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ABSTRACT

Radionuclides such as ^{99}Tc are by-products of fission reactions in high-level wastes. Technetium poses a serious environmental threat because it is easily oxidized into its highly leachable pertechnetate form. Magnesium potassium phosphate ceramics have been developed to treat ^{99}Tc that has been separated and eluted from simulated high-level tank wastes by sorption processes. Dense and hard ceramic waste forms were fabricated by acid-base reactions between mixtures of magnesium oxide powders and wastes, and acid phosphate solutions. Standard leaching tests, such as ANS 16.1 and the Product Consistency Test, were conducted on the final waste forms to establish their performance. The fate of the contaminants in the final waste forms was established with scanning electron microscopy techniques. In addition, stability of the waste forms in aqueous environments was evaluated by long-term water immersion tests.

INTRODUCTION

Technetium-99 is a long-half-life fission product isotope that is present in U.S. Department of Energy (DOE) high-level waste (HLW) along with other volatile fission products such as ^{137}Cs and ^{90}Sr. Over a wide range of oxidizing conditions, the predominant form of Tc is the pertechnetate anion (TcO_4^-), which is highly soluble in water and thus readily mobile in the environment. Because of its long half-life (2.13 x 10^5 yrs) and high solubility, immobilization of ^{99}Tc is of great concern to DOE. Conventional thermal treatments for the stabilization of fission-product (Tc, Cs) wastes generates volatiles that subsequently must be stabilized before disposal. Hence, we need technologies that stabilize these waste streams by nonthermal stabilization processes. To this end, we are developing and demonstrating a low-temperature stabilization technology based on chemically bonded phosphate ceramics (CBPCs).

Chemically bonded phosphate ceramics are inorganic materials that can be fabricated inexpensively at relatively low temperatures by acid-base reactions between an inorganic oxide/hydroxide powder and an acid-phosphate solution [1,2]. The resulting phosphate ceramics are extremely insoluble in aqueous media and exhibit excellent long-term durability. Using CBPC technology, we have successfully demonstrated superior stabilization of heavy metals such as Pb, Cd, Cr, Hg, Ni, and radioactive contaminants like ^{238}U [3].

In this work, magnesium potassium phosphate ceramics (MKPCs) were developed for the stabilization of Tc-containing waste streams generated by a complexation-elution process developed at Los Alamos National Laboratory (LANL). Performance of the phosphate ceramic waste forms was established with various leaching, strength, and durability tests. Investigations were carried out by incorporating rhenium (Re) as a surrogate (chemical but nonradioactive equivalent) for ^{99}Tc, as well as ^{99}Tc in the LANL waste. The results of this study show that MKPCs have several advantages that make them ideal candidates for the treatment of waste streams that contain ^{99}Tc.

WASTE STREAM COMPOSITION

As part of the DOE's Efficient Separations and Processing Crosscutting Program, several separation technologies are being developed to partition volatile fission products from HLW to reduce the overall volatiles and radioactivity levels in the wastes. These partitioning efforts also minimize waste handling operations. In this regard, LANL has developed a complexation-elution process to separate ^{99}Tc from HLW such as the Hanford supernatant process. However, this separated waste must be immobilized before disposal. The expected composition of the Tc waste that is obtained from the complexation-elution process is 1 M NaOH, 1 M ethylene-diamine, 0.005 M Sn (II), and 0.00005 M ^{99}Tc. Surrogate waste with this composition was prepared by using Re as a nonradioactive surrogate for Tc. Also, waste forms were fabricated from the ^{99}Tc-containing waste from LANL's complexation-elution process.

