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THE IMPACT OF BRANNERITE ON THE RELEASE OF PLUTONIUM AND GADOLINIUM DURING THE CORROSION OF ZIRCONOLITE-RICH TITANATE CERAMICS

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ABSTRACT

Titanate ceramics have been selected as the preferred waste form for the immobilization of excess plutonium. Corrosion tests are underway to try to understand the long-term behavior of this material. In this paper, results from PCT-B static dissolution tests are used to provide an explanation of the observed corrosion behavior of a zirconolite-based ceramic. Two important observations are made. First, Ca is released at a constant rate [7×10^{-5} g/(m^2 day)] in PCT-B tests for up to two years. Second, the release rates for Pu and Gd increase with time (up to two years) in PCT-B tests. The first observation suggests that the ceramics continue to corrode at a low rate for at least two years in PCT-B tests. The second observation suggests that the release rates of Pu and Gd are controlled by some process or processes that do not affect the release rate of other elements. Evidence indicates that this is due to the preferential dissolution of brannerite from the ceramic.

I. INTRODUCTION

The U. S. Department of Energy (DOE) has selected a hybrid approach for the disposal of up to 50 metric tons of surplus plutonium [1]. Approximately 17 metric tons will be immobilized in a titanate ceramic; the balance of the plutonium will be fabricated into a mixed oxide fuel. A pyrochlore-based titanate ceramic has been selected as the preferred waste form for immobilization [2,3]. Final disposition of the immobilized plutonium is slated for the proposed federal repository. The current baseline ceramic contains several phases, including pyrochlore [$(Ca,Gd,Pu)(Hf,Pu,U,Gd)\,Ti_2O_7$] and the related phase zirconolite, Hf-bearing rutile [$(Ti,Zr)O_2$], brannerite [$(Pu,Gd)Ti_2O_6$], and PuO_2. A backscatter SEM image of the baseline pyrochlore-based ceramic is shown in Figure 1.

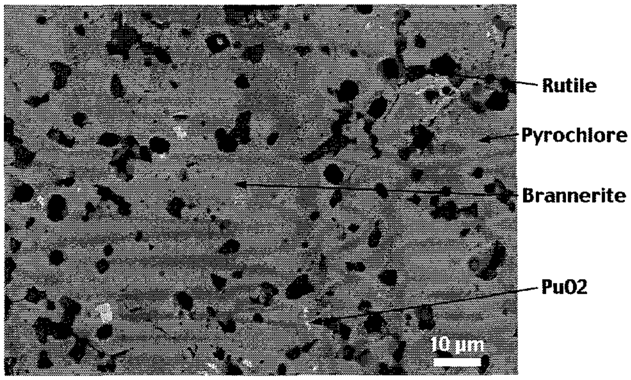

Figure 1. Scanning electron backscatter image of an unreacted baseline pyrochlore-based ceramic at a magnification of 1000X.

Corrosion tests are being conducted to describe the long-term corrosion behavior of titanate ceramics and to gain acceptance for its disposal in a federal repository. One such test that was started several years ago is a product consistency test (PCT, protocol B) with a

zirconolite-based ceramic. A backscatter SEM image of this ceramic is shown in Figure 2. Although this ceramic is composed mainly of zirconolite and the current baseline is composed primarily of pyrochlore, we expect that the tests described here will provide insight into the long-term corrosion behavior of the pyrochlore-based formulations. Reasons for this include (1) zirconolite and pyrochlore are chemically and structurally similar, and (2) their short-term corrosion behavior is similar [4]. Long-term tests have now been initiated with the pyrochlore ceramic.

