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journal homepage: www.elsevier.com/locate/jnucmatIron phosphate glass for immobilization of ^{99}Tc Kai Xu^{a,b}, Pavel Hrma^{a,c}, Wooyong Um^{a,c}, Jong Heo^{a,b,*}^a Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Gyeongbuk 790784, South Korea^b Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Gyeongbuk 790784, South Korea^c Pacific Northwest National Laboratory (PNNL), Richland, WA 99354, USA

HIGHLIGHTS

- ^{99}Tc (surrogated by Re) was immobilized in an iron phosphate glass.
- ~1.1 mass% Re was retained, possibly dissolved, in the iron phosphate glass.
- The 7-day PCT normalized release of Re was $<10^{-2} \text{ g/m}^2$.
- Re concentration in the glass rapidly decreased with increasing melting temperature and duration.

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ABSTRACT

Technetium-99 (^{99}Tc) can bring serious environmental threats because of its long half-life ($\tau_{1/2} = \sim 2.1 \times 10^5$ years), high fission yield (~6%), and high solubility and mobility in the ground water. The high volatility makes it difficult to immobilize ^{99}Tc in continuous melters vitrifying ^{99}Tc -containing nuclear wastes in borosilicate glasses. This work explores a possibility of incorporating a high concentration of ^{99}Tc , surrogated by the non-radioactive Re, in an iron phosphate glass by melting mixtures of iron phosphate glass frits with 1.5–6 mass% KReO_4 at ~ 1000 °C. The retention of Re achieved was ~1.1 mass%. The normalized Re release by the 7-day Product Consistency Test was $<10^{-2} \text{ g/m}^2$. Surprisingly, the Re escaped from the melt within a short time of heating, especially when the temperature was increased. Therefore, ^{99}Tc volatilization would still be a challenging task for its immobilization in iron phosphate glasses.

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1. Introduction

Technetium-99 (^{99}Tc), a fission product generated during the irradiation of ^{235}U -enriched fuel for commercial power generation or ^{239}Pu production for nuclear weapons, is present in the world-wide nuclear wastes. Because of its long half-life ($\tau_{1/2} = \sim 2.1 \times 10^5$ years) and high fission yield (~6%), ^{99}Tc bears serious environmental threats [1]. Moreover, the stable form of Tc in oxidizing environments, the pertechnetate anion, Tc(VII)O_4^- , is highly soluble and mobile in ground water, and thus easily migrates through geologic systems, resulting in potential harm to biospheres [2–5].

Vitrification technology is the preferred process for nuclear waste immobilization in the form of borosilicate glasses [6,7]. The primary concern in vitrifying nuclear wastes containing Tc is its low retention in the glass, which is caused by its high volatility at elevated temperatures [8,9]. The Tc solubility in a borosilicate glass is estimated to be ~1500 ppm [10], yet 18–66% of Tc out of

the projected <6 ppm is expected to be retained in the glass vitrified in conventional melters based on recent small-scale tests [11].

Although recycling of Tc into the waste glass is preferable, other option is the development of waste forms [12,13], including glass, with a high concentration of Tc. Glass has substantial advantages over crystalline and metallic waste forms in its easy processing and excellent durability. Volatilization can be minimized, if the Tc-containing waste, such as the off-gas recycle, is mixed with a premelted frit and then melted [9,14]. Powdered iron phosphate glass can melt within a narrow temperature interval at a relatively low temperature; this limits the time to evaporate, thus making iron phosphate glass a good candidate for Tc encapsulation. Also, it has reportedly additional advantages in its ability to dissolve larger fractions of sulfate, halides, and heavy metals, such as Cr, Bi, or Mo, that are troublesome in borosilicate glass [15–18]. Iron phosphate glass was recently proposed for immobilizing Cs and Re-containing low-activity wastes with high concentrations of sulfate [19]; Re is generally being used as a surrogate for Tc.

In this study, we added high fractions of Re to a powdered iron phosphate glass to estimate Re retention and its stability with respect to prolonged heating and elevated temperatures. We

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confirmed the good resistance of iron phosphate glass against aqueous corrosion with the Product Consistency Test (PCT).

2. Experimental methods

2.1. Preparation of iron phosphate glass

Table 1 lists the host glass composition and starting chemicals. Al₂O₃ and Fe₃O₄ provide the iron phosphate glass good chemical durability, while CaF₂ decreases the melt viscosity [15,18]. To imitate KTCO₄ that melts at 540 °C and decomposes at 1000 °C, we used KReO₄ that melts at 550 °C and boils at 1370 °C [9,20].

