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Magnesium potassium phosphate ceramic for ^{99}Tc immobilization ☆

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Abstract

Technetium-99, present in the US Department of Energy's (DOE) high-level waste (HLW) as a by-product of fission reactions, poses a serious environmental threat because it has a long half-life, is highly mobile in its soluble Tc^{7+} oxidation state and is volatile at high temperatures. Magnesium potassium phosphate (MKP) ceramics have been developed to treat ^{99}Tc that has been partitioned and eluted from simulated high-level tank wastes by means of sorption processes. Waste forms were fabricated by adding MKP binder and a reducing agent ($SnCl_2$) to the ^{99}Tc-containing aqueous waste. In addition, waste forms were fabricated by first precipitating ^{99}Tc from the waste and subsequently solidifying it in MKP. ^{99}Tc loadings in the waste forms were as high as 900 ppm by weight. Waste form performance was established through various strength, leaching, and durability tests. Long-term leaching studies, as per the ANS 16.1 procedure, showed leachability indices between 11 and 14 for ^{99}Tc under ambient conditions. The normalized leach rate for ^{99}Tc, according to the product consistency test, was as low as 1.1×10^{-3} g/m^2 d. The waste forms exhibited a compressive strength of $\approx$30 MPa and were durable in an aqueous environment. Containment of ^{99}Tc in MKP ceramics is believed to be due to a combination of appropriate reducing environment (determined from Eh–pH measurements) and microencapsulation in a dense matrix.

1. Introduction

Technetium-99 is present in the US Department of Energy's (DOE) high-level waste (HLW) along with other volatile fission products such as ^{137}Cs [1]. Under oxidizing conditions, the predominant form of technetium is the pertechnetate anion (TcO_4^-), which is highly soluble in water and thus readily mobile in the environment [2]. Because of the high leachability and long half-life (2.13×10^5 yr) of ^{99}Tc, its immobilization is of great concern to DOE. Conventional thermal treatments for stabilization of fission-product (^{99}Tc, ^{137}Cs) wastes,

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such as vitrification, generate volatiles that require subsequent stabilization before disposal. A nonthermal stabilization process with sufficient waste loading capability has the advantage of circumventing volatility problems. To this end, a low-temperature stabilization technology based on chemically bonded phosphate ceramics (CBPCs) is being developed at Argonne National Laboratory (ANL).

This approach is very timely with respect to the acceptability of waste treatment approaches. The National Academy of Sciences (NAS) [3] recently issued a report detailing these approaches and waste stream problems with vitrification and calling for development of alternative immobilization technologies, in particular, glass- and polyphase-ceramics. The NAS cites as technological risks not only the vitrification process, but also separation processes and borosilicate glass forms.

Besides the limitations of glass forms noted by the NAS, recent research [4] at Los Alamos National Laboratory (LANL) and Imperial College, London, has also called into question the long-term viability of glass under extended radiation, predicting that certain ceramics should hold up better than glass. Thus, we present in this paper CBPC as an alternative technology to treat the challenging issue of ^{99}Tc stabilization.

Various low- and high-temperature stabilization technologies (such as portland cement, ceramics, and borosilicate glasses) have been used to immobilize ^{99}Tc. Gilliam et al. [5] stabilized gaseous diffusion plant waste that contained 14 ppm ^{99}Tc in cement grout. It should be noted that all contaminant loadings referred to in the paper are in terms of weight. Long-term leach studies showed a leachability index (LI) of 6 for ^{99}Tc. However, after additives such as blast furnace slag were incorporated, the LI improved to $\approx$11. It is believed that the blast furnace slag modifies the pore structure of cement grout and thereby leads to better containment of pertechnetate ions. Similarly, Langton [6] demonstrated that an LI in the range of 9–12 could be achieved for ^{99}Tc in saltstone, a hydrated ceramic waste form.

Product consistency tests (PCTs) at 90 °C gave normalized ^{99}Tc losses from borosilicate glasses that ranged from 0.12 to 0.079 g/m^2 d for ^{99}Tc loadings of 30–2000 ppm [7,8]. Recently, Hart et al. [9] reported that in the SYNROC process, ^{99}Tc with a loading of 20000 ppm can be stabilized so that leach rates, from PCT tests, can reach as low as 10^{-4} g/m^2 d. It is believed that, in SYNROC, ^{99}Tc goes into the solid solution with rutile phase and is then chemically fixed, leading to its lower leachability. Uncertainties remain about the volatility of ^{99}Tc in the high-temperature borosilicate glasses and SYNROC processes. However, there is evidence that volatility of ^{99}Tc can be reduced by the pretreatment of the waste before its incorporation in SYNROC [10].

CBPCs are inorganic materials that can be fabricated inexpensively at relatively low temperatures by acid–base reactions between an inorganic oxide/hydroxide powder and an acidic phosphate solution [11,12]. These phosphates generally exhibit high solid–solution capacity for incorporating heavy metals, actinides, and rare-earth contaminants [13,14]. Also, very low solubilities of heavy metal, actinide, and rare earth phosphates [15] indicate that phosphate-bonded ceramics should be effective in stabilizing these contaminants. In addition, monazite and apatite minerals are durable natural analogs of phosphate-bonded ceramics [13], suggesting that phosphates are good hosts to radionuclides. Furthermore, phosphate ceramics can be fabricated at room temperature or slightly elevated temperatures, thus minimizing off-gassing of contaminants. Heavy metals such as Pb, Cd, Cr, Hg, and Ni and radioactive contaminants like ^{238}U have been successfully stabilized in CBPC ceramics [16].