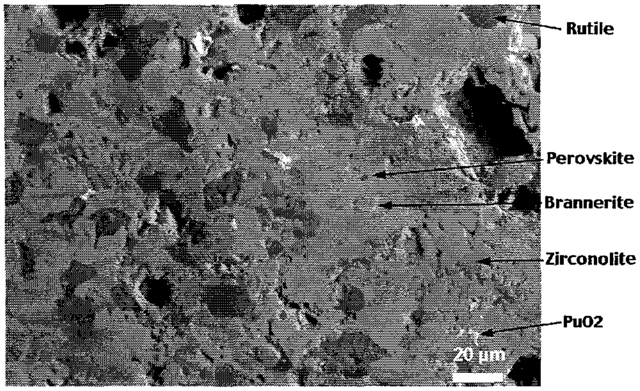

Figure 2. Scanning electron backscatter image of an unreacted zirconolite-based ceramic at a magnification of 500X.

Previous corrosion studies with this zirconolite-rich ceramic, based on MCC-1 test data, have shown an initial rapid release of cations followed by a much slower release [5]. The NL(Ca) data show rapid corrosion in the first three days and slower corrosion after that. Similar changes were observed in the release rates of other elements found in this ceramic [5], and similar behavior has been observed with SYNROC ceramics [6]. Possible explanations for this behavior are discussed in more detail by Bakel et al. [7], and include solution saturation, formation of a protective layer, corrosion of small-grained material on the surface of the ceramic, or the corrosion of more soluble material from grain boundaries. Of these, selective dissolution from grain boundaries appears to be most likely [7]. In this paper, we show that the presence of brannerite in this ceramic impacts the long-term release of Pu and Gd. Earlier, we attributed differences in the short-term uranium release in pyrochlore-rich ceramics to the presence or absence of brannerite [8,9].

II. EXPERIMENTAL

The zirconolite-rich ceramic was fabricated at Lawrence Livermore National Laboratory. The precursor material was ground, dried, pulverized, and calcined in air at 600°C for 1 hour. The calcined material was then broken up and mixed with PuO_2. The resulting powder was cold pressed and sintered at 1325°C for about 4 hours. The bulk density of this material after sintering is 5.4 g/cm^3. Further details of the fabrication method are described by Buck et al. [10].

The bulk composition of the zirconolite-based ceramic is reported in Table 1. The phase composition of the ceramic is 60-70 vol.% zirconolite, about 30% rutile, less than 5% perovskite and brannerite, and less than 1% PuO_2. For comparison, the composition of the pyrochlore-based baseline ceramic is included in Table 1.

Table 1. Oxide weight percents for the two ceramics described in this study.

Element	Zirconolite ceramic[1,2]	Pyrochlore Ceramic[3]
Al_2O_3	8.0	
CaO	7.3	12.7
Cr_2O_3	0.37	
Fe_2O_3	0.27	
NiO	0.10	
ZnO	0.26	
CuO	0.21	
Ga_2O_3	0.32	
BaO	3.6	
CeO_2	0.31	
Gd_2O_3	9.5	7.7
TiO_2	37	34.8
ZrO_2	16	
HfO_2	0.35	10.3
UO_2	0	23.0
PuO_2	14	11.5
Total	97.59	100.0

[1] The ceramic was dissolved at 150°C in mineral acids, and the resulting solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

[2] The composition of this ceramic contains a series of impurities that are expected with the various Pu feed streams. These components not included in this version of the pyrochlore ceramic.

[3] As-batched ceramic composition.

The product consistency tests (PCT-B) were conducted according to ASTM procedure C-1285-94 [11]. The purpose of these tests is to evaluate the corrosion behavior of materials in concentrated solutions. These tests were conducted for two years. Initially, a number of tests were started and then periodically during the test period of two years, a sample was terminated. Solutions were analyzed by ICP-MS; solids were collected and examined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

For the PCT-B tests, the ceramic was crushed and sieved to isolate the -100+200 mesh fraction. The powder was ultrasonically cleaned in deionized water and ethanol. The crushed ceramic was sealed in a 22 mL stainless steel vessel with enough water to yield an surface area to volume ratio of approximately 10,000 m^{-1}. Upon the completion of a test, the leachate was removed and analyzed for pH and for cations with ICP-MS. The test vessel was then filled with 1% HNO_3, and placed in a 90°C oven for at least 8 hours to remove material fixed to the vessel wall. This "acid strip" solution was also analyzed with ICP-MS. The normalized mass loss [NL(i)] values presented here represent the amount of the ceramic dissolved based on the amount of an element in the leachate and the acid strip solutions. Experimental blanks were conducted, and background concentrations were subtracted from concentrations measured from leachates.