The iron phosphate glass was first prepared without KReO₄; ~15-g batches were heated in alumina crucibles at 1050 °C for 30 min under the ambient atmosphere and the quenched melts were crushed into fine powders. Then, ~6.5-g samples of powdered glass were mixed with different amounts of KReO₄ (1.5, 2, 3, 4 and 6 mass%), heat-treated at 1000 °C for 10 min, poured into a brass mold, and annealed at ~350 °C for 3 h.

2.2. Characterization of iron phosphate glass

The chemical composition of the host glass was analyzed with X-ray fluorescence (XRF). Crystals in samples were identified with optical microscopy and X-ray diffraction (XRD). The retention of Re was determined with the inductively coupled plasma mass spectrometry (ICP-MS). The distribution of Re in samples were checked with energy dispersive X-ray spectroscopy (EDX).

2.3. Chemical durability test

The PCT was performed on duplicate samples following the procedures specified in American Society for Testing and Materials (ASTM) C 1285-02 [21]. The glass samples were crushed manually in an agate mortar and sieved to -100 to +200 mesh (75–150 μm). Powders were ultrasonically washed five times with deionized water (DIW) to remove fines, then ultrasonically washed three times with ethanol to dissolve any organic impurities, and finally dried at 90 ± 5 °C overnight. 1.5 g of sample powders (±0.1 mg) were mixed with 15 mL of DIW in a Teflon vessel and kept at 90 ± 2 °C temperature in an oven for 7, 14 or 21 days. The solution was filtered through a 0.45 μm filter to remove particulates and the concentration of elements in the solution was measured by ICP-MS.

Normalized elemental mass releases, r_i (g/m²), were calculated using the formula:

$$r_i = \frac{C_i}{f_i(A/V)} \quad (1)$$

where C_i is the i th element concentration in the solution (mg/L = g/m³), f_i is the i th element mass fraction in the glass (unitless), and A/V

Table 1

Glass composition (nominal and analyzed by XRF) and starting chemicals used for the host glass.

Component	Nominal Composition (mol%)	Analized ^a (mass%)	Starting chemicals
P ₂ O ₅	42	45.5	NH ₄ H ₂ PO ₄ , Na ₃ PO ₄
Na ₂ O	25	11.8	Na ₃ PO ₄
Al ₂ O ₃	5	3.9	Al(OH) ₃
Fe ₃ O ₄	18	31.8	Fe ₃ O ₄
CaF ₂	10	–	CaF ₂
CaO	–	4.3	
F	–	2.7	
Total	100	100	99.3

^a Average of pentaplicate measurements.

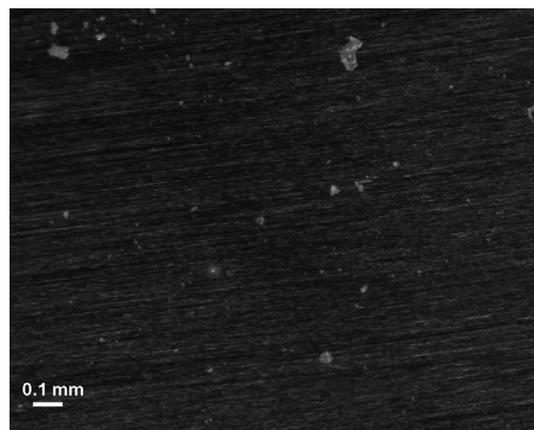


Fig. 1. Optical micrograph of fracture surface in the 1.5-mass% KReO₄ sample under dark field mode.

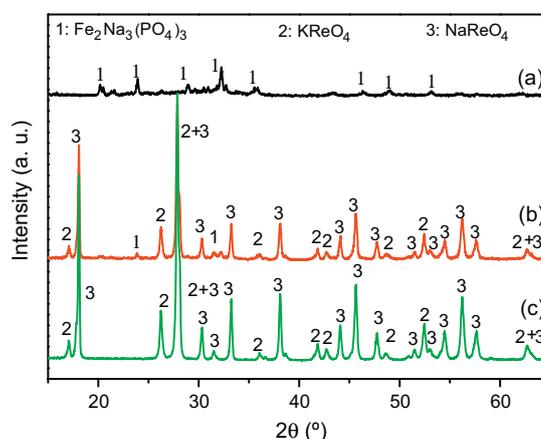


Fig. 2. XRD patterns of crystals in samples with additions of (a) 2 or 3 (b) 4 and (c) 6 mass% KReO₄.

