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## The Long-Term Corrosion Behavior of Titanate Ceramics for Pu Disposition: Rate-Controlling Processes

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### ABSTRACT

The corrosion behavior of a titanate ceramic was investigated with the aim of describing the rate-controlling process or processes. These titanate ceramics are similar to SYNROC and are proposed as immobilization materials for surplus Pu. The corrosion behavior was described with results from MCC-1 and PCT-B static dissolution tests. Three important observations were made: a) Ca is released at a constant rate [ $6 \times 10^{-5}$  g/(m<sup>2</sup> day)] in PCT-B tests for up to two years, b) all of the test leachates are oversaturated with respect to rutile and anatase, and c) 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 2 years in PCT-B tests. The second observation shows that the rate of the corrosion reaction is not affected by the concentration of Ti in solution, suggesting that the approach to saturation with respect to either rutile or anatase is not a rate-limiting process. The third observation shows that the rate of Pu and Gd release increases with time in these tests. While this observation cannot be fully explained at this point, two possible explanations, alteration phase formation and grain boundary corrosion, are forwarded.

### INTRODUCTION

The dismantlement of nuclear weapons and the cleanup of weapons production sites have generated large quantities of surplus weapons-grade Pu, contaminated Pu stock, and Pu scrap existing in the United States [MYERS-1998]. Two options for the disposition of surplus Pu are currently being considered by the U.S. Department of Energy: incorporation into mixed oxide fuel and immobilization in a titanate ceramic. The ceramic described and tested in this study represents a zirconolite-rich formulation that is compositionally similar to the current pyrochlore-rich material. The goals of this study are to describe the long-term corrosion of titanate ceramic materials and to evaluate several possible rate-controlling steps for the corrosion of these titanate ceramics.

### TEST METHODS

Tests in this study were conducted according to the standard MCC-1 [ASTM-1992] and PCT-B [ASTM-1994] procedures. For the MCC-1 tests, the ceramic samples were prepared as wafers (about 10 mm in diameter and 1 mm in thickness) and the surfaces were ground to a 240-grit finish. All samples were ultrasonically cleaned in deionized water (DIW) and ethanol. Tests were conducted by sealing one ceramic wafer in a stainless steel (Type 304L) 22 ml vessel with about 18 ml of DIW, leading to a ratio of the geometric surface area to leachant volume (S/V) of about 10 m<sup>-1</sup>. For the PCT-B tests, the ceramic was crushed and sieved (-100+200 mesh). The powder was ultrasonically cleaned in DIW and ethanol. The crushed ceramic was sealed in a 22 ml stainless steel vessel with enough water to yield an S/V of about 10,000 m<sup>-1</sup>.

Upon the completion of a test, the leachate was removed and analyzed for pH and cations with inductively coupled plasma-mass spectrometry (ICP-MS). The test vessel was then filled with 5% HNO<sub>3</sub>, and placed in a 90°C oven for at least 8 hours to remove any 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 test results.

### TEST MATERIALS

The zirconolite-rich ceramic studied here is a formulation that was proposed several years ago at the beginning of the testing program. Long-term tests were initiated with this material. Newer formulations are dominated by pyrochlore. Since zirconolite and pyrochlore are similar, we expect the long-term corrosion behavior of the newer formulation to be similar to that of the zirconolite-rich ceramic. The chemical composition of the ceramic was determined by dissolving it at 150°C in mineral acids, and analyzing the resulting solution with ICP-MS. The composition of the ceramic was measured to be: 8.0

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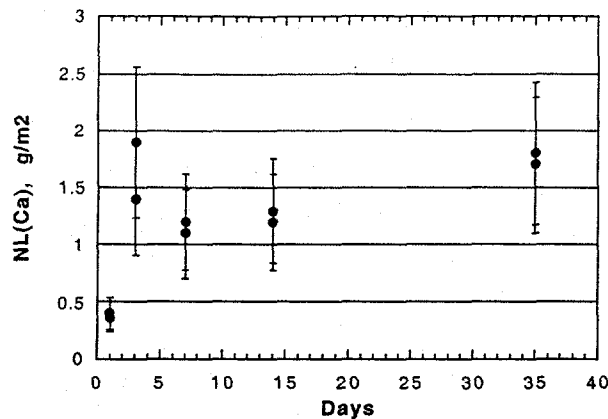


