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Aqueous leachability of lanthanide and plutonium titanates [1]

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Abstract

The leachabilities of titanate and zircono–titanate solid solutions, $Ce_2Ti_2O_7$, $Er_{1.78}Ce_{0.22}Ti_2O_7$, $Er_{1.78}Pu_{0.22}Ti_2O_7$ (9.5 wt% Pu) $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$, $SrCe_2Ti_4O_{12}$, $SrPu_2Ti_4O_{12}$ (50.7 wt% Pu) and $Sr_2Ce_2Ti_5O_{16}$, have been investigated in WIPP 'A' brine, 0.1 M NaCl, and 0.1 M HCl solutions using a modified MCC-3 procedure with a duration of 60 days. The concentrations of plutonium leached by the brine were less than 1 ppm. Where cerium was used as a surrogate for plutonium, its concentration in WIPP brine was below the limit of detection (10 ppm) established for the inductively coupled plasma (ICP) atomic emission spectrometer used. Concentrations of strontium leached by WIPP brine from stable strontium-containing titanate compounds, considered as possible immobilizers of both ^{90}Sr and actinide elements, were on the order of 30–60 ppm.

1. Introduction

The need for developing host forms for immobilizing radionuclides originated with the discovery and use of radioactive materials as energy sources, in nuclear weapons, and in medical applications. Glasses, titanate-based ceramic materials, especially SYNROC, and zircon have been and continue to be aggressively studied by researchers, such as Ewing et al. [1,2], Roy [3], Ringwood et al. [4,5], Nesbitt et al. [6], Vance et al. [7–9], Burakov et al. [10], Hart et al. [11], and Newkirk et al. [12], to understand their potential and their limitations as immobilizing matrices.

The formation of compounds and solid solutions in lanthanide- and actinide-containing titanate and/or zircono–titanate systems has been investigated by Bamberger et al. [13,14] and Shoup et al. [15–18]. Establishing the existence of compounds that can incorporate elements of interest is only the first step in proposing the use of such compounds and solid solutions as host matrices for radioactive elements. The durability of a compound or solid solution with respect to leaching is an equally important consideration.

Underground salt repositories have been chosen as possible sites in which to store immobilized transuranic nuclear waste. A test facility designed to study this possibility is the Waste Isolation Pilot Plant (WIPP) in New Mexico. In the event that a breach by water occurred in such a repository, leaching studies using a brine, denoted WIPP 'A' brine, considered to simulate the WIPP repository conditions, can provide valuable information about the stability of compounds considered as potential immobilizers in such sites.

Thus, to obtain an initial perspective on the feasibility of titanate and zircono–titanate compounds as hosts, the aqueous leachabilities of several representatives of the systems, previously studied by the present authors [13–18], were investigated. Modified MCC-3 leaching procedures established by the Materials Characterization Center [19] were followed, and the leachants used were the WIPP 'A' brine [20], 0.1 M NaCl, and 0.1 M HCl solutions. Ce(III) was used in some compounds as a surrogate for Pu(III) based on the comparable ionic radii from Shannon [21] and

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observed similarities in compound formation [13,16]. The cerium-containing compounds and solid solutions studied were $Ce_2Ti_2O_7$ [13] (I), $Er_{1.78}Ce_{0.22}Ti_2O_7$ [13] (II), $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$ [18] (III), $SrCe_2Ti_4O_{12}$ [15] (IV), and $Sr_2Ce_2Ti_5O_{16}$ [14] (V). These compounds were chosen to provide several comparisons, e.g., from (I) and (II) the effect of crystal structure and dilution of cerium; from (II) and (III) the effect of zirconium substitution and thus another crystal structure change, and from (IV) and (V) the effect of the oxidation state of cerium and, when compared to (I)–(III), the effect of the presence of strontium. Cerium is trivalent in all of these compounds and solid solutions except for $Sr_2Ce_2Ti_5O_{16}$ where cerium is tetravalent. The plutonium-containing solid solutions studied were $Er_{1.78}Pu_{0.22}Ti_2O_7$ and $SrPu_2Ti_4O_{12}$ [16] where plutonium is in the (III) oxidation state and the plutonium content is, respectively, 9.5 and 50.7 wt%.