Table 2

Analized (ICP-MS) Re concentration and retention in samples with various KReO₄ additions.

KReO ₄ addition (mass%)	Added Re (mass%)	Analized Re ^a (mass%)
1.5	0.97	0.50
2	1.29	0.65
3	1.93	0.88
4 ^b	2.57	1.12
6 ^b	3.86	1.13

^a Average of duplicate measurements.

^b White crystals of (Na, K)ReO₄ were removed.

V is the ratio of the powder surface area to solution volume (m⁻¹). The A/V value, 1790 m⁻¹, was obtained per the procedures specified in ASTM C 1285-02.

2.4. Additional heat treatment for Re volatilization

To investigate the stability of Re retention in the glass, ~6.5-g samples of powdered glass were mixed with 2 mass% KReO₄ and subjected to two series of heat-treatment: first, samples were heat-treated at 1000–1300 °C at 50 °C steps for 10 min; second, samples were heat-treated at 1000 °C for durations from 10 to 140 min. The concentration of Re in samples was determined with ICP-MS.

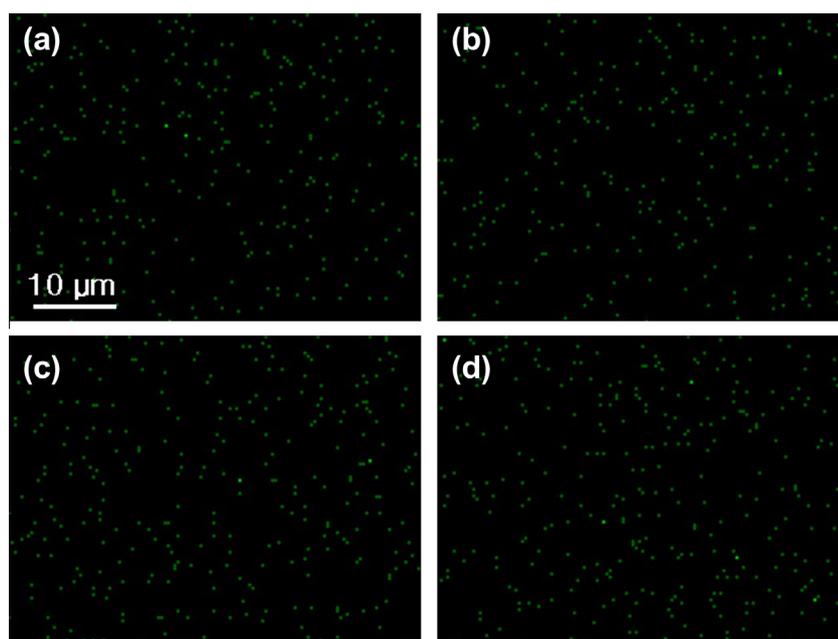


Fig. 3. EDX mapping of Re in samples with additions of (a) 1.5 (b) 2 (c) 3 and (d) 4 mass% KReO_4 .

Table 3

Normalized elemental releases (r_i , in g/m^2) for PCT from samples with various KReO_4 additions and 2-mass% KReO_4 sample leached for 1–3 weeks.

KReO_4 addition (mass%)	Duration Weeks	r_{Re}	r_{Na}	r_{P}	r_{Al}	r_{Ca}	r_{Fe}
1.5	1	8.4×10^{-2}	0.15	4.3×10^{-2}	1.9×10^{-2}	1.5×10^{-3}	$<10^{-4}$
2	1	6.3×10^{-2}	0.19	3.8×10^{-2}	5.8×10^{-3}	3.7×10^{-3}	$<10^{-4}$
	2	7.2×10^{-2}	0.23	4.6×10^{-2}	8.3×10^{-3}	3.7×10^{-3}	$\sim 10^{-4}$
	3	9.4×10^{-2}	0.27	5.5×10^{-2}	1.1×10^{-2}	3.9×10^{-3}	$\sim 10^{-4}$
3	1	6.4×10^{-2}	0.17	5.1×10^{-2}	1.5×10^{-2}	2.8×10^{-3}	$<10^{-4}$
4	1	6.8×10^{-2}	0.19	5.8×10^{-2}	9.4×10^{-3}	3.7×10^{-3}	$<10^{-4}$

3. Results and discussion

3.1. Glass composition and appearance

All samples with KReO_4 additions were completely fused. The analyzed chemical composition of the host glass was in satisfactory agreement with the nominal composition, as seen in Table 1. In the sample with 6 mass% of KReO_4 added, a thin compact layer of white crystals was located below the bulk of black glass. No such settled layer was seen in other samples.