Figure 1. Normalized mass loss, based on Ca release for the zirconolite-rich ceramic in MCC-1 tests. The error bars represent 35% relative uncertainty.

mass %  $\text{Al}_2\text{O}_3$ , 7.3%  $\text{CaO}$ , 0.37%  $\text{Cr}_2\text{O}_3$ , 0.27%  $\text{Fe}_2\text{O}_3$ , 0.10%  $\text{NiO}$ , 0.26%  $\text{ZnO}$ , 0.21%  $\text{CuO}$ , 0.32%  $\text{Ga}_2\text{O}_3$ , 3.6%  $\text{BaO}$ , 0.31%  $\text{CeO}_2$ , 9.5%  $\text{Gd}_2\text{O}_3$ , 37%  $\text{TiO}_2$ , 16%  $\text{ZrO}_2$ , 0.35%  $\text{HfO}_2$ , and 14%  $\text{PuO}_2$ . The phase composition of the ceramic is 60-70 vol % zirconolite, about 30% rutile, less than 5% perovskite and brannerite, and less than 1%  $\text{PuO}_2$ .

## RESULTS AND DISCUSSION

Previous extended MCC-1 studies on the corrosion of titanate ceramics have shown an initial rapid release of material, followed by a much slower release [BAKEL-1999]. The NL(Ca) data shown in Figure 1 illustrate this initial rapid corrosion in the first three days. Further, the rate of Ca release decreases after 3 days. Similar changes have been shown in the release rates of other elements found in this ceramic [BAKEL-1999].

One explanation for the decrease in the corrosion rate over time is that the leachate solutions approach saturation. As the solutions approach saturation with respect to some solid phase, we expect the release of certain elements and, possibly, the overall corrosion rate to decrease. Potential saturation solid phases include  $\text{TiO}_2$  and  $\text{ZrO}_2$ . In addition, the rapid corrosion of fine-grained material, particularly soluble phases or materials on grain boundaries, could account for the observed decrease in corrosion rate.

Similar changes in the corrosion rates of titanate ceramics during long-term replacement tests have been attributed to the formation of a protective  $\text{TiO}_2$ -rich alteration layer [RINGWOOD-1981]. While continuous  $\text{TiO}_2$  layers have been observed on corroded Ti metal surfaces [FONTANA-1986], no direct observations of such a layer on titanate ceramics have been reported. Titanium-rich alteration phases have been found on several corroded titanate ceramics [BUCK-1997, SMITH-1997]. In each of these cases, however, the alteration phases were not continuous and, therefore, could not have been protective. The results of various tests are discussed below, and are interpreted in terms of rate-controlling processes.

### Ca Release

Figure 2 shows the amounts of Ca released, as a function of test duration, for a series of PCT-B tests with the zirconolite-rich ceramic. The release of Ca in these PCT-B tests increases linearly with time at a rate corresponding to about  $7 \times 10^{-5} \text{ g}/(\text{m}^2 \text{ day})$ ; the R value for this linear fit is 0.997. The rate estimated using Bourcier's pH and temperature dependence model [BOURCIER-1999] at  $90^\circ\text{C}$  and pH of 8 is about  $1 \times 10^{-4} \text{ g}/(\text{m}^2 \text{ day})$ .

These Ca release data indicate that the corrosion of the ceramic continues in these tests for up to two years. The constant rate also suggests that no protective layer formed during these tests, and that the solutions were not approaching any limiting saturation condition. In addition, the constant rate up to 728 days is inconsistent with the idea of a transport-controlled rate-limiting process.

The similarity of the corrosion rates measured in our PCT-B tests and the single pass flow through (SPFT) tests suggests that the corrosion mechanisms is the same during these two tests. On the other hand, the corrosion rates have been shown to decrease with time during SPFT tests [BOURCIER-1999]. This decrease has been taken as evidence of a transport-controlled rate-limiting process in SPFT tests. In contrast, the data from PCT-B tests indicate that transport is rate-limiting in the corrosion of this ceramic.