In this work, magnesium potassium phosphate (MKP) ceramics were used to stabilize technetium wastes generated by a complexation/elution process developed at LANL to separate ^{99}Tc from HLW [17]. Waste forms were fabricated from LANL's partitioned technetium waste solution and from ^{99}Tc that was precipitated from the partitioned solutions. Performance of the ceramic waste form was evaluated by various strength, leaching, and durability tests. Further, the MKP process was modified to enhance stabilization of ^{99}Tc in phosphate ceramic. Stabilization mechanisms of ^{99}Tc in phosphate ceramics were investigated. Experimental results reveal many beneficial features of MKP ceramics that make them suitable candidates for stabilization of waste streams containing ^{99}Tc.

2. Experimental methods

2.1. Waste stream composition

As part of DOE's Efficient Separations and Crosscutting Program (ESP), several technologies are being developed to separate volatile fission products from HLW (in particular, Hanford tank waste) to reduce the overall volatility and radioactivity levels of the waste and minimize waste volume. In this regard, LANL has developed a complexation–elution process to separate ^{99}Tc from HLWs such as Hanford supernatant [17]. However, the elution solution that captures ^{99}Tc in this process must be stabilized before disposal. A typical composition of waste solution generated in the complexation–elution process is 1 M NaOH, 1 M ethylene–diamine, and 0.005 M Sn(II). The technetium concentration in this waste can be as high as 150 ppm by weight or 0.0015 M.

2.2. Fabrication of MKP ceramic waste forms

Ceramic waste forms of MKP were fabricated by incorporating either surrogate formulations or the actual technetium waste generated by the LANL complexation–elution process into MKP binder. The binding matrix is formed by reacting calcined magnesium oxide (MgO) powder with potassium phosphate (KH_2PO_4) in aqueous conditions. The reaction can be represented as:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O. \quad (1)$$

The resulting $MgKPO_4 \cdot 6H_2O$ (MKP) phase is extremely stable, with a solubility product of 2.4×10^{-11} under ambient conditions [18]. In addition, fly ash and tin chloride were added to the binder powder mixture. Fly ash, added to a level of ≈38 wt% of the total binder powder content, improves the structural integrity of the final waste form [19], whereas addition of a reducing agent, such as $SnCl_2$ (2–3 wt% of binder mix), is helpful in maintaining ^{99}Tc in its relatively insoluble Tc^{4+} form [20].

The fabrication process involves adding a binder powder mixture to the elution solution, stirring the resultant mixture to a desired consistency, and then transferring it into a mold and allowing it to set. The mix hardens in ≈2 h to form a dense, monolithic waste form. After >14 days of curing, the waste form monoliths are removed from molds and subjected to tests for strength, leaching, and water immersion.

For waste treatability studies, waste forms were fabricated in an inert nitrogen atmosphere (in a glove box) by two approaches. In the first approach, eluted aqueous waste was directly stabilized. The water in the waste was used in the waste form fabrication process. To establish the role of $SnCl_2$, samples were fabricated with and without $SnCl_2$. In the second approach, ^{99}Tc was precipitated from the eluted solution by a process described in Ref. [21], and subsequently, the precipitated ^{99}Tc (in 4+ state) was incorporated into the MKP ceramic. The black precipitate is believed to be $TcO_2 \cdot 2H_2O$. In the first approach, the optimal loading of elution solution in MKP waste forms was 36 wt%, and the concentration of ^{99}Tc in the waste forms ranged from 20 to 150 ppm. In the second approach, ^{99}Tc loadings in the waste forms were as high as 900 ppm.

2.3. Characterization of the waste forms

The measured physical properties of waste forms included density, porosity, and unconfined compressive strength. The apparent density of the waste forms was measured by determining the mass and geometric volume; porosity (water immersion method); and compression strength (Instron machine in compressive mode). To determine the presence, if any, of crystalline phases in the waste forms, X-ray diffraction (XRD) analyses were performed with a Scintag XDS 2000 diffractometer operated at 40 kV and 35 mA with a Cu-K_α wavelength of 1.5406 nm. The microstructure of the waste forms was investigated by scanning electron microscopy (SEM). Energy dispersive X-ray (EDX) spectrometry was used to identify the various microstructures by determining their elemental composition. The distribution of ^{99}Tc in the waste forms was studied via X-ray dot mapping.

2.4. Leaching and water immersion tests

Leaching and water immersion studies were performed on the final waste forms fabricated with 36% elution loading and with precipitated ^{99}Tc. Long-term leach tests (90 days) were conducted in an anoxic (nitrogen) atmosphere, in accordance with the procedure of the American Nuclear Society's ANS 16.1 standard [22] on monolithic cylindrical waste forms of about 2.5 cm length and 2.0 cm diameter. Water volume used is 10 times the total surface area of the test sample. In this test, leachate solutions were changed periodically to simulate dynamic leaching conditions. The average values of effective diffusivity and leachability index were calculated from

$$D_e = \sum [(a_n/A_0)/(\Delta t)_n]^2 (V/S)^2 (T), \quad (2)$$

$$LI = 1/n \sum [\log(\beta/D_e)]_n. \quad (3)$$

In Eqs. (2) and (3), a_n represents the amount (g) of contaminant leached from the waste form during the leaching interval n ($t_{n-1} < t < t_n$); A_0, the amount (g) of contaminant in the waste form at the beginning of leach test (g); $(\Delta t)_n (= t_n - t_{n-1})$, the duration of the nth leaching interval (s); D_e, the effective diffusivity (cm^2/s); V, the volume of the waste form (cm^3); S, the external surface area of waste form (cm^2); T, the mean time of leaching interval (s); and β, unity ($1\ cm^2/s$).