3.2. Crystal characterization

Crystals were visible on fracture surfaces in all samples. Gray clusters of crystals appeared in samples with <4 mass% KReO_4 added and white spherical inclusions were visible in samples with ≥ 4 mass% KReO_4 added. In the 1.5-mass% KReO_4 sample, the tiny crystals, <0.1 mm in diameter, were only visible with optical microscopy (Fig. 1). Except for the 1.5-mass% KReO_4 sample, clusters and inclusions were large, between 0.5 and 1.5 mm in diameter, in all other samples and could be separated from crushed glasses with tweezers. The gray clusters were identified by XRD as $\text{Fe}_2\text{Na}_3(\text{PO}_4)_3$ crystals, see Fig. 2a. The white spherical inclusions were crystallized droplets of $(\text{Na}, \text{K})\text{ReO}_4$ (Fig. 2b) and the compact white layer in the 6-mass% KReO_4 sample was a segregated $(\text{Na}, \text{K})\text{ReO}_4$ (Fig. 2c). The black matrix was amorphous by XRD analysis.

3.3. Re retention

Crushed samples with <4 mass% KReO_4 additions and samples with ≥ 4 mass% KReO_4 additions from which the white crystals $(\text{Na}, \text{K})\text{ReO}_4$ were manually removed were digested by HNO_3 , and analyzed with ICP-MS for Re retention. The results are shown in Table 2. In the case of samples with <4 mass% KReO_4 added, retained Re concentration in the glass increased as initial Re addition increased. When ≥ 4 mass% KReO_4 was added into samples, Re retained in the glass reached the maximum amount (~ 1.1 mass%), no matter how much Re was added. This result indicates that 1.1 mass% was a solubility limit of Re in the glass at 1000°C . The EDX mapping shown in Fig. 3 supports this assertion: Re is uniformly distributed and no isolated Re-rich inclusions are seen; visible white inclusions, $(\text{Na}, \text{K})\text{ReO}_4$, or a segregated white layer, $(\text{Na}, \text{K})\text{ReO}_4$, precipitated in samples with ≥ 4 mass% KReO_4 .

3.4. Chemical durability

Table 3 lists normalized 7-day PCT elemental releases, r_i , from samples with different KReO_4 additions and 14 and 21-day PCT releases from sample with 2 mass% KReO_4 addition. Fig. 4 shows r_{Na} , r_{Re} and r_{P} as functions of the Re addition and test duration, demonstrating excellent chemical durability. As expected, normalized releases of Na, Re and P slightly increased with the test duration. The KReO_4 addition had little effect on 7-day PCT normalized releases