### Ti Release

Figure 3 shows the concentrations of Ti in the leachate solutions at 90°C as a function of pH. The solubility of rutile at 100°C [KNAUSS-1999] and our analytical detection limit are also shown. Knauss et al. [1999] showed that temperature has little effect on the solubility of rutile under these conditions. The solubility of anatase (the low temperature polymorph of  $\text{TiO}_2$ ) is about an order of magnitude lower than that of rutile, about 1 ppb [ROBIE-1979, LENCKA-1993]. Most of the leachate solutions appear to be oversaturated with respect to anatase as well.

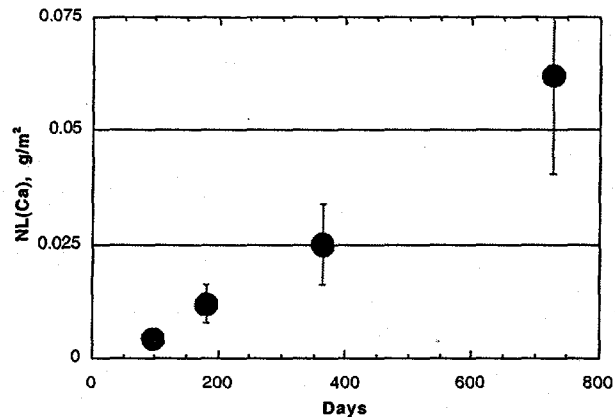


Figure 2. Normalized mass loss, based on Ca release for the zirconolite-rich ceramic in PCT-B tests. The error bars represent 35% relative uncertainty.

Based on the data shown in Figure 3, all of the leachate solutions are oversaturated with respect to rutile and anatase and, therefore, are not in equilibrium with these phases. Further, the data suggest that, on this time scale, the precipitation of  $\text{TiO}_2$  is slow relative to the corrosion. Therefore, the approach to the  $\text{TiO}_2$  solubility limit does not appear to be the rate-controlling process for the corrosion of these ceramics.

### Gd and Pu Release

In contrast to the release of Ca (Figure 2) in PCT-B tests, the releases of Pu and Gd do not increase linearly with time (Figure 4). The release rates of Gd and Pu are significantly higher in the interval between 364 and 728 days [ $2 \times 10^{-5}$  and  $7 \times 10^{-5}$  g/(m<sup>2</sup> day), respectively] than in the intervals between 182 and 364 days [ $8 \times 10^{-6}$  and  $1 \times 10^{-5}$  g/(m<sup>2</sup> day), respectively], or between 98 and 182 days [ $3 \times 10^{-6}$  and  $7 \times 10^{-6}$  g/(m<sup>2</sup> day), respectively]. At the same time, the release rates of Ca are about the same for each interval,  $7 \times 10^{-5}$  g/(m<sup>2</sup> day) between 98 and 182 days,  $9 \times 10^{-5}$  g/(m<sup>2</sup> day) between 182 and 364 days, and  $6 \times 10^{-5}$  g/(m<sup>2</sup> day) between 364 and 728 days. These results show that the release behaviors of Gd and Pu differ from the release behavior of Ca, and that some process or processes affect the release of Gd and Pu that do not affect the release of Ca.