A static leaching test, the product consistency test (PCT) per ASTM C 1285-94, was performed on the waste forms to evaluate the chemical durability of phosphate ceramic waste forms at temperatures below 100 °C [23] in an oxygen-containing laboratory atmosphere. The test was carried out at room temperature and 90 °C for 7 days in Teflon containers with >1 g of crushed waste form particles that measured between 74 and 149 μm (sieve fractions −100 to +200 mesh). The normalized ^{99}Tc leaching rate is calculated by the following equation:

$$L = C_i V / f_i A \cdot d, \quad (4)$$

where C_i is the concentration of ^{99}Tc in the leachate (g/mL); V, the leachate volume (mL); f_i, the initial fraction of ^{99}Tc in the solid waste form; A, the surface area of the test specimen (m^2); and d, the duration of the test (days). Deionized water was the leachant, and the S/V ratio in this test was held constant at $3000\ m^{-1}$. The radionuclide concentration in all leachant solutions was determined by liquid scintillation counting.

Long-term water immersion tests were used to establish the durability of the final waste forms in an aqueous environment. Three waste form specimens were immersed in deionized water for 90 days. One of the specimens was removed every week, dried, and weighed to determine the weight change over the 90-day period. The other two specimens were not disturbed during the test period, and the weight change in these samples was determined at the end of the test period. The percent change in weight of the waste forms was computed with respect to the initial weight of the waste forms. The compressive strength of the above three specimens was also determined at the end of a 210 day immersion period in water.

2.5. Electrochemical experiments

Because leaching of ^{99}Tc is strongly dependent on its oxidation state, it was important to establish the redox conditions in the MKP slurry during the fabrication of the waste forms in the presence of the reducing agent $SnCl_2$. The redox conditions of the MKP slurry were studied by cyclic voltammetry measurements made with a potentiostat connected to a three-electrode electrochemical cell [24]. A time-dependent potential was imposed on the working electrode of the electrochemical cell, and the resulting current was measured. The working electrode used in the electrochemical cell was a Pt wire; the auxiliary electrode, a Pt plate; and the reference electrode, a standard calomel electrode. The electrodes were connected to a potentiostat that imposes a selected potential on the working electrode of the electrochemical cell relative to the reference electrode and measures the resulting current between the working and auxiliary electrodes.

Rhenium (a nonradioactive surrogate of ^{99}Tc) and ^{99}Tc have the same valence states and exhibit similar crystal and chemical behavior [25]. Therefore, Re was used as an analog for ^{99}Tc to predict the redox behavior of ^{99}Tc under MKP slurry conditions in the presence of $SnCl_2$. Variations in current and potential during these experiments exhibit peaks, indicative of the reduction or oxidation of polyvalent ions.

The redox state of the MKP slurry was identified by measuring Eh (the oxidation–reduction potential with reference to the hydrogen electrode) and pH values of the slurry. The possible valence states of the contaminant (Re) under the measured Eh–pH conditions were determined with the help of standard Eh–pH diagrams. Eh was measured as the electromotive force E between a platinum electrode, which is a substitute for a hydrogen electrode, and a saturated calomel reference electrode [26]. All measurements were done under ambient (oxygen-containing) conditions. The platinum electrode and saturated calomel reference electrode were connected to the millivolt input of a standard pH meter. In this case,

$$\mathrm{Eh} = E + E(\mathrm{ref}), \quad (5)$$

with E(ref) being 244 mV for the saturated calomel electrode at 25 °C.

3. Results and discussion

3.1. Fabrication of waste forms

Formation of MKP, as described by Eq. (1), is spontaneous since the Gibbs free energy change for the reaction given by this equation is −969.8 kJ/mol at 25 °C. Formation of $MgKPO_4 \cdot 6H_2O$ involves two steps: dissociation and dissolution of the binding components in water, and an acid–base reaction between the dissociated ions. Dissolution of the dissociated KH_2PO_4 in water is an endothermic reaction with the absorption of 250.6 kJ/mol of heat, whereas the reaction that governs formation of magnesium potassium phosphate is exothermic, generating 66.8 kJ/mol of heat. Because dissolution of reactant ions in water occurs before the exothermic reaction, an initial drop in temperature occurs and is followed by an increase in the slurry temperature as reaction takes place and the slurry starts to set into a solid waste form. Because the rise in temperature occurs at the time the waste form sets, a temperature increase in the exothermic reaction does not cause any problems in waste form fabrication. Typically, the temperature rises to 50 °C with a ≈40-cc sample, and to ≈75 °C with a 2-gal sample. Inasmuch as volatization and boiling temperatures of ^{99}Tc (300 and 900 °C, respectively) are far higher than these temperatures, this process is suitable for stabilizing wastes that contain ^{99}Tc and other volatile contaminants. The pH value of the slurry at the time of setting is typically in the range of 6–7.

