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Leach resistance of murataite-based ceramics containing actinides

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Abstract

Leach resistance of murataite-based ceramics containing 10 wt.% of either UO_2 or ThO_2 was measured using an SPFT procedure, and leach rates of Pu and Am from murataite-based 10 wt.% $^{239}PuO_2$/0.1 wt.% $^{241}Am_2O_3$-bearing ceramic was studied by the MCC-1 method. The ceramics exhibited very low leachability of the actinide elements comparable to or lower than that from Synrocs and pyrochlore-based ceramics for excess weapons plutonium immobilization.

Keywords: Ceramics; Liquid–solid reactions; Corrosion

1. Introduction

Pyrochlore, murataite and related phases with fluorite-derived structure are considered as host phases for actinide (An) and rare earth elements (REE) [1]. Producing combined structures consisting of pyrochlore (two-fold fluorite unit cell) and murataite (three-fold) modules [2], we can adjust ceramic formulations for immobilization of An/REE-bearing waste with variable chemical composition. In our previous work [3] we have proposed a baseline composition (wt.%): 5 Al_2O_3, 10 CaO, 55 TiO_2, 10 MnO, 5 Fe_2O_3, 5 ZrO_2, and 10 (An,REE)O_2 or (An,REE)$_2O_3$ yielding >90% of the phases containing murataite modules in their structure. Preliminary studies have demonstrated high leach resistance of the murataite-based ceramics [3]. Zoned structure of the murataite grains with depletion of An and REEs in the rim protects the core with the highest An/REE content from leachate attack and reduces leach rates to levels that are lower than those for zirconolite and pyrochlore by 1–3 orders of magnitude. In this paper we present new data on leaching of ^{239}Pu and ^{241}Am from the murataite-based ceramic and preliminary results of an SPFT test for the Th- and U-bearing murataite-based ceramics with the above-mentioned formulation [4].

2. Experimental

Ceramic samples with a specified composition (wt.%): 5 Al_2O_3, 10 CaO, 55 TiO_2, 10 MnO, 5 Fe_2O_3, 5 ZrO_2, and 10 wt.% of either $^{239}PuO_2$, UO_2, or ThO_2 were prepared and characterized in details as described in Refs. [4,5]. ^{241}Am was present in the PuO_2 used for specimen preparation as an impurity in the amount of 0.1 wt.%. Leach resistance of the ceramics in deionized water at 90 °C was studied by MCC-1 [6] and single-pass-flow-through (SPFT) [7] tests.

The SPFT test was performed using an apparatus (Fig. 1) delivered by Pacific Northwest National Laboratory, USA, under a contract between US DOE and SIA Radon. The apparatus consisted of syringe pumps that transfer solution from input vessels to the reactors via Teflon tubing. Reactor vessels were 60–1000 mL capacity perfluoroalkoxy (PFA) Teflon jars (Savillex, Minnetonka, MN) that were housed in a constant-temperature oven. The temperature (90 °C) was measured with an accuracy of ±2 °C. Input leachant (deionized water, pH 6–6.5) contacted with powdered ceramics in the reactor without stirring. The effluent from the reactor was fed through Teflon tubes and collected continuously in polypropylene bottles (100 mL) placed outside the oven. Leachant flow rates were 1 and 3 mL/h for the U- and Th-bearing ceramics. The particle size of the U- and Th-bearing powdered ceramics was 87.5 and 112.5 μm, respectively. The measured density of both of the ceramics was 4.52 g/cm^3.

3. Results and discussion

Murataite ceramics doped with PuO_2, UO_2 or ThO_2 are composed of major murataite polytypes with five- (M5), eight- (M8), and three-fold (M3) fluorite unit cells as well as minor crichtonite and rutile [4,5]. Murataite polytypes are predominant hosts for actinides. Crichtonite contains only traces of actinide

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Table 1
Leach data for the Pu/Am bearing murataite ceramic (MCC-1 test in teflon container with deionized water at 90 °C)

Leach time (d)	Concentration in leachate (g/L)		Mass of the nuclide leached (g)		Leach rate g/(m^2 day)	
	Pu	Am	Pu	Am	Pu	Am
3	2.22×10^{-5}	3.39×10^{-8}	3.02×10^{-7}	4.62×10^{-10}	8.37×10^{-3}	5.48×10^{-3}
7	4.25×10^{-6}	3.23×10^{-8}	5.79×10^{-8}	4.41×10^{-10}	6.88×10^{-4}	5.23×10^{-3}
14	7.19×10^{-6}	3.12×10^{-8}	9.79×10^{-8}	4.26×10^{-10}	5.82×10^{-4}	2.39×10^{-3}
21	2.40×10^{-6}	$2{,}88 \times 10^{-8}$	3.27×10^{-8}	3.93×10^{-10}	1.30×10^{-4}	1.55×10^{-3}
28	4.73×10^{-7}	4.25×10^{-9}	6.44×10^{-9}	5.78×10^{-11}	1.91×10^{-5}	2.34×10^{-4}
35	6.51×10^{-7}	6.53×10^{-9}	8.87×10^{-9}	8.90×10^{-11}	2.11×10^{-5}	2.88×10^{-4}
42	6.05×10^{-7}	7.28×10^{-9}	8.24×10^{-9}	9.92×10^{-11}	1.63×10^{-5}	2.68×10^{-4}
49	7.76×10^{-7}	6.60×10^{-9}	1.06×10^{-8}	8.99×10^{-11}	1.79×10^{-5}	2.08×10^{-4}
56	4.99×10^{-7}	9.42×10^{-9}	6.80×10^{-9}	1.28×10^{-10}	1.01×10^{-5}	1.90×10^{-4}
63	6.64×10^{-7}	1.19×10^{-8}	9.04×10^{-9}	1.62×10^{-10}	1.19×10^{-5}	2.14×10^{-4}

elements (1–2 wt.%) thus we can assume that actinide elements are leached only from the murataite polytypes.