III. RESULTS AND DISCUSSION

Figure 3 shows the NL(Ca) as a function of test duration for a series of PCT-B tests with the zirconolite-rich ceramic. The NL(Ca) increases linearly with time at a rate corresponding to about 7×10^{-5} g/(m^2 day); the R value for this linear fit is 0.997. The bounding rate estimated using Bourcier's pH and temperature-dependence model [12] at 90°C and pH of 8 is about 1×10^{-4} g/(m^2 day).

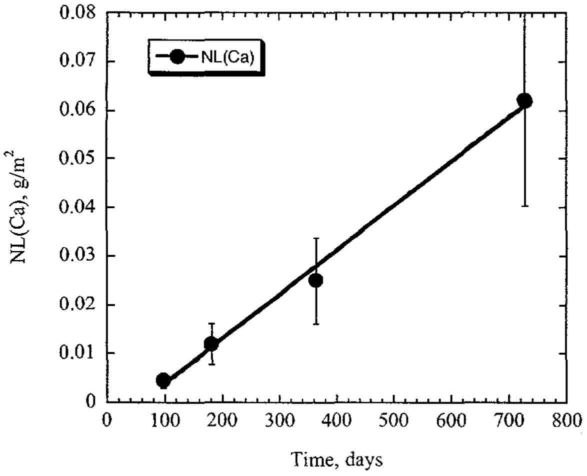

Figure 3. Normalized mass loss, based on Ca release for the zirconolite-rich ceramic in PCT-B tests. The error bars represent 35% relative uncertainty.

The similarity of the corrosion rates measured in our PCT-B tests and Bourcier's single-pass flow-through (SPFT) tests [12] suggests with those measured from corrosion mechanisms are the same for these two tests. On the other hand, the corrosion rates have been shown to decrease with time during SPFT tests [12]. This decrease has been taken as evidence of a transport-controlled rate-limiting process in SPFT tests. In contrast, the constant rate observed in long-term PCT-B tests indicates that the release of Ca is not rate limiting.

These Ca release data indicate that the corrosion of the ceramic continues unchanged in these tests for up to two years, suggesting that no protective layer formed on the phase(s) controlling the release of Ca during these tests. Also, the solutions do not approach a limit due to saturation with a calcium-bearing phase.

In contrast to the release of Ca (Figure 3), NL(Pu) and NL(Gd) do not increase linearly with time in the PCT-B tests (Figure 4). Instead, the release rates increase with time. The data in Table 2 show that the release rates of Pu and Gd are highest in the longest-term tests. At the same time, the release rates of Ca are similar in all three intervals (Table 2). These results show that the release behaviors of Gd and Pu differ from the release behavior of Ca, and that the process or processes affecting the release of Gd and Pu are not the same as those that affect the release of Ca. This is not unexpected because the ceramic contains several phases that may have different corrosion behaviors.

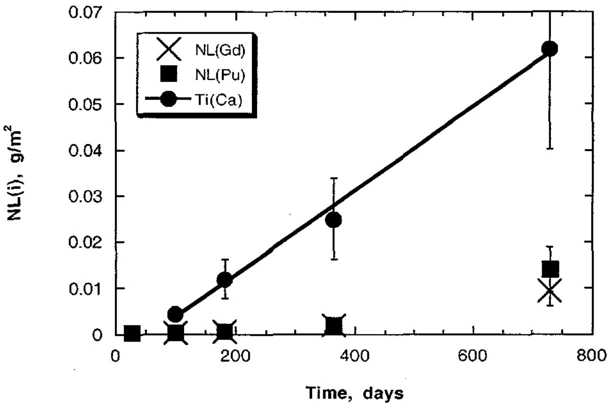

Figure 4. Normalized mass loss values based on Gd, Pu, and Ca from PCT-B tests. The error bars represent 35% relative uncertainty.

