

## Immobilization of $^{99}\text{Tc}$ (Re) using Iron-Phosphate Glasses

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### 1. Introduction

Technetium-99 ( $^{99}\text{Tc}$ ) is a fission product artificially generated during the irradiation of  $^{235}\text{U}$  for commercial power production or  $^{239}\text{Pu}$  for nuclear weapons. Under oxidizing conditions, the dominant species of Tc, the pertechnetate anion ( $\text{TcO}_4^-$ ), is highly soluble in ground water and thus easily transports through the geologic systems. In addition, because of its high fission yield (~6 %) and long half-life ( $2.1 \times 10^5$  yr), immobilization of  $^{99}\text{Tc}$  has been investigated for decades [1,2]. Several waste forms such as metallic alloys, sintered titanate ceramics and chemically bonded phosphate ceramics have been proposed to encapsulate  $^{99}\text{Tc}$ . They have not yet been realized in the industrial-scale, mostly either due to the high volatilization of  $^{99}\text{Tc}$  during high temperature process (>1300°C), or the low  $^{99}\text{Tc}$  loading [3-5].

Iron-phosphate (FeP) glasses have been developed as alternative waste forms because of their chemical durability equivalent to borosilicate glasses [6]. Additionally, vitrification of radioactive waste by FeP glasses can be done at a relatively low temperature (~1000°C) and the low-temperature process can reduce the volatilization of  $^{99}\text{Tc}$  significantly. Thus, this work reports the immobilization of  $^{99}\text{Tc}$  by FeP glasses using rhenium (Re) as a surrogate. We also examine the chemical durability of Re-containing FeP glasses using product consistency test (PCT). Experimental results reveal that FeP glass can become a promising candidate for immobilizing  $^{99}\text{Tc}$ .

### 2. Experimental Methods

FeP waste forms were prepared by a two-step procedure. First, base glasses with a nominal composition of  $42\text{P}_2\text{O}_5-25\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-10\text{CaF}_2-18\text{Fe}_3\text{O}_4$  (mol %) were melted at 1050°C for 30 min. Melt was then quenched and crushed into powder. Then, the powdered glass was mixed with different amounts of  $\text{KReO}_4$  (1.5, 2, 3, 4 and 6 wt. %) and re-melted at 1000°C for 10 min before pouring into a brass mold.

Crystalline phases in the waste forms were identified with X-ray diffraction (XRD). The retention of Re was determined with the inductively coupled plasma mass spectrometry (ICP-MS). Distribution of Re in the glass was ascertained with the energy

dispersive X-ray spectroscopy (EDX). Chemical durability of Re-containing phases was examined with 7-day PCT following ASTM C 1258-02. Elements in the solution were analyzed with ICP-MS. Normalized elemental mass release,  $r_i$  ( $\text{g}/\text{m}^2$ ), was calculated as:

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

where  $C_i$  is the concentration of element  $i$  in the solution ( $\mu\text{g}/\text{ml}$  or  $\text{g}/\text{m}^3$ ),  $f_i$  is the mass fraction of element  $i$  in the glass (unitless), and  $A/V$  is the ratio of the sample surface area to volume of leachate ( $\text{m}^{-1}$ );  $A/V = 1790 \text{ m}^{-1}$ .

### 3. Results and Discussion

FeP glass with 1.5 wt. % of  $\text{KReO}_4$  addition contained tiny crystals only visible under optical microscopy, while other glasses had <10 wt. % of crystals in the form of spherical inclusions. These crystals were removed from the glass and analyzed with XRD as shown in Fig. 1. The main crystalline phase was  $\text{Fe}_2\text{Na}_3(\text{PO}_4)_3$  when < 3 wt. % of  $\text{KReO}_4$  was added. With > 3 wt. %  $\text{KReO}_4$  added,  $\text{NaReO}_4$  and  $\text{KReO}_4$  crystals settled down in the glass. This result suggests that the initial addition of  $\text{KReO}_4$  in FeP base glasses should be < 3 wt. %.