2. Experimental

2.1. Compound preparation

The method used to prepare the compounds studied here consisted of dry grinding the appropriate oxides (CeO_2, Er_2O_3, $^{242}PuO_2$, TiO_2, ZrO_2) together with $SrCO_3$ (as a source of SrO) and TiN (a reductant used to convert Ce(IV) to Ce(III) and Pu(IV) to Pu(III)) when needed. These mixtures were calcined between 1350–1400°C and were reground 1–4 times until no changes in composition were seen by X-ray diffraction (XRD). This method was the main analytical tool used to determine the purity of solids. Typical reaction times were between 20 and 100 h. $Ce_2Ti_2O_7$, $Er_{1.78}Ce_{0.22}Ti_2O_7$, and $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$ were calcined in Ar, while $SrCe_2Ti_4O_{12}$ and $Sr_2Ce_2Ti_5O_{16}$ were calcined in Ar–4%H_2 and air, respectively. $Er_{1.78}Pu_{0.22}Ti_2O_7$ and $SrPu_2Ti_4O_{12}$ were calcined in Ar–4%H_2. Additional details concerned with phase purities and crystal structures have been described in [13–18].

Each cerium-containing product was ground in an agate ball grinder (Spex Industries, cat. no. 8000) fine enough to be sieved through a 325 mesh nylon screen (44 μm pore size) (Spex Industries). The plutonium-containing products were ground with a porcelain mortar and pestle and also sieved through 325 mesh screens. The cerium-containing products were re-analyzed by XRD to insure that grinding had not caused polymorphic changes or separation of phases. Because of the limited amounts available, the plutonium-containing solid solutions were not analyzed after grinding.

2.2. Leachant preparation and procedure

The leachants were: WIPP 'A' brine [20], a synthetic substitute for that found in nature at the Waste Isolation Pilot Plant (WIPP) site in New Mexico, 0.1 M NaCl solution, used as a constant ionic strength solution, and 0.1 M HCl solution, to test the effect of low pH. Because of the small amounts of plutonium-containing solid solutions available, only their leachabilities in WIPP 'A' brine solution were studied. The pH of each solution before and after leaching the cerium-containing compounds was measured using a pH meter (Beckman Zeromatic) standardized with buffers of pH 4.01 and 7.00.

The ratio 1 g solid/10 mL leachant, as stated in the MCC-3 procedures [19], was used in all the leaching tests. Hermetic Teflon containers were cleaned and used following the MCC procedures. The volumes of the solutions remaining at the end of the testing period were measured, and it was found that the loss of volume was within the limits acceptable by the MCC standards.

2.3. Temperature control and agitation methods

The leachability of the cerium-containing compounds and solid solutions were studied at two temperatures, room temperature and 50°C, while the plutonium-containing solid solutions were studied only at room temperature. The MCC-3 procedures [19] call for constant agitation of the samples at the test temperature. Constant agitation at room temperature was achieved by magnetic stirring. The samples held at 50°C were kept in a water bath equipped with a shaker (Magni Whirl Constant Temperature Bath, Blue M Electric, model MSB-1122A-1). Constant temperature and agitation were maintained throughout the test period (1344 h) except for approximately 3 h during a general power outage.