FABRICATION OF MKPC WASTE FORMS

Magnesium potassium phosphate ceramic waste forms were fabricated by incorporating simulated formulations of the Tc waste stream obtained from LANL's complexation-elution process [4]. The magnesium potassium phosphate matrix is fabricated by reacting calcined magnesium oxide powder with an acid-phosphate solution. Phosphate ceramic waste forms were fabricated by mixing a surrogate waste stream with the magnesium potassium phosphate binder. Reducing agents such as $SnCl_2$ were added to the waste form formulation to keep the Re/Tc in its reduced state. The binder was continuously added to the waste solution, and the mixture was vigorously mixed to a desired consistency and then transferred to a mold and allowed to set. The mix hardened in 2 h to form hard, dense monoliths. After curing for >7 days, the monolithic waste forms were removed from the molds and subjected to various performance tests. Waste forms were fabricated so that the waste loading in the final waste forms was 36%. Concentration of the contaminants in the final waste forms ranged from 5 to 225 ppm.

RESULTS AND DISCUSSION

Physical and Mechanical Properties of Final Waste Forms

The physical properties most relevant to the final waste form are density, porosity, and compression strength. Therefore, these properties were measured on the MKPC waste forms fabricated from surrogate formulations of LANL's elution wastes. The density of the samples was measured by determining the mass and geometric volume; the porosity, by water immersion; and the compression strength, with an Instron machine in the compression mode. The density and open porosity of the waste forms were 1.8 g/cm^3 and 4%, respectively. The average compression strength of the MKPC ceramic waste forms was 4320 ± 954 psi. The land disposal requirement for the final waste forms is 500 psi. When compared with the required value, the strengths of the phosphate ceramic waste forms are much higher, indicating that MKPCs form superior waste forms. Overall, the waste forms are dense and hard materials, with very low open porosity and high strength.

X-ray Diffraction Analysis

To identify the crystalline phases in the MKPC waste forms, X-ray diffraction (XRD) using CuK_α radiation were performed. Figure 1 shows the XRD pattern of the MKPC waste form with 36% waste loading. Phosphate ceramic waste forms are highly crystalline. The prominent peaks in Fig. 1 represent those of the magnesium potassium phosphate system, which is the binding phase in the waste forms. Magnesium potassium phosphate is a highly insoluble phase (solubility in water is $\approx 10^{-9}$ mol/L); hence, it is desirable in the final waste forms. Also present in Fig. 1 are peaks of unreacted magnesium oxide, which acts as a filler material.

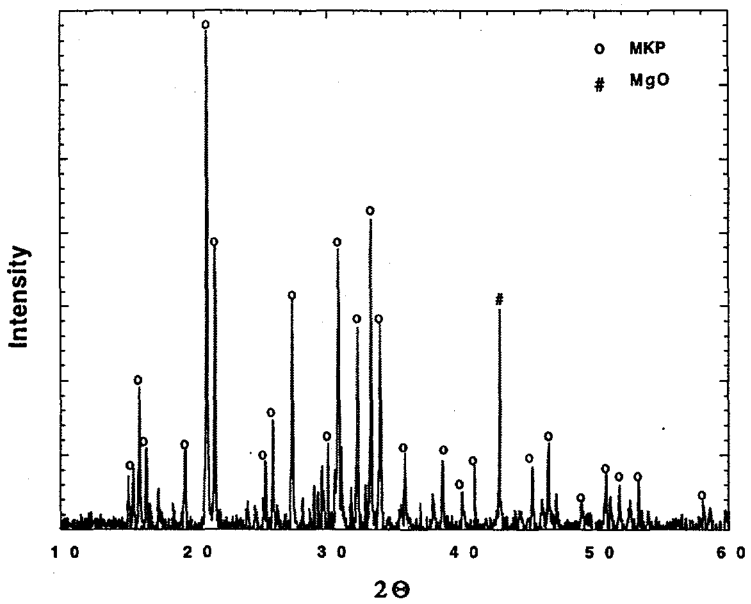

Fig. 1. X-ray diffraction pattern of magnesium potassium phosphate ceramic (MKPC) waste form with 36% waste loading.