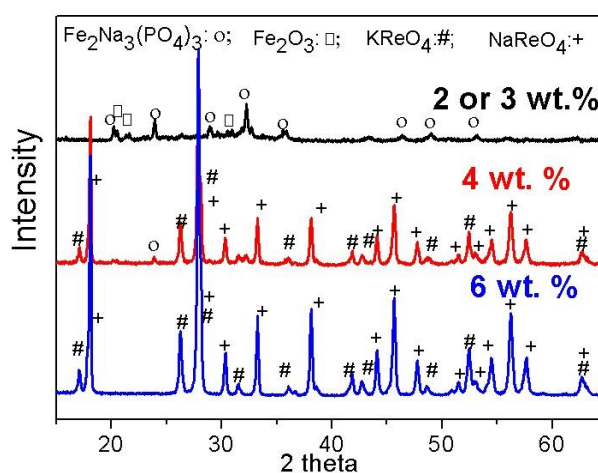


Fig. 1. XRD patterns of crystals in samples with 2, 3, 4 and 6 wt. %  $\text{KReO}_4$  addition.

Actual concentration of Re retained in waste forms analyzed by ICP-MS was as high as ~1.1 wt. %

when more than 4 wt. % of  $\text{KReO}_4$  was added into FeP glasses (Table I). As Table I shows, Re volatilization can be reduced to ~50 % and it is considerably smaller than those (~90 %) found from normal borosilicate glasses [7]. EDX mapping of Re in FeP waste forms shows Re distribution was uniform and no Re-rich phase was detected (Fig. 2).

Table I: Re retention in FeP glass with different  $\text{KReO}_4$  additions.

$\text{KReO}_4$ addition (wt. %)	Re addition (wt. %)	Re Retained (wt. %)	Volatilization (%)
1.5	0.97	0.50	48
2	1.29	0.65	50
3	1.93	0.88	54
4*	2.57	1.12	56
6*	3.86	1.13	71

\*: White crystals of  $\text{NaReO}_4$  or  $\text{KReO}_4$  persisted in the glass.

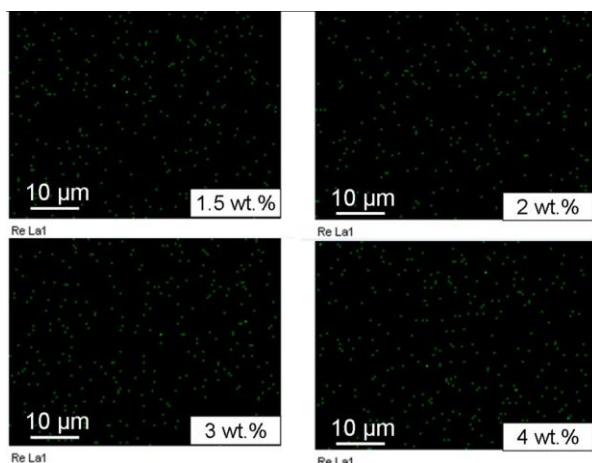


Fig. 2. EDX mapping of Re in FeP glass with different  $\text{KReO}_4$  addition.

The normalized 7-day PCT elemental releases,  $r_i$ , of Re, Na, P and Al are listed in Table II. Values of  $r_{\text{Re}}$  were  $< 10^{-2} \text{ g/m}^2$  and are comparable with values measured from other waste forms [3, 5, 7]. Releases of other elements (Na, P and Al) indicate that the FeP glass used has a high chemical durability.

Table II: Normalized 7-day PCT elemental mass releases ( $\text{g/m}^2$ ) from FeP glass with different  $\text{KReO}_4$  additions.

$\text{KReO}_4$ (wt. %)	$r_{\text{Re}}$	$r_{\text{Na}}$	$r_{\text{P}}$	$r_{\text{Al}}$
1.5	$8.4 \times 10^{-2}$	0.15	$4.3 \times 10^{-2}$	$1.9 \times 10^{-2}$
2	$6.3 \times 10^{-2}$	0.19	$3.8 \times 10^{-2}$	$5.8 \times 10^{-3}$
3	$6.4 \times 10^{-2}$	0.17	$5.1 \times 10^{-2}$	$1.5 \times 10^{-2}$
4	$6.8 \times 10^{-2}$	0.19	$5.8 \times 10^{-2}$	$9.4 \times 10^{-3}$

#### 4. Conclusions

The FeP glass with a nominal composition of  $42\text{P}_2\text{O}_5\text{-}25\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}10\text{CaF}_2\text{-}18\text{Fe}_3\text{O}_4$  (in mol %) was used for the immobilization of Re. The maximum retention of Re in the glass was as high as ~1.1 wt. % and its volatilization can be reduced to below ~50 %. The 7-day PCT normalized release of Re was less than  $10^{-2} \text{ g/m}^2$ , well below the current US DOE specification for high-level waste. Therefore, the FeP glass offers a significant potential for the immobilization of  $^{99}\text{Tc}$ .

#### ACKNOWLEDGEMENTS

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