The major results of the MCC-1 test for the ^{239}Pu/^{241}Am-bearing murataite-based ceramic are given in Table 1. The leach rate of both Pu and Am reduced gradually with time and, after 63 days of leaching, achieved values of $\sim 1 \times 10^{-5}$ g m^{-2} d^{-1} and $\sim 2 \times 10^{-4}$ g m^{-2} d^{-1}, respectively. Am existing in a trivalent form is a more leachable element due to a higher electronegativity than Pu, which is tetravalent in this ceramic [8].

The main results of SPFT leach testing show that the ceramic specimens exhibit extremely low leachability of U and Th in deionized water at 90 °C. Average leach rates for these elements were found to be 2.40×10^{-5} and 1.14×10^{-7} g m^{-2} d^{-1}, respectively (Fig. 2).

The Pu leach rate (MCC-1 test at 90 °C in deionized water) from the murataite ceramic ($\sim 10^{-5}$ g m^{-2} d) was similar to that of Pu-bearing Synroc-C [9] and zirconolite-rich Synroc [10].

For the pyrochlore-based ceramics designed for excess weapons plutonium immobilization, the 7-day Pu leach rate ranged between 4×10^{-5} and $\sim 10^{-3}$ g m^{-2} d^{-1} (depending on type and amount of impurities) reducing to $\sim 1 \times 10^{-4}$ after 50–100 days and to $(0.8–3) \times 10^{-5}$ g m^{-2} d^{-1} after more than 300 days of leaching [11]. Thus, the Pu leach rate from the murataite-based ceramic under steady-state conditions was lower than that of the pyrochlore-based ceramics by about one order of magnitude. Higher leach rates during the initial period (3–7 days) of leaching are probably due to dissolution of the defect surface layer.

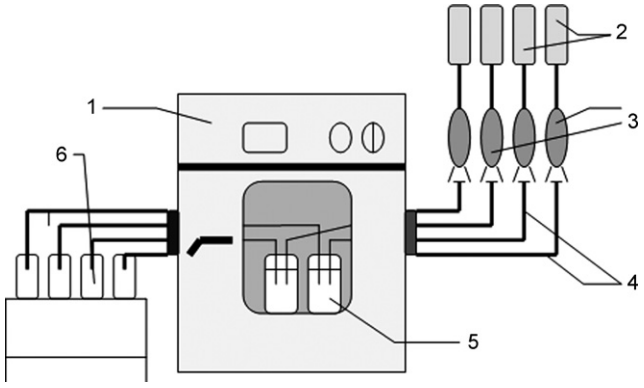

Fig. 1. Schematic representation of the SPFT apparatus used to test the corrosion durability of the murataite-based ceramics. 1, oven; 2, vessels for leaching solutions; 3, pumps; 4, solution feeding lines; 5, reactor vessels; 6, collection bottles.

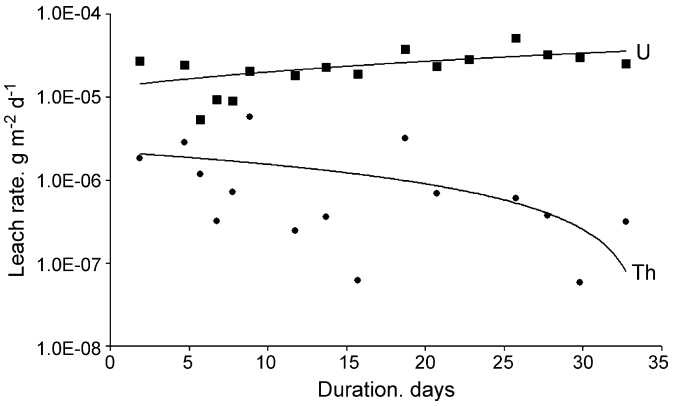

Fig. 2. Plots of $\log_{10}$(leach rate) [g m^{-2} d^{-1}] vs. test duration [d] for U- and Th-doped murataite-based ceramics at pH 7.

The Ti release rate measured by the SPFT test at 90 °C was found to be about 1×10^{-6} g/(m^2 d) at pH 7 and it increased to $\sim 2 \times 10^{-4}$ g m^{-2} d^{-1} at pH 2 [12]. U and Th leach rates measured in our tests were 2.40×10^{-5} and 1.14×10^{-7} g m^{-2} d^{-1}, respectively. Therefore, it can be expected that their release rates at pH 2 should be about $\sim 10^{-4}$–10^{-5} and $\sim 10^{-5}$–10^{-6} g m^{-2} d^{-1}, respectively. Steady-state U and Pu dissolution rates from the pyrochlore-based ceramics at 85 °C and pH 2 were found to be about $\sim 10^{-4}$ g m^{-2} d^{-1} [13]. Therefore, actinide release rates from the murataite-based ceramics are suggested to be lower than those from the pyrochlore-based ceramics by 1–2 orders of magnitude. Additional SPFT measurements of U and Th release from the murataite-based ceramics at pH 2 are in progress.

4. Conclusion

The murataite ceramics containing 10 wt.% of either UO_2 or ThO_2 exhibit extremely high leach resistance to water attack. Leach rates of Pu and Am in tests with a duration of leaching for 28 days and longer using the MCC-1 test are $(1–2) \times 10^{-5}$ and $(2–3) \times 10^{-4}$ g m^{-2} d^{-1}. Average leach rates in the SPFT test at 90 °C for these elements were found to be 2.40×10^{-5} and

1.14×10^{-7} g m^{-2} d^{-1}, respectively. These data are preliminary and need to be refined in a future study.

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