3.2. Characterization of waste forms

Density and open porosity of magnesium potassium phosphate ceramic (MKPC) waste forms fabricated with the 36% LANL's elution loading were 1.8 g/cc and 4%, respectively. The compression strength of MKP waste forms was 30 ± 7 MPa, which is significantly higher than the land disposal requirement of 3.4 MPa. The strength of phosphate ceramic waste forms greatly exceeds this requirement; hence, MKPs form waste forms that are dense (very low porosity) and hard (exhibiting high strength). Although these characterizations were not conducted on the waste form samples fabricated with precipitated ^{99}Tc, we believe that the results with precipitated ^{99}Tc will be similar.

The X-ray diffraction pattern of the MKP waste forms fabricated with 36% elution loading is presented in Fig. 1. Phosphate ceramic waste forms are highly crystalline structures. The prominent peaks in the figure represent those of MKP, which is the binding phase in the waste forms. In addition, the XRD plot shows peaks of silicates from fly ash and unreacted magnesium oxide, which acts as a filler material in the waste form.

An SEM photomicrograph of a fractured surface of an MKP waste form fabricated with 36% elution loading is presented in Fig. 2. Although SEM on polished surface would have provided increased resolution, it was not conducted because of the difficulty related to polishing of radioactive samples. This photomicrograph indicates a dense structure.

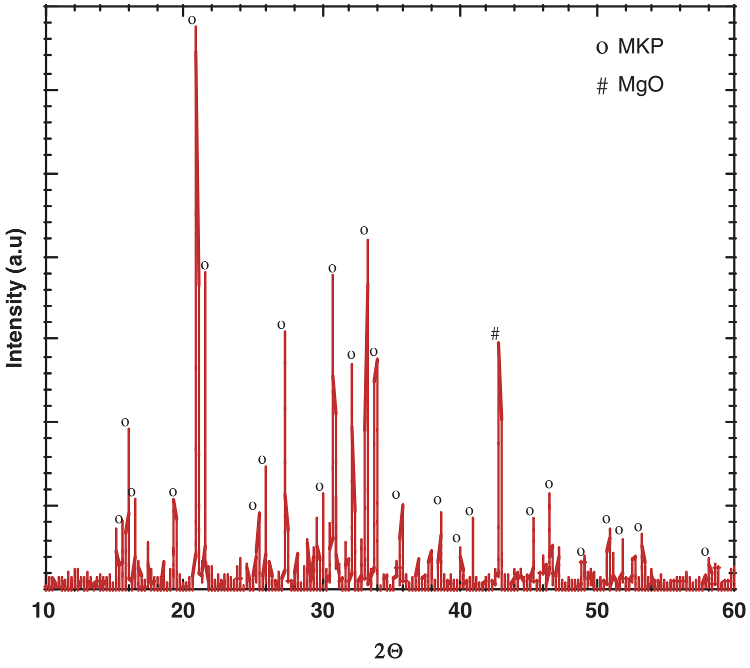

Fig. 1. XRD pattern of MKP waste forms with 36 wt% elution loading.

The EDX output on the area in the SEM photomicrograph is shown in Fig. 3. The elemental spectrum indicates that this area is composed of MKP, which is the binding phase. The technetium peak is noticeable in the spectrum, indicating the presence of technetium in an area identified as MKP phase, and suggesting microencapsulation of technetium in the matrix. X-ray dot mapping was performed in the same location to study the distribution of technetium in the waste form (Fig. 4). The distribution of technetium is homogeneous, without any segregation into localized clusters. The uniform distribution of ^{99}Tc in the binding matrix promotes efficient microencapsulation and/or chemical bonding and thereby inhibits leaching of the radionuclide from the waste form.

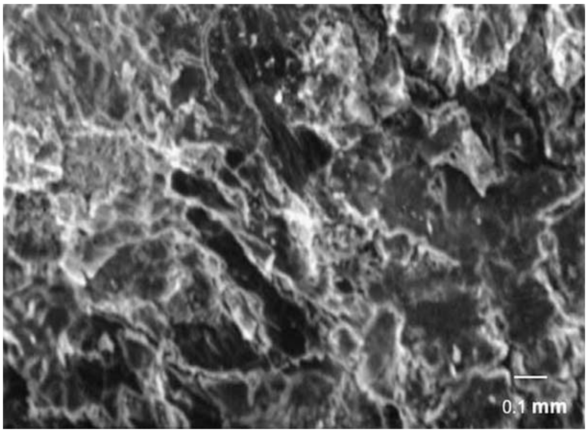

Fig. 2. SEM micrograph of MKP waste form with 36 wt% elution loading.

3.3. Leaching test results

3.3.1. American Nuclear Society's 16.1

The ANSI/ANS 16.1 standard assumes that diffusion controls the leaching of a contaminant from the waste form. Based on this assumption, the cumulative fraction of a contaminant species in the leachant varies with leaching time as per the following relation [22]:

$$\left(\sum a_n/A_0\right)V/S = 2[D_e/\pi]^{0.5}t_n^{0.5}. \tag{6}$$

To determine if diffusion is the rate-limiting process, the cumulative fractions of ^{99}Tc leached from the two sets of waste forms were plotted as a function of time as shown in Figs. 5 and 6. The release rates for the contaminants follow two distinct