Microstructural Studies

The microstructure of the phosphate ceramic waste forms was investigated by scanning electron microscopy (SEM). Figure 2 is an SEM photomicrograph of a fractured surface of a magnesium phosphate ceramic waste form with 36% waste loading. The photomicrograph shows a very dense, crystalline structure, with a small number of pores. The crystalline phase is the magnesium potassium phosphate binding matrix. The waste form microstructures were further analyzed by X-ray mapping of the contaminant in the waste form. The inset in Fig. 2, which shows the distribution of Re within the area of the photomicrograph, indicates that Re is evenly distributed. This implies that the distribution of the contaminant is homogeneous and the contaminant is not segregated into localized regions. In addition, contaminants are thoroughly encapsulated by the crystalline binding matrix of the MKPC. This makes the contaminant less leachable and accounts for the extremely low leachability of Re during leach testing of final waste forms.

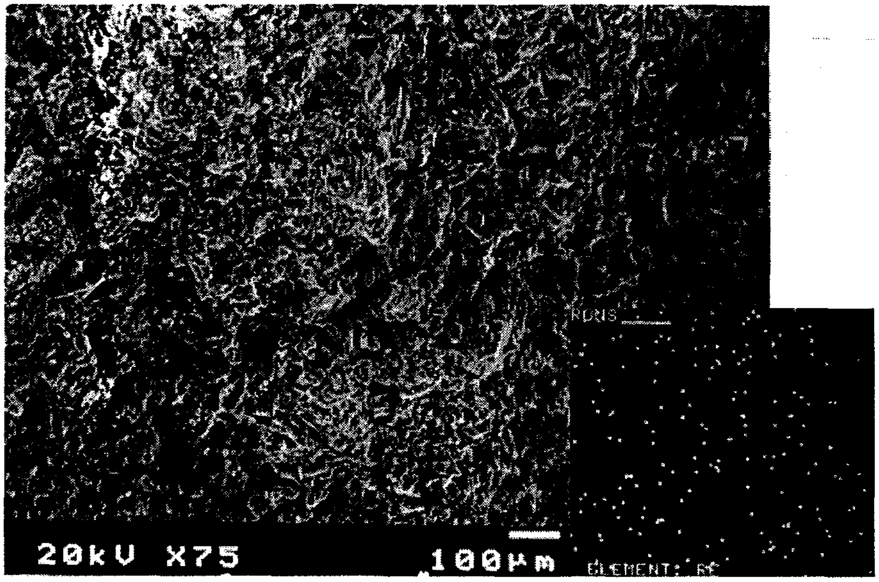

Fig. 2. Photomicrograph of fractured surface of MKP waste form with 36% waste loading; inset shows distribution of Re within the area of the photomicrograph.

Leaching Studies

To establish the effectiveness of the MKPC waste forms in stabilizing the contaminants, leaching studies were performed on the fabricated final waste forms according to American Nuclear Society's ANS 16.1 and Product Consistency Test (PCT).

MKPC waste forms with 36% elution waste loading were subjected to ANS 16.1 leach testing for 90 days under oxidizing conditions, in accordance with the procedure given in Ref. 6. This testing was conducted on waste forms made with Re (surrogate for Tc), and on wastes that contained ^{99}Tc. In this procedure, lechate solutions are periodically changed to simulate continuous flow of water. At the end of the 90-day test, parameters that are obtained are the effective diffusivity and leachability index of the contaminant. The effective diffusivity is given by

$$D_e = \pi[(a_n/A_0) / (\Delta t)_n]^2 (V/S)^2 (T) \qquad (1)$$

where

a_n = Amount of contaminant leached from sample during leaching interval n,

A_0 = Total amount of contaminant in sample at tbeginning of leach test,

$(\Delta t)_n$ = $t_n - t_{n-1}$, duration of nth leaching interval, s,
D_e = Effective diffusivity, cm^2/s,
V = Volume of sample, cm^3,
S = Surface area of sample, cm^2, and
T = Mean time of leaching interval, s,