Table 2. Interval release rates for Ca, Pu, and Gd for PCT-B tests with the zirconolite-rich ceramic. Units of g/(m^2 day).

	98-182 days	182-364 days	364-428 days
NR(Ca)	7×10^{-5}	9×10^{-5}	6×10^{-5}
NR(Pu)	7×10^{-6}	1×10^{-5}	7×10^{-5}
NR(Gd)	3×10^{-6}	8×10^{-6}	2×10^{-5}

The solids from the two-year PCT-B test were examined with SEM. Examination of the starting material showed that brannerite surrounds the PuO_2 (Figure 5 and 6). This morphology is typical of these titanate ceramics [13]. Based upon standardless energy dispersive spectrometry (EDS) analysis, the brannerite contains about 60% plutonium oxide, 10% gadolinium oxide, with the balance being titanium oxide. (Note that this early formulation does not contain uranium.)

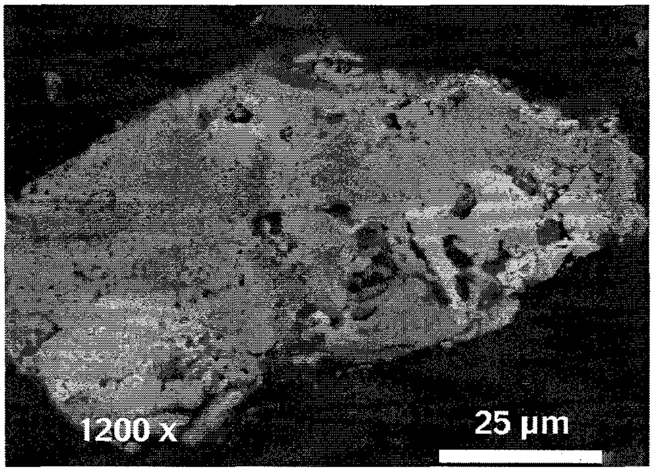

Figure 5. Scanning electron backscatter image of an unreacted PCT grain showing the phase brannerite surrounding PuO_2. The porosity of the ceramic can also bee seen in this image.

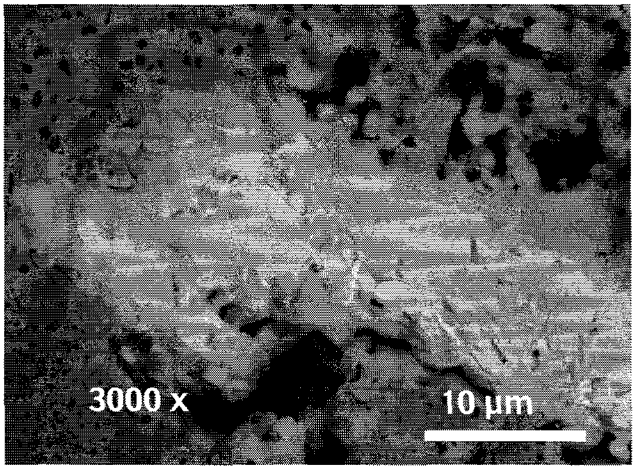

Figure 6. Higher magnification SEM image of an unreacted PCT grain showing the phase brannerite surrounding PuO_2. This image is representative of the brannerite and PuO_2 phases in this sample.

Examination with SEM of a PCT particle that had been reacted for 2 years under PCT-B conditions showed that the brannerite is absent or reduced (Figures 7 and 8). Voids are now present in the reacted sample where the brannerite would occur in unreacted samples. The apparent corrosion of brannerite would release Pu, Gd, and Ti to solution. Samples of reacted solids have been prepared and are currently being examined with TEM.