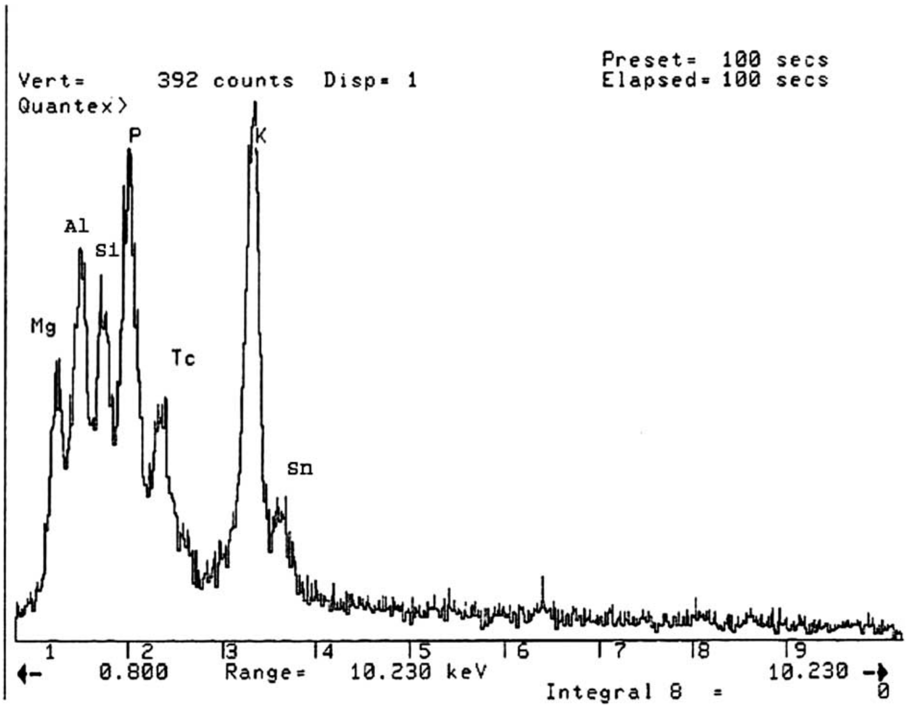

Fig. 3. EDX output of area shown in Fig. 2.

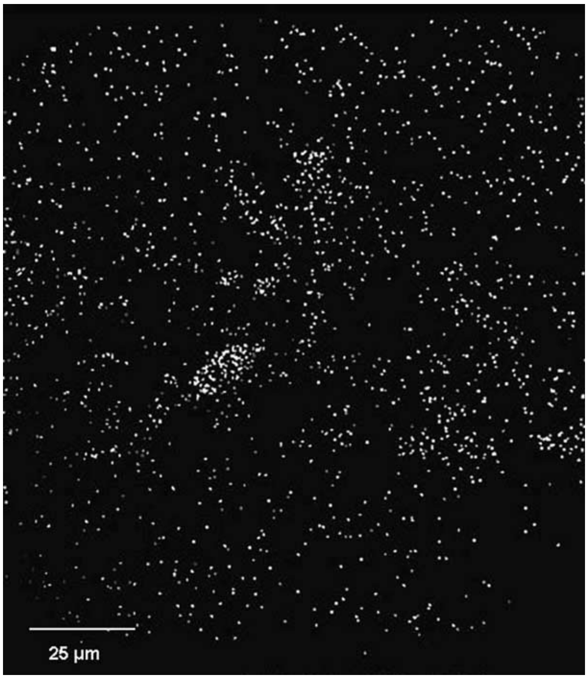

Fig. 4. X-ray dot mapping of Tc in area as shown in Fig. 2.

regimes. During the initial 100 h, the leaching of the contaminants from the waste forms is relatively rapid. This is because the contaminant that is deposited on the surface of a waste form leaches or is washed off over a relatively short period, causing an initially high leaching rate. As expected, the leaching is higher for waste forms with higher ^{99}Tc loadings. After the initial wash-off period, a linear relationship is obtained between cumulative fraction leached and square root of leaching time, indicating diffusion of ^{99}Tc as the main leaching mechanism.

The D_e and LI for the two sets of waste forms with varying ^{99}Tc concentrations were calculated from Eqs. (2) and (3); results are presented in Table 1. The LI for the specimens made by eluted wastes ranged from 11.3 to 14.4; these values are significantly higher than the NRC criterion for LI to be at least 6.0 [6]. The higher the LI and lower the D_e, the better the retention of contaminant in the matrix. Leachability indices for specimens without $SnCl_2$ are 8–9, as shown in Table 2. The role of $SnCl_2$ in effectively stabilizing ^{99}Tc by reducing it from the 7+ to 4+ oxidation state is evident from these results. The role of stannous chloride is discussed in the next section.

For ^{99}Tc concentrations as high as 900 ppm in the waste form, the LI values of samples with precipitated ^{99}Tc ranged from 13.3 to 14.6 (Table 1). It is well known that $TcO_2 \cdot 2H_2O$ is highly insoluble, with a solubility of 10^{-7}–10^{-8} mol/l in water under mildly reducing conditions [27]. This implies that precipitation of ^{99}Tc as $TcO_2 \cdot 2H_2O$ followed by microencapsulation in an MKP matrix yields a superior waste form. In addition, encapsulation of precipitated ^{99}Tc leads to a significantly higher loading of the radionuclide in the waste form, with higher LI as compared to waste forms fabricated without precipitated ^{99}Tc.