The logarithm of the average effective diffusivity (cm^2/s) is defined as leachability index

$$L_i = 1/n\ \Sigma[\log(\beta/D_e)]_n \tag{2}$$

where β is a defined constant (1 cm^2/s) and D_e is the effective diffusivity of the contaminant. Larger values of the leachability index are desirable because they represent lower values of contaminant diffusivity. Moreover, based on Godbee's model [7], a cumulative fraction of the contaminant species in the leachant solution after a particular time t can be expressed by

$$F = \Sigma a_n/A_0 = [2.\ D_e/\pi]^{0.5}.\ t^{0.5}\,(S/V) \tag{3}$$

Figure 3 shows the cumulative fraction of the contaminants (Re or ^{99}Tc) plotted against the square root of the leaching time. A straight line was not obtained for the first four days, indicating that the removal of the contaminant in the first four days was likely to be by washoff from the surface and the inner pore walls of the specimen. After four days, a linear relationship between the cumulative fraction leached and the square root of the leach time was obtained, indicating that diffusion was the rate-limiting mechanism. At present, it is not clear why the samples with higher contaminant loadings showed a lower cumulative leached fraction. It is possible that the amount of contaminant released depends on the rate at which oxygen diffuses into the specimen and oxidizes the reduced contaminant species. Thus, the diffusion of oxygen is probably the rate-limiting step and, hence, even though the contaminant concentration in the waste form is high, only a limited amount is oxidized and released into the lechant.

Effective diffusivity and leachability index values were obtained from the ANS 16.1 standard equations given above. The results are presented in Table I. Diffusivities of the contaminants are extremely low, indicating excellent stabilization of the contaminants in the phosphate matrix. The determined leachability indices

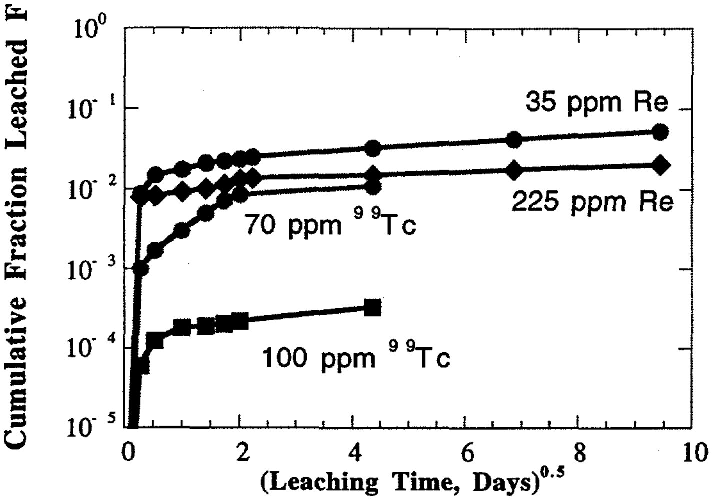

Fig. 3. ANS 16.1 test results, showing square root of leach time vs. cumulative fraction contaminant in leachate.

Table I. Results of ANS 16.1 test on MKP waste forms with 36% waste loading

Contaminant Conc., ppm	Effective Diffusivity, cm^2/s	Leachability Index
Re: 35	6.55×10^{-11}	10.2
Re: 225	6.39×10^{-12}	11.2
Tc: 70	2.13×10^{-11}	10.8
Tc: 100	2.36×10^{-14}	14.2

ranged from 10 for specimens with 35 ppm Re loading to as high as 14 for specimens with 100 ppm Tc loading. These figures of merit are significantly higher than the Nuclear Regulatory Commission's passing criterion of 6.

A static leaching test, such as the PCT [8], was performed to evaluate the chemical durability of MKPC waste forms at temperatures <100°C for various surface-area-to-volume (S/V) ratios. The PCT is designed to evaluate chemical durability of crushed homogeneous and vitrified glasses. To allow a comparison of leach test results of waste forms with differing compositions, results are given in terms of normalized elemental loss and normalized elemental leach rate in both tests. These tests simulate the worst-case leaching conditions. Product Consistency Tests were carried out at 90°C for seven days in teflon containers on >1 g from -100 to +200 mesh crushed waste form particles. Deionized water was the leachant and the S/V ratio in this test was held constant at 3000 m^{-1}. These leaching tests were performed under oxidizing conditions.