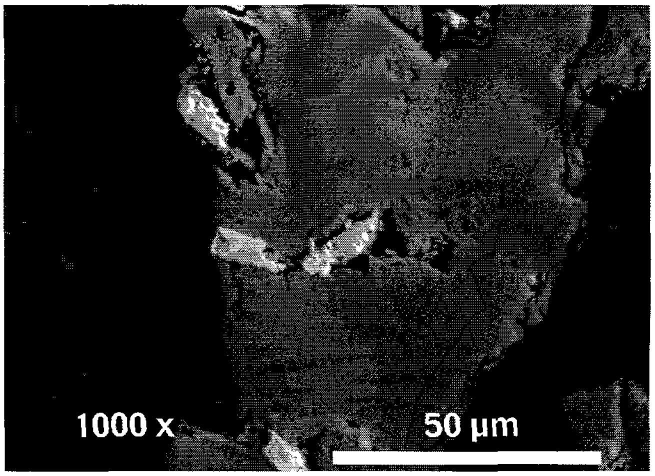

Figure 8. Scanning electron backscatter image following two years of corrosion under PCT-B conditions, showing voids surrounding the PuO_2 where the brannerite was expected.

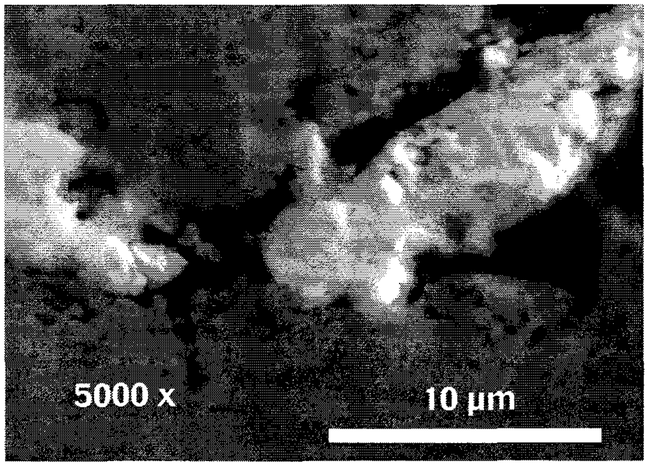

Figure 8. Scanning electron backscatter image following two years of corrosion under PCT-B conditions, showing voids surrounding the PuO_2 where the brannerite was expected. This image is representative of the PuO_2 phase in this sample.

These data corroborates data collected in MCC-1 and SPFT tests showing that brannerite is less durable than either zirconolite or pyrochlore. In MCC-1 tests reported by Bakel et al. [8,9], they observed an increase in the uranium release rates in brannerite-rich ceramics relative to brannerite-poor ceramics. Bourcier reported that singlephase brannerite also appears to be significantly less durable than either zirconolite or pyrochlore [12]. This observation was based upon 70°C SPFT data collected by Australian Nuclear Science and Technology Organisation (ANSTO). In these tests, the normalized release rate for uranium from brannerite was about 100 times greater over the pH range of 5 to 10.

The preferential dissolution of brannerite would lead to increasing surface area of exposed brannerite as a function of time, until this phase is exhausted. This process explains the increasing release rate of Pu and Gd observed in PCT-B tests. Alternative explanations such as incorporation of Pu and Gd into colloids are being investigated.

IV. CONCLUSIONS

The observations made in this study lead to several important observations regarding the corrosion of titanate ceramics. First, the release of Ca in these tests continues at a constant rate for up to two years. The measured Ca release is consistent with corrosion rates previously measured in SPFT tests. The corrosion rates for these ceramics are also very low, with rates typically several orders of magnitude below those of many high-level waste glasses [14].

Second, the release rates of Pu and Gd (but not Ca) increase with time in long-term PCT-B tests. We believe that this increase is due to preferential release of Gd and Pu from brannerite. Data from other researchers have shown that brannerite is significantly less durable than either zirconolite or pyrochlore.

The results from PCT-B tests of the zirconolite-rich ceramic are valuable for describing its long-term behavior. In particular, the results shown here provide important feedback for waste-form development activities and for potential criticality issues. Although significant quantities of plutonium are present in the brannerite, so is Gd and both are released together as the brannerite corrodes.

ACKNOWLEDGMENTS

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