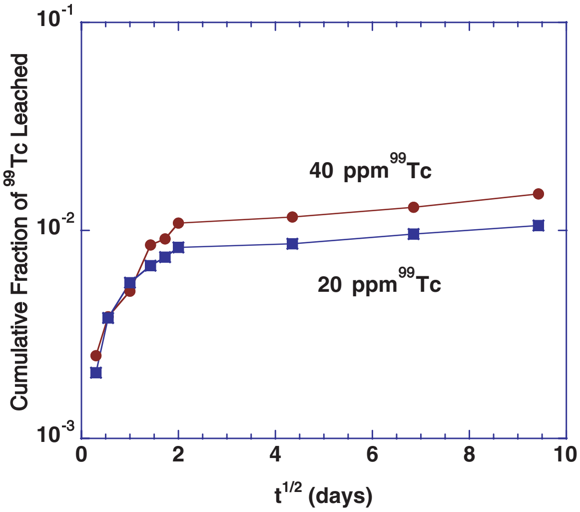

Fig. 5. Cumulative fraction of ^{99}Tc leached from eluted waste forms at room temperature.

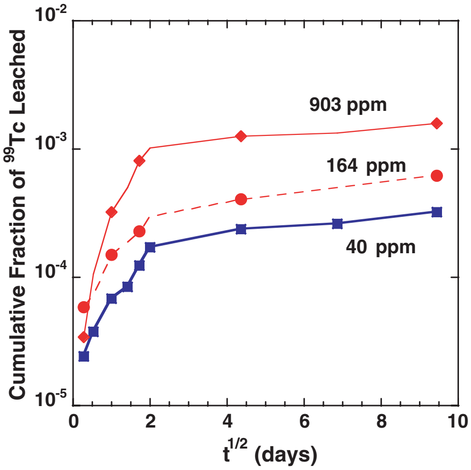

Fig. 6. Cumulative fraction of ^{99}Tc leached from waste form fabricated with precipitated ^{99}Tc at room temperature.

Table 1
ANS 16.1 results from MKP specimens fabricated with ^{99}Tc that contained eluted waste and precipitated ^{99}Tc

Composition	^{99}Tc conc. (ppm)	Effective diffusivity (cm^2/s)	Leachability index
MKP + $SnCl_2$ + eluted waste	20	2.9×10^{-12}	11.54
	40	5.4×10^{-12}	11.27
	124	3.8×10^{-15}	14.42
MKP + $SnCl_2$ + precipitated ^{99}Tc	41	2.2×10^{-14}	14.6
	164	2.3×10^{-13}	13.3
	903	7.2×10^{-15}	14.6

Table 2
ANS 16.1 results from MKP specimens with ^{99}Tc but without $SnCl_2$ addition

Composition	^{99}Tc conc. (ppm)	Effective diffusivity (cm^2/s)	Leachability index
MKP + eluted waste	20	1.20 *E* – 09	8.92
	40	2.95 *E* – 09	8.53

3.3.2. Product consistency test (PCT)

Results of PCTs conducted on specimens with precipitated ^{99}Tc are presented in Table 3. Normalized leaching rates of ^{99}Tc after a 7-day test period at room temperature are as low as 1×10^{-3} g/m^2 d for MKP waste forms. At 90 °C, the dissolution rate of the matrix increases; thus, the normalized leaching rate for ^{99}Tc increases to 10^{-2}–10^{-1} g/m^2 d. For both room- and elevated-temperature tests, the samples with highest loading of ^{99}Tc demonstrated the lowest normalized leach rate. The PCT was designed to evaluate the chemical durability of crushed borosilicate glass, which has been used to stabilize ^{99}Tc wastes. During tests conducted at 90 °C, the leaching rate of ^{99}Tc was as low as 10^{-2} g/m^2 d for borosilicate glass waste forms [8]. Therefore, we concluded that, when compared with high-temperature technologies, low-temperature fabrication of MKP waste forms provides reasonably good stabilization of ^{99}Tc.

Table 3
PCT results of MKP specimens fabricated with precipitated ^{99}Tc

Composition	Test temperature (°C)	Tc conc. (ppm)	Normalized leaching rate (g/m^2 d)
MKP + $SnCl_2$ + precipitated ^{99}Tc	25	40	3.9×10^{-3}
		164	8.5×10^{-3}
		903	1.1×10^{-3}
MKP + $SnCl_2$ + precipitated ^{99}Tc	90	40	7.2×10^{-2}
		164	1.1×10^{-1}
		903	3.6×10^{-2}

The concentration of ^{99}Tc in the leachant during the PCTs conducted at room temperature and 90 °C was used to determine the activation energy. Tests were not conducted for waste forms with ^{99}Tc greater than 903 ppm because of limited supply of waste stream available. The activation energy determined from samples with three loadings of ^{99}Tc was quite similar. Average activation energy value was 10.1 ± 1.2 kcal/mol, in agreement with the free energy change of 10.4 kcal/mol associated with solvation of Tc_2O_7 in water to form pertechnic acid in the reaction [28]:

$$Tc_2O_7 + H_2O \rightarrow 2HTcO_4. \tag{7}$$

Thus, during the PCT, ^{99}Tc leaching is probably controlled by the dissolution of Tc_2O_7 in water. It is expected that when crushed waste form is placed in water for testing, oxygen dissolved in water oxidizes the exposed $TcO_2 \cdot 2H_2O$ particulates and converts them to Tc_2O_7, which subsequently dissolves into the leachant.