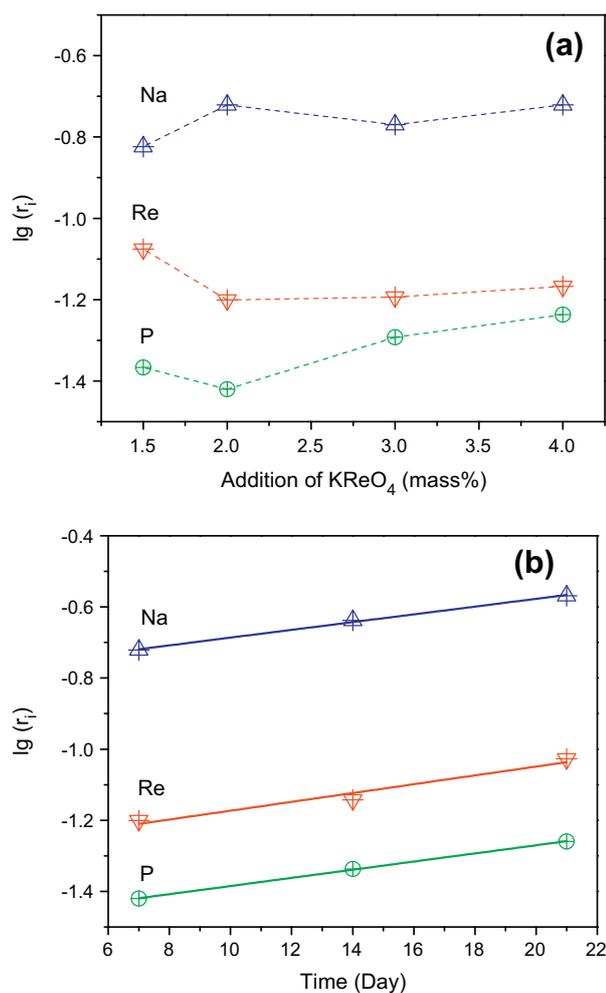


Fig. 4. (a) 7-day PCT normalized elemental releases versus KReO_4 addition; (b) normalized elemental releases from 2-mass% KReO_4 sample versus PCT duration with linear trend lines.

(Fig. 4a). Fig. 4b indicates that Re is released with the phosphate matrix. All r_{Re} values were $<10^{-2} \text{ g/m}^2$.

3.5. Re volatilization

Fig. 5 displays Re concentration in 2-mass% KReO_4 heat-treated samples as a function of temperature after a 10-min hold and as a function of duration at 1000°C . Heating for 10 min at 1300°C and for 40 min at 1000°C were enough to reduce the Re retained to $<10\%$ of the initial addition. Both high temperatures and prolonged melting time dramatically decreased the content of Re in the glass.

Though large fractions of Re ($\sim 1.1 \text{ mass}\%$) could retain in the iron phosphate glass, the sensitivity of the Re content to heating is both worrying and difficult to understand. However, one can expect that the loss of Re from a larger body of melt will be small compared to the laboratory crucible. Moreover, glass formulation can be optimized to further decrease the melting time and temperature of glass powder to encapsulate the Tc concentrate. Thus, a durable glass, whether iron phosphate or borosilicate, can still be considered a promising candidate for Tc immobilization.

4. Conclusions

The iron phosphate glass $42\text{P}_2\text{O}_5-25\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-10\text{CaF}_2-18\text{Fe}_3\text{O}_4$ (mol%) retained, and possibly dissolved, $\sim 1.1 \text{ mass}\%$ Re when KReO_4 , a KTcO_4 surrogate, was mixed with the powdered

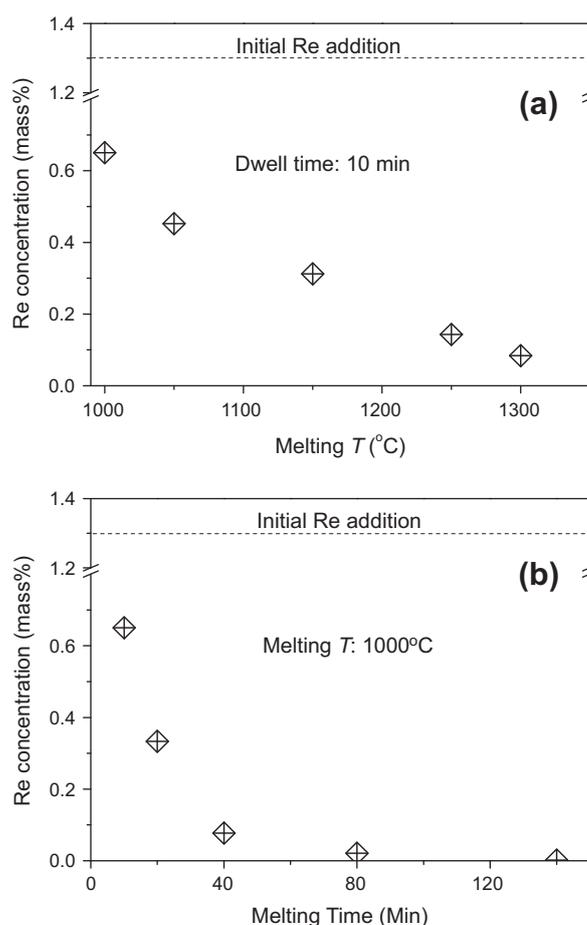


Fig. 5. Concentrations of Re retained in 2-mass% KReO_4 samples versus (a) melting temperature (T) or (b) time.

glass and melted at 1000°C for 10 min. The 7-day PCT normalized release of Re was $<10^{-2} \text{ g/m}^2$. The Re content rapidly decreased from the melt with increasing melting temperature and prolonged duration at a constant temperature. Though the rapid loss of Tc from molten glass could be a challenge in practical application, encapsulating Tc by melting powdered glass with a Tc concentrate remains a viable option.

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