2.4. Leachate filtering

The compounds and solid solutions were in contact with the leachant for eight weeks, a reasonable contact time based on several other studies using MCC procedures [4,6,22], for preliminary leachability results. At the end of the eight-week test period, approximate aliquots of 5 mL or 1 mL of the leachate solutions in contact with, respectively, the cerium- or plutonium-containing solids were filtered from each container using 0.45 μm pore size syringe-filters connected to disposable syringes and needles. Filters and syringes were warmed to 50°C before the aliquots of leachate held at 50°C were taken. The filtered aliquots were transferred to small polyethylene bottles and analyzed for the concentrations of each element of interest; in the case of the cerium-containing samples, by Inductively Coupled Plasma (ICP) atomic emission spectrometry, while plutonium-containing samples were analyzed only for the amount of plutonium present using gross alpha counting and alpha pulse height analyses.

2.5. Analysis by ICP atomic emission spectrometry

The filtered leachates which had been in contact with the cerium-containing solids were analyzed using an ICP

Table 1
Detection limits established for each element in the different leachants [a]

	Strontium (ppm)	Erbium (ppm)	Cerium (ppm)	Titanium (ppm)	Zirconium (ppm)
WIPP 'A' brine	1	0.1	10	0.1	0.04
0.1 M NaCl	1	4	2	3	1
0.1 M HCl	0.001	0.01	0.2	0.002	0.004

[a] These pre-dilution limits of detection (except for cerium in the brine solution) were taken as three times the standard deviation of the background signal for each element in the blank leachants. The pre-dilution limit of detection for cerium in the blank brine solution was established based on the actual instrumental reading, which greatly exceeded its standard deviation.

atomic emission spectrometer (Thermo Jarrell Ash PolyScan Iris) with an argon plasma excitation source. The following plasma conditions were used: auxiliary gas, 3 psig; RF power, 1150 W; nebulizer pressure, 32.0 psi, nebulizer flush pump rate, 100 rpm; nebulizer analysis pump rate, 100 rpm; relaxation time, 0.0 s. The following wavelengths (in nm), calibrated from an internal mercury lamp, were used to identify the indicated element: Ce, 413.765; Er, 323.058; Sr, 338.071; Ti, 336.121; and Zr, 343.823 or 349.621. A 1 ppm yttrium internal standard, detected at 360.073 nm, was used in all analyses. The sample flush time was between 20.0 and 40.0 s. Blanks of every leachant solution were analyzed. The blanks and leachates were diluted before analysis with 0.45 M HNO_3 (2% by volume) according to the following arbitrary ratios: WIPP brine, 1:10; 0.1 M NaCl, 1:2; and 0.1 M HCl, 1:2. The pre-dilution detection limits established for each element in the different leachants are given in Table 1. Each sample was analyzed three times to obtain average concentrations of the elements of interest, and the concentrations reported are the pre-dilution values. The percent relative standard deviation values determined for the concentrations were typically lower than 5 and are not included in Table 2 for clarity.

2.6. Gross alpha counting and alpha pulse height analyses

The leachates which had been in contact with the plutonium-containing solids were analyzed by gross alpha counting using a gas-flow proportional counter (Tennelec LB 4000, Oxford Instrument Co.). The instrument, which had a low alpha background (0.2 cpm), was calibrated using an Am-241 NIST traceable standard. Each sample was plated onto a stainless steel planchet and counted following the EPA-600/900.0 procedure [23]. The counting time for each sample was 20 min. Alpha pulse height

Table 2
Concentrations of elements leached at (room temperature and) 50°C and XRD results of the residues [a]