Table II summarizes the PCT leaching rates observed with waste form samples fabricated with 35 and 225 ppm Re loading. Normalized leaching rates of Re after a seven-day test period are extremely low ($\approx 10^{-4}$ g/cm^2-d) for both of the waste forms. These values are as good as those observed in high-temperature technologies applied to materials like borosilicate glass, vitrified glass, etc. The low leach rate values observed with phosphate ceramic waste forms in PCTs are attributed to the reduction of Re to its lower oxidation state. It should be noted that maintenance of low-oxygen conditions, to prevent oxidation and thus to reduce the mobility of Re, significantly improves the leaching rates of the contaminant in phosphate ceramic waste forms. We are currently performing a PCT on waste forms that were fabricated with the actual Tc waste.

Table II. Test results of product consistency

Waste Form	Re conc., ppm	Leach Rate, g/m^2-d
MKPC + 36% Eluted Waste	35	1.26×10^{-3}
MKPC + 36% Eluted Waste	225	4.90×10^{-4}

Water Immersion Tests on Final WasteForms

Immersion studies were initiated to study 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 periodically removed, dried, and weighed to determine weight change over the 90-day period. The other two specimens were not disturbed. The procedure we followed was similar to that outlined in ANS 16.1. Figure 4 shows the weight change in the waste form containing 36% LANL-eluted waste loading. The percent change in weight is

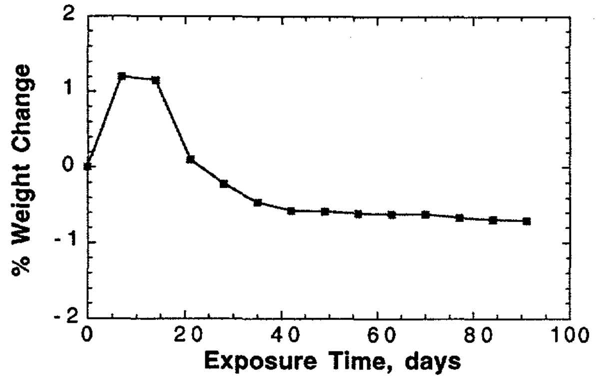

Fig. 4. Percent weight change of waste form during 90-day water immersion test.

computed with respect to the weight of the waste form before immersion study. Initially, there was an increase in weight. After three weeks of immersion, the weight of the sample started to decrease, and from five weeks onwards, it remained nearly constant. At the end of 90 days, there was an ≈0.5% net decrease in weight. However, specimens that were not disturbed for 90 days showed a 0.2 wt.% increase in weight.

X-ray diffraction analyses (Fig. 5) of as-fabricated and long-term-water-immersed waste forms provide insight into the initial gain and subsequent loss in weight of water-immersed specimens. All of the peaks of the magnesium potassium phosphate binding matrix that were present in the XRD plot of the as-fabricated waste forms were also present in the water-immersed samples. This finding indicates that the matrix of the fabricated waste forms is not being dissolved even after long-term exposure to water and demonstrates the insolubility of the phosphate binding phase in water, a highly desirable characteristic for the durability of the final waste forms in aqueous environments. Furthermore, it was observed that the relative intensity of the magnesium oxide peak at 42° has decreased significantly in the water-exposed samples. It can be inferred from this observation that the initial weight gain might be due to the hydration of magnesium oxide to mganesium hyroxide. The weight loss in the following weeks is probably due to the release of these reaction products, along with some unreacted MgO, into the water. The increase in the pH of the deionized water from 5.5 to 8 after 210 days

