

DURABILITY OF ACTINIDE CERAMIC WASTE FORMS UNDER CONDITIONS OF GRANITOID ROCKS

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ABSTRACT

Three samples of ^{239}Pu - ^{241}Am -doped ceramics obtained from previous research were used for alteration experiments simulating corrosion of waste forms in ion-saturated solutions. These were ceramics based on: pyrochlore, $(\text{Ca,Hf,Pu,U,Gd})_2\text{Ti}_2\text{O}_7$, containing 10 wt.% Pu and 0.1 wt.% Am; zircon, $(\text{Zr,Pu})\text{SiO}_4$, containing 5-6 wt.% Pu and 0.05 wt.% Am; cubic zirconia, $(\text{Zr,Gd,Pu})\text{O}_2$, containing 10 wt.% Pu and 0.1 wt.% Am. All these samples were milled in an agate mortar to obtain powder with particle sizes less than 30 micron. Sample of granite taken from the depth 500-503 m was studied and then used for preparing ion-saturated water solutions. A rock sample was ground, washed and classified. A fraction with particle size 0.10-0.25 mm was selected for alteration experiments.

Powdered ceramic samples were separately placed into deionized water together with ground granite (approximately 1gram granite per 12-ml water) in special TeflonTM vessels and set at 90°C in the oven for 3 months. After alteration experiments, the ceramic powders were studied by precise XRD analysis. Aqueous solutions and granite grains were analyzed for Am and Pu contents. The results show that alteration did not cause significant phase transformation in all ceramic samples. For all altered samples, the Am contents in aqueous solutions after experiments were similar (approximately $n \times 10^2$ Bq/ml) as well as Am amounts absorbed on granite grains (approximately $n \times 10^5$ Bq/g). Results on Pu contents were varied: for the solutions – from 60 Bq/ml for pyrochlore ceramic to 2.1×10^3 Bq/ml for zircon ceramic; and for the absorption on granite – from 2.6×10^4 Bq/g for zirconia ceramic to $1.4\text{-}6.8 \times 10^5$ Bq/g for pyrochlore and zircon ceramics.

INTRODUCTION

At present, the Nizhnekanskiy granitoid massif in Krasnoyarsk Region, Russia, is under consideration as a prospective site for building the HLW underground repository in Russia (1). In order to develop technology of HLW underground disposal, it is important to evaluate chemical durability of different waste forms, in particular, actinide ceramics, under conditions of a real geological environment of selected site. Although different ceramic waste forms such as those based on: zircon (1-5,9); zirconia (6-9,11,12) and titanate pyrochlore (10) were developed and justified for actinide immobilization, there is still a lack of information concerning actinide release from their matrices in ion-saturated solutions occurred in granitoid massif. Main goal of this paper is to discuss first preliminary results of alteration experiments simulating actinide ceramic corrosion by underground water of granitoid rocks.

EXPERIMENTAL PROCEDURE

A sample of granite taken at Nizhnekanskiy massif from the depth 500-503 m was studied and then used for preparing ion-saturated water solutions. This granite is characterized of the following mineral composition (from XRD, in wt.%): quartz, SiO_2 – 35-40; feldspar, $(\text{K,Na})\text{AlSi}_3\text{O}_8$ – 45; plagioclase, $(\text{Ca,Na})\text{Al}_2\text{Si}_2\text{O}_8$ – 15-20; biotite, $\text{K}(\text{Mg,Fe})_3[\text{Si}_3\text{AlO}_{10}][\text{OH,F}]_2$ – 2; muscovite, $\text{KA}_2[\text{AlSi}_3\text{O}_{10}][\text{OH}]_2$ – 1-2; magnetite, Fe_3O_4 – 0.1-0.3. Bulk chemical analysis of this sample was as follows (in wt. %): SiO_2 – 76.9; Al_2O_3 – 12.9; K_2O – 5.5; Na_2O – 3.1; CaO – 0.6; Fe_2O_3 – 0.3; FeO – 0.3; MgO – 0.1. The rock

sample was ground, washed and classified. Obtained fraction with particle size 0.10-0.25 mm was selected for preparing ion-saturated solutions.

Three samples of Pu-Am-doped ceramics obtained from previous research (5,13) were used for alteration experiments. Principal features of these ceramics are summarized in Table I. All samples were milled in agate mortar to obtain powder with particle sizes less than 30 micron.

Table I. Main features of Pu-Am-doped ceramics used for alteration experiment.

Ceramic type and average EPMA data of main phase, wt.% element	Phase composition from XRD, wt. %	Approximate actinide content, wt.% element		Ceramic density, g/cm ³
		Pu	Am	
Zircon-based, (Zr,Pu)SiO₄ Zr – 46.5; Si – 14.1; Pu – 6.1	Zircon – 94-96; Zirconia (tetrag.) – 3-5; Zirconia (mon.) – 1-3	5-6	0.05	3.8
Zirconia-based, (Zr,Gd,Pu)O₂ Zr – 48.6; Gd – 20.9; Pu – 10.3	Cubic zirconia – 100	10	0.1	5.6
Pyrochlore-based, (Ca,Pu,Gd,Hf,U)₂Ti₂O₇ Ca – 8.2; Pu – 10.7; Gd – 7.4; Hf – 7.1; Ti – 19.0; U – 23.1	Pyrochlore – 90-95; Brannerite, (U,Pu)Ti₂O₆ – 1-3; Rutile, TiO₂ – 1-3	10	0.1	4.9

Powdered ceramic samples (in amount 200 mg each) were separately placed into deionized water together with ground granite (approximately 1gram granite per 12-ml water) in a sealed TeflonTM vessels (Fig.1) and set at 90°C in the oven for 3 months.