	$Ce_2Ti_2O_7$		$Er_{1.78}Ce_{0.22}Ti_2O_7$		$Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$		$SrCe_2Ti_4O_{12}$		$Sr_2Ce_2Ti_5O_{16}$	
Leachant	Ion	ppm	Ion	ppm	Ion	ppm	Ion	ppm	Ion	ppm
WIPP 'A' brine	Ce	BDL	Ce	BDL	Ce	BDL	Sr	25	Sr	40
	Ti	BDL	Ti	BDL	Ti	BDL	Ce	BDL	Ce	BDL
			Er	10	Er	15	Ti	BDL	Ti	BDL
					Zr	BDL				
XRD of residues	M: NC m: pyroch.		NC		M: NC m: $Ce_2Ti_3O_{9-3m}$		M: NC m: $Ce_2Ti_2O_7$-type, Ti_nO2_{n-1}		NC	
0.1 M NaCl	Ce	BDL	Ce	BDL	Ce	BDL	Ce	BDL	Ce	BDL
	Ti	BDL	Ti	BDL	Ti	BDL	Ti	BDL	Ti	BDL
			Er	BDL	Er	BDL	Sr	*	Sr	*
					Zr	BDL				
XRD of residues	NC		NC		NC		M: NC m: $Ce_2Ti_2O_7$		NC	
0.1 M HCl	Ce	300	Ce	150	Ce	45	Ce	150	Ce	110
	Ti	BDL	Ti	3	Ti	15	Ti	30	Ti	35
			Er	1375	Er	1200	Sr	80	Sr	190
					Zr	BDL				
XRD of residues	NC		NC		NC		NC		NC	

[a] BDL = below detection limits; M = major phase, NC = no change; m = minor phase; pyroch. = pyrochlore-type phase; * = values too high above calibration curves.

analyses were performed on the same samples used to obtain the gross alpha counts using an alpha spectrometer (Tennelec TC 257, Oxford Instrument Co.) and the Genie-ESP Data Acquisition and Processing System (Canberra, Nuclear Data). The acquisition time for each sample was 1 h.

2.7. Analysis by XRD of leached solids

Solids remaining from the leaching tests at 50°C were analyzed by XRD. The solid remnants were washed with distilled water and isopropyl or methyl alcohol, dried, and examined by XRD to detect any change of the solid phase during the course of leaching.

3. Results and Discussion

3.1. Leaching results for cerium-containing compounds

The concentrations of elements present in the different leachates held at 50°C and determined by ICP are given (reported as ppm (or mg/L solution)) in Table 2. The results from the leachates held at room temperature are not given here because they are similar to the values at 50°C. XRD analyses of the solids remaining after contact with the leachants at 50°C are also given in Table 2.

The compound $Ce_2Ti_2O_7$ was selected to provide a basis for the aqueous leachability of the monoclinic dititanates because no such data have been found in the literature. The solid solution $Er_{1.78}Ce_{0.22}Ti_2O_7$ was selected in order to (a) compare the aqueous leachability of monoclinic $Ce_2Ti_2O_7$ to that of a solid solution of Ce(III) in a pyrochlore-type heavy lanthanide dititanate and (b) as a surrogate for the analogous Pu(III) compound. Both compounds were quite stable in the brine and 0.1 M NaCl solution, but it is interesting to note that in 0.1 M HCl a combined higher concentration of erbium and cerium was observed than the amount of cerium solubilized from $Ce_2Ti_2O_7$. This suggests that the pyrochlore-type structure is less stable in dilute HCl than the monoclinic phase.

Only the brine solution degraded sufficiently the solid $Ce_2Ti_2O_7$ so that differences could be detected by XRD. The major phase after contact with the brine was still $Ce_2Ti_2O_7$; however, significant amounts of a pyrochlore-type phase were also present. Since the leaching of $Ce_2Ti_2O_7$ was below the ICP detection limits, the presence of pyrochlore can be speculated to have originated from small amounts of Ce(IV) formed by oxidation, which could have allowed the radius ratio of the Ce(III) and Ce(IV) to Ti(IV) ions present to fall within the range necessary for pyrochlore formation [24].

No major structural damage was done to the $Er_{1.78}Ce_{0.22}Ti_2O_7$ samples by any of the leachants. There was virtually no change detected in the XRD results of the solids remaining after contact with the leachants as compared to the results of $Er_{1.78}Ce_{0.22}Ti_2O_7$ before leaching.

To compare the effect of the presence of zirconium and of a crystal structure different from the pyrochlore $Er_{1.78}Ce_{0.22}Ti_2O_7$, leaching was also tested on the defect fluorite-type solid solution $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$. Little effect on the leachability by the various leachants was seen.