3.4. Role of redox conditions in stabilization of ^{99}Tc

A cyclic voltammogram of a MKP slurry that contains 500 ppm Re and the reducing agent $SnCl_2$ is presented in Fig. 7. The upper curve represents cathodic (reducing) scan, and the lower curve, the anodic (oxidizing) scan. The peaks in current-vs.-potential curves are related to the half-wave

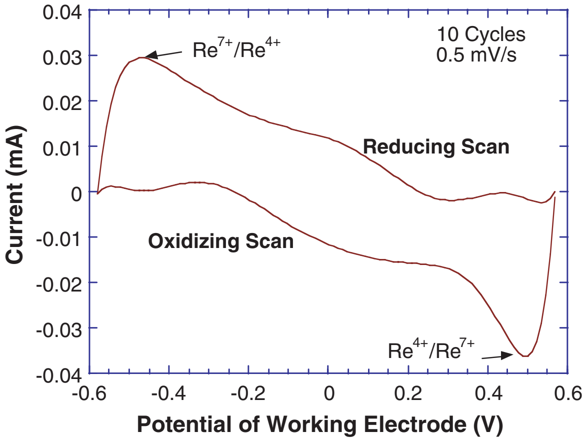

Fig. 7. Cyclic voltammogram of MKP waste form with 500 ppm Re.

potential $E_{1/2}$, which is equal to the standard potential E_0 of a redox reaction. The standard redox potential of the Re^{4+}/Re^{7+} system is 510 mV [29]. The voltammogram obtained for the slurry that contained $SnCl_2$ shows both oxidation and reduction peaks. The peaks observed in voltammogram, in both anodic and cathodic scans are at ≈ ±500 mV, indicating that the reversible oxidation–reduction reaction from Re(IV) to Re(VII) occurs in an MKP slurry in the presence of $SnCl_2$. The anodic peak is sharper than the cathodic peak in the voltammogram, indicating that the net effect involves oxidation of Re(IV) to Re(VII). These results reveal that $SnCl_2$ is a strong reductant that is capable of reducing Re and, hence, ^{99}Tc from their 7+ to 4+ states under similar conditions.

Fig. 8(a) shows the superimposed Eh–pH diagrams of Re–O–H and Tc–O–H systems [27]. As the pH increases, the Eh at which Re and ^{99}Tc are oxidized decreases. Furthermore, in the pH range 0–7, Re is relatively more easily oxidizable [to ReO_4^-] than is ^{99}Tc.

Fig. 8(b) shows the Eh–pH diagram for Re–O–H and Tc–O–H systems in the pH range 5–10. Also shown are the experimentally determined Eh values as a function of pH for the MKP slurries that contained eluted waste solution. These values were measured in MKP slurries with differing elution loadings. (Note that Re was added to the elution as a substitute for ^{99}Tc.) The Eh and pH values of the slurry with 36% elution loading under the normal setting conditions are +225 mV and 6.5, respectively. It is evident from this diagram that over the entire pH range of measurement, Eh values are in the highly soluble heptavalent oxidation state of Re. Even though cyclic voltammetry experiments showed that $SnCl_2$ is capable of reducing Re from the 7+ to the 4+ valence state, the reductant agent fails to reduce Re under actual Eh–pH conditions of the slurry.

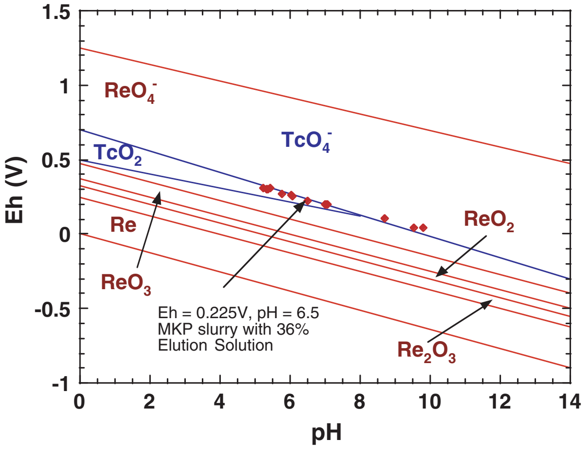

Fig. 8(a). Eh–pH diagram for Tc–O–H (blue) and Re–O–H (red); Eh value for MKP system at the time of setting = 225mV; pH = 6.5. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

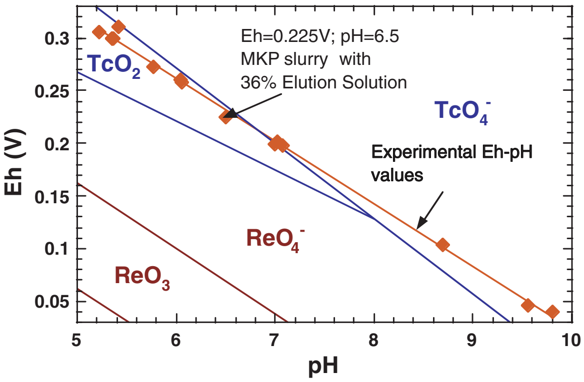

Fig. 8(b). Eh–pH diagram for Tc–O–H and Re–O–H system (enlarged).