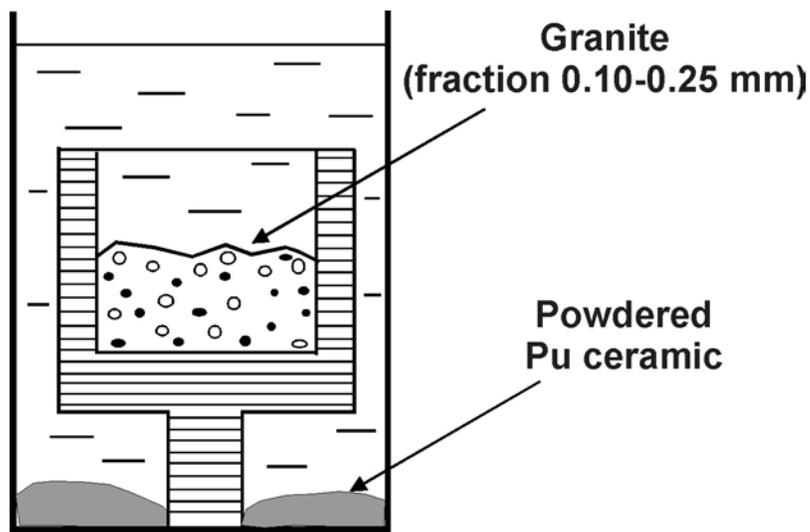


Fig. 1. Cross-section view of special TeflonTM vessel used for alteration experiment.

After the alteration experiment the aqueous solutions (carefully passed through a filter with pore size less than 1µm) and granite grains (washed several times in distilled water under strong shaking) were analyzed for Am and Pu contents. Initial and altered ceramic samples were studied in comparison by X-ray diffraction analysis (XRD) under the same conditions.

The XRD analyses were carried out under following conditions: CoK_α irradiation; current – 40 mA; tube voltage – 30 kV, scan speed 2°/min., step sampling – 0.01°. The XRD measurements were done using technique developed at the V.G. Khlopin Radium Institute [13]. In this method, the highly radioactive ceramic sample is placed into a regular XRD handler which is then hermetically covered by a thin (50-100 µm) Be-window. This minimizes any contamination of the X-ray spectrometer during analysis.

For leaching experiment, a single ceramic pellet of known surface area was placed on the thin Pt-support at the bottom of TeflonTM test vessel with deionized water and then set at 90°C in an oven for 28 days. The ratio of surface area to water volume was maintained at 1:10. The measurement of the Pu content in the leaching solution, and one measurement of material absorbed on the walls of test vessels were carried out after 28 days. Normalized Pu mass loss (NL) was calculated as follows: $NL = A \times W_0 \times (A_0)^{-1} \times S^{-1}$, where *A* – total activity of Pu or Am in the water solution and one absorbed on the walls of test vessels after leaching, Bq; *A*₀ – the initial activity of Pu or Am in the specimen, Bq; *W*₀ – the initial mass of the specimen, gram; *S* – specimen surface area without correction on ceramic porosity, m².

RESULTS AND DISCUSSION

Results of MCC-1 leach tests done at 90°C in deionized water (Table II) demonstrate that in general, a ceramic based on zirconia is characterized with the lowest Pu mass loss, but the highest Am mass loss. The opposite tendency, the highest Pu and lowest Am mass losses, was observed for pyrochlore-based ceramic.

Table II. Normalized actinide mass loss (in g/m²) from ceramic matrices after MCC-1 leach test done in deionized water at 90°C for 28 days. Correction on ceramic porosity was not estimated.

Actinide-doped ceramics	Normalized mass loss, g/m ²	
	Pu	Am
Zircon-based	0.008	0.18
Zirconia-based	0.001	0.33
Pyrochlore-based	0.009	0.04

After alteration experiments no significant changes of phase composition of all ceramic samples were identified by XRD method.

It is interesting to note that the Am contents (Table III) in solutions for all altered samples were similar (approximately $n \times 10^2$ Bq/ml) as well as Am amounts absorbed on granite grains (approximately $n \times 10^5$ Bq/g). Plutonium contents in solutions and Pu amounts absorbed on granite grains after alteration experiments varied significantly for different types of ceramic (Table III). However, the interpretation of these observations is unclear because Pu occurs in aqueous solution mainly in colloid forms.

Table III. Contents of Pu and Am in solutions (including colloid forms) and those absorbed on granite grains after alteration experiment at 90°C for 3 months.

Actinide-doped ceramics	Radionuclide content			
	In solution (Bq/ml)		Absorbed on granite grains (Bq/g)	
	Pu	Am	Pu	Am
Zircon-based	2.1E+3	4.2E+2	6.8E+5	1.3E+5
Zirconia-based	3.2E+2	1.3E+2	2.6E+4	5.9E+5
Pyrochlore-based	6.0E+1	1.3E+2	1.4E+5	3.4E+5

CONCLUSION

1. Actinide-doped crystalline ceramics based on zircon, $(Zr,Pu)SiO_4$, gadolinia-stabilized cubic zirconia, $(Zr,Gd,Pu)O_2$, and titanate pyrochlore, $(Ca,Pu,Gd,Hf,U)_2Ti_2O_7$, demonstrated high physico-chemical resistance to alteration by ion-saturated solutions simulating underground water in granitoid massif. After alteration experiments at 90°C for 3 months no significant changes of ceramic phase compositions were identified by XRD method.
2. Although, ceramics based on zircon, zirconia and pyrochlore are characterized with different Am mass loss from their matrices in deionized water, they are similar for Am release in ion-saturated solutions (approximately $n \times 10^2$ Bq/ml) and the amount of Am absorbed on granite grains (approximately $n \times 10^5$ Bq/g) after alteration experiments.

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