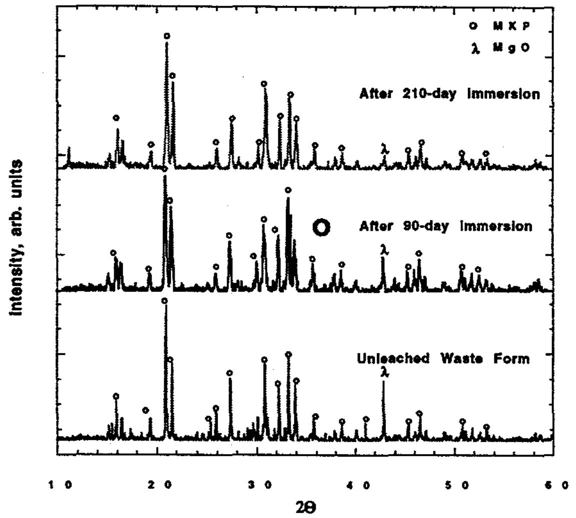

Fig. 5. XRD plots of as-fabricated and long-term-water-immersed MKPC waste forms with 36% waste loading.

of immersion suggests the release of the unreacted magnesium oxide from the water-immersed specimens. Over all, there was a very small decrease (≈0.5%) in the weight of the specimens after 90 days of immersion in water. We believe that this small weight loss can be further reduced by optimizing the processing conditions so that the residual MgO content in the final waste form is minimized.

In addition to monitoring the weight change of the waste forms, we immersed three specimens in water and tested them for compression strength at the end of 210 days. Figure 6 shows the strength of the as-fabricated final waste forms and of the phosphate ceramic waste forms after a 210-day water immersion. The compressive strength of the waste forms is ≈3000 psi, which is significantly higher than the regulatory requirement of 500 psi, even after a 210-day exposure to an aqueous environment. The observed weight change and compression strength results clearly indicate that MKPC waste forms have the potential to form highly insoluble and durable waste forms.

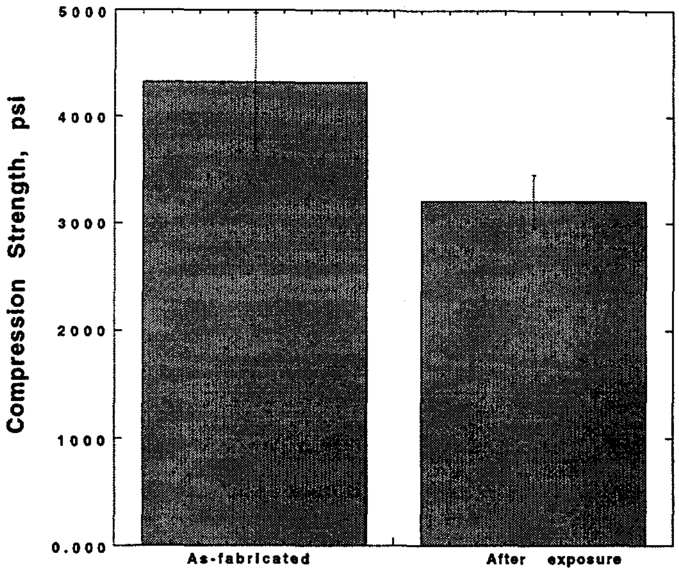

Fig. 6. Average strengths of as-fabricated MKPC waste forms and after 210-day immersion in water.

SUMMARY

Magnesium potassium phosphate ceramics were used to stabilize separated ^{99}Tc waste stream from LANL's complexation-elution process. Waste forms were produced with low open porosity, and hence low permeability, and high compression strength. Preliminary investigations were carried out by incorporating Re in the phosphate matrix as a nonradioactive surrogate for ^{99}Tc. The waste forms were subjected to various leaching tests to demonstrate retention of the contaminants in the surrogate wastes. Magnesium potassium phosphates are extremely effective in stabilizing Re, the surrogate of Tc. A Product Consistency Test conducted on MKPC-LANL-eluted waste forms showed leaching rates of Re of $\approx 10^{-3}$-10^{-4} g/m^2-d. Similarly, ANS 16.1 tests on the waste forms indicated leachability indices from 10-14 for ^{99}Tc. Ninety-day water immersion tests showed an $\approx$0.5% change in sample weight, indicating no apparent dissolution of the matrix material. Overall, MKPCs have several advantages that make them candidates for the treatment of waste streams that contain ^{99}Tc.

Acknowledgments

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