The XRD results of $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$ after leaching do not differ much from those before leaching. Only the solid which had been in contact with the brine solution shows any change. A small amount of a phase identified as $Ce_2Ti_3O_{9-3m}$ was detected in addition to the main phase of a defect fluorite-type compound. It may be speculated that some Ti(III) would have been initially present since the solid solution was calcined in Ar–4%H_2. It is possible that the separation of a small amount of $Ce_2Ti_3O_{9-3m}$ would leave a phase having a slightly different composition than $Er_{1.78}Ce_{0.22}Ti_{0.5}Zr_{1.5}O_7$ but which would still exhibit a defect fluorite-type structure.

The compound $SrCe_2Ti_4O_{12}$, a member of the series $Sr_{4-x}Ce_{2x/3}Ti_4O_{12}$, where $x = 3.0$ and cerium is trivalent, was selected to determine its potential as a host matrix for both ^{90}Sr and, ultimately, Pu(III). The amounts of strontium leached by the 0.1 M NaCl solution were quite high (Table 2) suggesting, in a first approximation, that this compound may not be a good candidate for strontium immobilization. In general, no dramatic change in pH was found for the WIPP and HCl solutions in contact with $SrCe_2Ti_4O_{12}$, but the pH of the 0.1 M NaCl solutions held at both room temperature and 50°C was higher by 1–2 units.

The effect of 0.1 M NaCl indicated by a large amount of strontium in solution, while not readily apparent, may be explained by the following reaction:

$$SrCe_2Ti_4O_{12(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + Sr^{2+}_{(aq)} + Ce_2Ti_2O_{7(s)} + 2TiO_{2(s)}. \qquad (1)$$

No TiO_2 was seen in the XRD pattern of the remaining solid, however it would be expected from a hydrolysis reaction such as that depicted by Eq. (1) that the TiO_2 would be amorphous.

Several changes were observed via XRD for the solid $SrCe_2Ti_4O_{12}$ that had been in contact with the brine. The major phase present was $SrCe_2Ti_4O_{12}$ together with two additional phases, an unknown $Ce_2Ti_2O_7$-type phase, having a slightly smaller cell volume than that of pure $Ce_2Ti_2O_7$, and another phase, possibly a titanium suboxide. The presence of a reduced titanium species is likely because the compound was originally calcined in Ar–4%H_2, thus allowing for some reduction of some Ti(IV) to Ti(III).

The compound $Sr_2Ce_2Ti_5O_{16}$ was selected because it contains cerium in the tetravalent state and has a similar

Table 3
Concentrations of plutonium leached at room temperature [a]

	$Er_{1.78}Pu_{0.22}Ti_2O_7$		$SrPu_2Ti_4O_{12}$	
Leachant	Ion	ppm	Ion	ppm
WIPP 'A' brine	Pu	0.2 (0.1)	Pu	0.2 (0.1)

[a] The errors are given at two standard deviations.

structure to $SrCe_2Ti_4O_{12}$ with Ce(III). It was found that the leaching behavior of both compounds was similar in all leachants, i.e., there was also a significant difference between the amounts of strontium leached by the brine and 0.1 M NaCl solutions, the latter giving high values. The pH of the leachates was virtually the same as the solutions before contact with $Sr_2Ce_2Ti_5O_{16}$ except for 0.1 M NaCl solution where the pH of the leachates was 1–2 units higher than the original solution. A similar reasoning used for $SrCe_2Ti_4O_{12}$ can be used to explain the increase in pH with the significant amount of strontium dissolved. No major structural damage had occurred to the $Sr_2Ce_2Ti_5O_{16}$ compound in the WIPP 'A' brine, 0.1 M NaCl, or 0.1 M HCl solutions.