However, for ^{99}Tc, the Eh values correspond to its insoluble TcO_2 (Tc^{4+}) oxidation state in the pH range 0–7. When pH >7, ^{99}Tc is present as TcO_4^- (Tc^{7+}). Under the setting conditions of the MKP slurry, the pH for a 36% elution loading lies between 6 and 7, and the Eh is +225 mV. These conditions are highly conducive in maintaining Tc in the 4+ state. Under these conditions, addition of $SnCl_2$ will further help in reducing TcO_4^- (Tc^{7+}) to its stable and insoluble (4+) oxidation state [Fig. 8(b)]. From these voltammetry and Eh/pH experiments we concluded that, by maintaining favorable reducing conditions, one could keep ^{99}Tc in its insoluble (4+) state in MKP slurry and hence achieve a low egress of ^{99}Tc. This conclusion was corroborated by the leaching test results.

3.5. Water immersion test

The variation in weight of one of the waste form samples immersed in water for 90 days is shown in Fig. 9. Initially, the mass of the water-immersed specimen increased. After three weeks of immersion, the specimen weight started to decrease, and from five weeks onwards, it remained nearly constant. At the end of 90 days, there was a ≈0.5% net decrease in mass. However, specimens that were

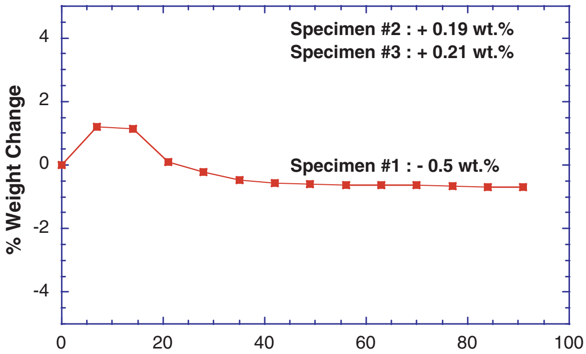

Fig. 9. Variation in mass of waste form during 90-day water immersion test.

not disturbed for 90 days showed a 0.2% net increase. These observations indicate that phosphate ceramic waste forms are extremely durable in aqueous conditions and show no significant material loss by matrix dissolution or congruent leaching.

X-ray diffraction analyses (Fig. 10) provide an insight into the initial gain and subsequent loss in the mass of water-immersed specimen. All of the MKP peaks observed in the XRD plot of the as-fabricated waste form were also observed in the XRD plot of waste forms subjected to the water immersion test. This finding indicates that even after long-term exposure to water, the matrix of fabricated waste forms is not being dissolved, presumably because of the insolubility of the phosphate-binding phase in water. This is a highly desirable characteristic for the durability of the final waste forms in aqueous environments. Furthermore, the relative intensity of the magnesium oxide peak at 42° decreases significantly in the specimens exposed to water. We infer that the initial weight gain is probably due to hydration of magnesium oxide to form magnesium hydroxide. The weight loss in subsequent weeks is due to release of magnesium oxide reaction products, along with some unreacted MgO, into water. The increase in pH of the deionized water from 5.5 to 8 after 90 days of immersion of the specimen indicates the release of magnesium oxide and its reaction products from the specimens exposed to water. The weight loss, which already is very low (≈0.5%), can further be decreased by reducing the residual MgO content of the waste form and optimizing the waste form processing.

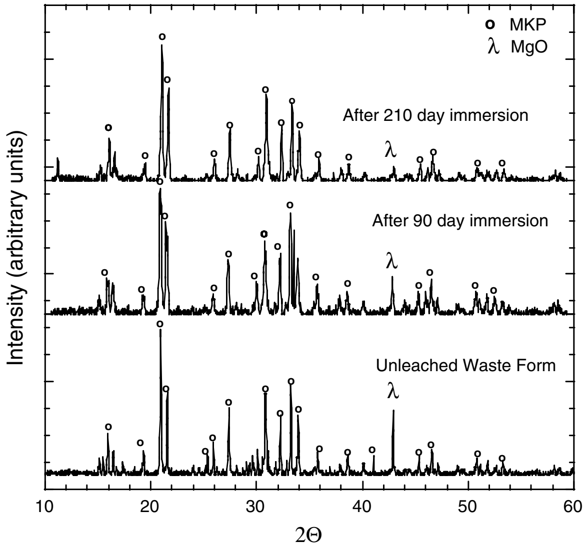

Fig. 10. XRD plots of as-fabricated specimen and waste forms immersed in water for 90 and 210 days.

The average compressive strength of three waste forms immersed in water for 210 days is ≈22 MPa, which is significantly higher than the regulatory requirement of 3.4 MPa. Observed mass changes and compression strengths clearly indicate that MKP waste forms have the potential to form highly insoluble and durable waste forms.

4. Summary

Magnesium potassium phosphate ceramics, which are formed at low temperature by the acid–base reaction between magnesium oxide and potassium phosphate in aqueous environments, were used to stabilize ^{99}Tc waste solutions generated by complexation/elution processes. Two approaches were used to fabricate the waste forms: directly adding the binder powders to the waste solution and precipitating ^{99}Tc from the waste solution followed by microencapsulation of the precipitate in the phosphate matrix. The fabricated waste forms possess low open porosity and high compression strength. ANS 16.1 and PCTs demonstrated the effectiveness of MKP waste forms in stabilizing ^{99}Tc. The ANS 16.1 test indicated LI values of ^{99}Tc as high as 14 for the waste forms. The PCTs showed ^{99}Tc leaching rates as low as 10^{-2} g/m^2 d. Eh/pH measurements of the MKP slurry indicate that redox conditions are favorable for ^{99}Tc to exist in its insoluble ^{99}Tc^{4+} state. The 90-day water immersion test showed insignificant change in sample weight, indicating little dissolution of the matrix material.

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