0 wt. % by EDX analysis, which is parallel with that measured by ICP-AES.

Product Consistency Test

Table IV compares the 7-day PCT release of Re from the glass with ~1.2 wt. % of Re retention with the published Tc release data for phosphate-bonded ceramics and borosilicate glass. Note that the Re content in the FeP glass is two orders of magnitude higher than the Tc content in the other waste forms. The high Re loading with low volatilization and acceptable leaching rate of Re imply that the FeP glass can be a good glass form candidate for immobilization of Tc-99.

Table IV. Normalized 7-day PCT Releases of Re from the FeP Glass with 4 wt. % of KReO₄ Addition and Tc from Phosphate-Bonded Ceramics and Borosilicate Glass.

Normalized Leaching Releases (<i>L</i>) (g/m ²)		
FeP Glass (Re)	Phosphate Ceramics [6] (Tc)	Borosilicate Glass [8] (Tc)
0.39	0.25	~0.07

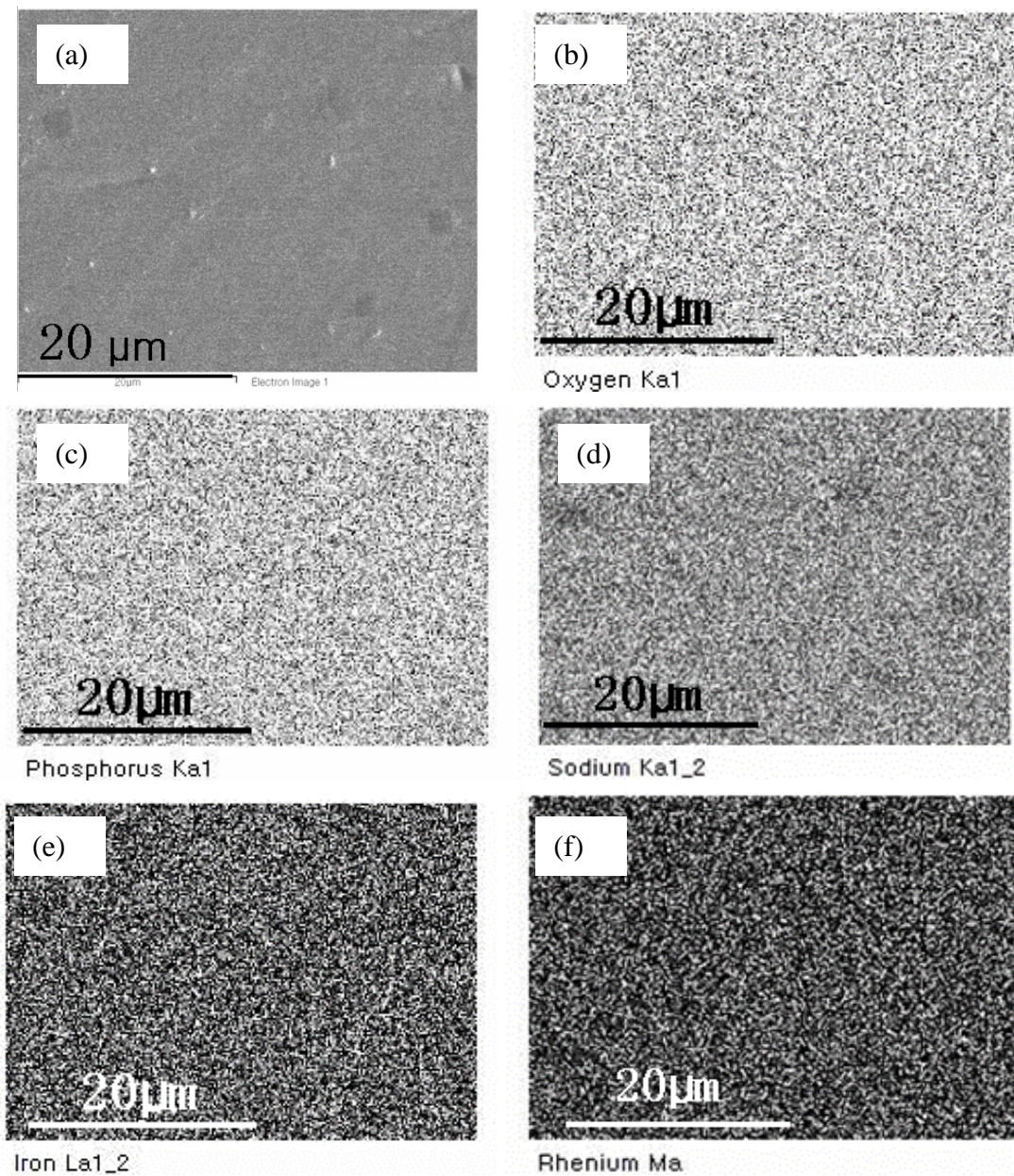


Fig. 3. (a) SEM image and EDX elemental mapping of (b) O, (c) P, (d) Na, (e) Fe and (f) Re in the glass with 4 wt. % $KReO_4$ addition.

CONCLUSION

The FeP glass with a nominal composition of $42P_2O_5-25Na_2O-5Al_2O_3-18Fe_3O_4-10CaF_2$ (in mol %) retained as much as ~1.2 wt. % of Re while the loss by $KReO_4$ evaporation was as low as ~50%. The low melting temperature and short melting time of the FeP glass help minimize the evaporation losses. The EDX elemental mapping showed uniform distribution of Re in the glass.

The 7-day PCT normalized release of Re, 0.39 g/m^2 , is acceptable for a high-level waste form. Accordingly, the FeP glass qualifies as a promising candidate for immobilizing Tc-99.

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