3.2. *Leaching results for plutonium-containing compounds*

Two plutonium-containing solid solutions, $Er_{1.78}Pu_{0.22}Ti_2O_7$ and $SrPu_2Ti_4O_{12}$ were contacted at room temperature only with WIPP 'A' brine. The results from gross alpha counting and alpha pulse height analyses are given in Table 3. (The pulse height analysis of the leachates indicated that ^{241}Am was present as a trace impurity in $Er_{1.78}Pu_{0.22}Ti_2O_7$ and ^{241}Am and ^{239}Pu were trace impurities in $SrPu_2Ti_4O_{12}$.)

The amounts of plutonium leached by WIPP brine may be of the same order of magnitude as the amounts of cerium leached by the WIPP brine from both of the cerium-containing analog solid solutions, $Er_{1.78}Ce_{0.22}Ti_2O_7$ and $SrCe_2Ti_4O_{12}$, since the concentrations of cerium determined by ICP were below 10 ppm, the limit of detection.

4. Conclusions

The results of a scoping study performed to determine the relative stabilities of various candidate compounds potentially useful for immobilizing radioactive waste have been presented here. Although there are limitations and difficulties in using ICP to analyze such complex matrices as the leachants used in this work, preliminary leachability data have been gathered for several systems of cerium- and plutonium-containing titanate and zircono–titanate solid solutions.

$Ce_2Ti_2O_7$ and $Er_{1.78}Ce_{0.22}Ti_2O_7$ were both quite stable in the WIPP 'A' brine and the 0.1 M NaCl. Higher concentrations of erbium and cerium were leached from $Er_{1.78}Ce_{0.22}Ti_2O_7$ in the 0.1 M HCl solution than cerium from $Ce_2Ti_2O_7$, maybe an effect of crystal structure. Little difference is seen between $SrCe_2Ti_4O_{12}$ and $Sr_2Ce_2Ti_5O_{16}$ with regards to their stabilities in the different leachants. The concentrations of strontium leached by the WIPP brine are in the same order of magnitude as the amounts of strontium dissolved in cold and hot water from compounds such as $SrCO_3$ and $SrSO_4$. However, in 0.1 M NaCl the amounts of strontium leached were significantly higher.

It has been previously established that cerium appears to be an adequate surrogate for plutonium in the (III) oxidation state regarding titanate solid solution formation and thus solid solubility limits. The aqueous leachability studies obtained in this work indicate that Ce(III)- and Pu(III)-containing titanate compounds behave similarly when in contact with WIPP brine thus suggesting that Ce(III) is also an adequate surrogate for aqueous leachability tests.

Since the WIPP brine was the most realistic leachant used, conclusions regarding the potential usefulness of the solid solutions tested as host matrices should be drawn from the leaching data using the brine solution. Overall, all of the compounds and solid solutions fared well in WIPP brine with concentrations of cerium, as a surrogate for plutonium in some compounds, below the ICP detection limit (10 ppm). The concentrations of strontium were also quite low. The leachability tests on the plutonium-containing solid solutions showed concentrations of less than 1 ppm leached by the brine and were comparable to the concentrations found for cerium in the analogous solid solutions. In general, the results obtained in this study compare well with results of similar studies; e.g., Vance et al. [7] give 1.9×10^{-6} g/m^2/d for plutonium leached at 90°C from a titanate-based ceramic containing 10 wt% Pu. Conversion of ppm (Table 3) to g/m^2/d gives estimates of 1.8×10^{-6} for a similar plutonium-loading and about 3.3×10^{-6} for 50 wt% Pu at room temperature. These estimates were obtained assuming spherical particles of 44 μm diameter and a density of 7 g/cm^3 for $Er_{1.78}Pu_{0.22}Ti_2O_7$ and of 13 g/cm^3 for $SrPu_2Ti_4O_{12}$.

Finally, the leachability studies reported here suggest that the types of strontium-free titanates and the zircono–titanate studied might be useful as host matrices for nuclear waste immobilization.

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