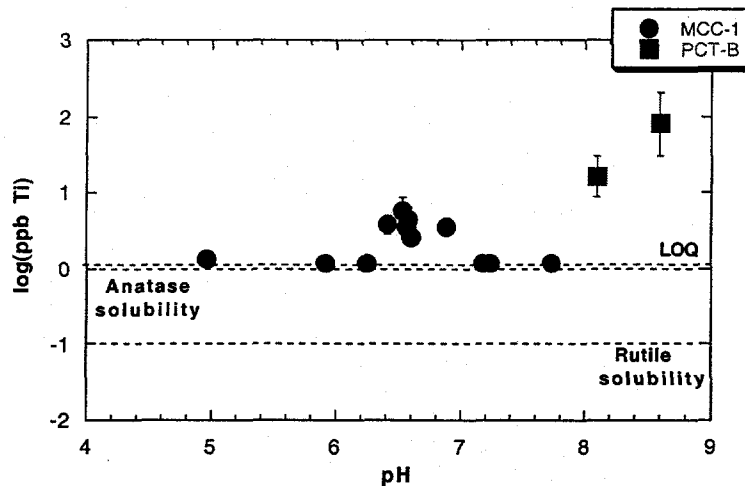


Figure 3. Measured Ti concentrations from MCC-1 test solutions as a function of pH. The error bars represent 22% analytical uncertainty. The limit of quantitation (LOQ) is also shown. The rutile solubility shown was determined at 100°C by Knauss et al. [1999].

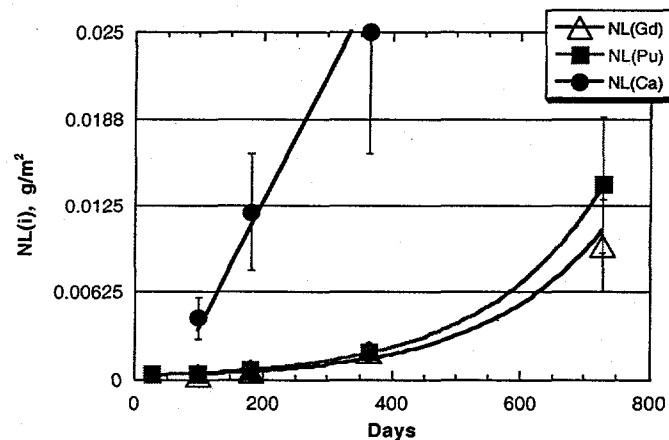


Figure 4. Values of NL(Ca), NL(Gd) and NL(Pu) for the zirconolite-rich ceramic in PCT-B tests as a function of time. The error bars represent 35% uncertainty.

We propose two possible mechanisms that could lead to increasing release rates with time. First, the formation of alteration phases has been shown to accelerate the corrosion rate of borosilicate glasses [BAKEL-1995]. Precipitation of alteration phases presumably alters the leachate chemistry, leading to an increase in the corrosion rate. Previous studies of corroded titanate ceramics have shown only small amounts of alteration products on the corroded ceramic surface [BUCK-1997]. We do not expect that their precipitation would affect the corrosion of the ceramic as observed. In the case of borosilicate glasses, the precipitation of alteration phases leads to an increase in the release rate of all elements. We have already shown that the release rate of Ca remains constant in these tests throughout the two-year test period.

Second, if the surface area of the reacting ceramic increases throughout the course of the reaction (for example, by grain boundary corrosion), then the release rate would increase. An increase of at least 100-fold would be needed to explain the change in release rate of Pu/Gd between 98 and 728 days. Such

an increase appears reasonable if corrosion occurs at grain boundaries, which could significantly increase the reactive surface area.

The increase in the release rates of Pu and Gd observed in these tests is an interesting result. However, since these observations are based on a single set of tests, all conclusions regarding the corrosion behavior of Pu and Gd must be considered tentative. Similar long-term tests are underway with pyrochlore-rich ceramics. In addition, higher temperature PCT-B tests are planned. We expect that increasing the temperature will serve to accelerate the corrosion.

## SUMMARY

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 is constant for up to two years. The measured Ca release is consistent with rates previously measured in SPFT tests. Second, all of the test leachates appear to be oversaturated with respect to  $TiO_2$ . This suggests that the corrosion of this ceramic is not controlled by the Ti concentrations of the leachates. Third, the release rates of Pu and Gd increase with time in long-term PCT-B tests. Two processes that could lead to the observed increases, formation of alteration phase and grain boundary corrosion, are discussed.

Due to the complexity of the ceramic and the observed incongruent dissolution, it may be difficult to derive a simple equation to describe the dissolution of this ceramic. We believe that the results from PCT-B tests are valuable in describing the long-term behavior of this ceramic. It is interesting to note that our results are not in all cases predicted by the current model of titanate ceramic corrosion.

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