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A. J. Bakel, E. C. Buck, S. F. Wolf, B. Ebbinghaus,* J. K. Bates
and D. B. Chamberlain

ARGONNE NATIONAL LABORATORY
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439-4837

*LAWRENCE LIVERMORE NATIONAL LABORATORY
P. O. Box 808
Livermore, CA 94550

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A. J. Bakel, E. C. Buck, S. F. Wolf, B. B. Ebbinghaus,* D. B. Chamberlain, and J. K. Bates
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
*Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, CA 94550

ABSTRACT

As part of a large Pu disposition program, a zirconolite-rich titanate ceramic is being developed at Lawrence Livermore National Laboratory (LLNL) as a possible immobilization material. This same material is being tested at Argonne National Laboratory (ANL). The goal of this study is to describe the corrosion behavior of this ceramic, particularly the release of Pu and Gd, using results from several static corrosion tests (MCC-1, PCT-A, and PCT-B). The release of relatively large amounts of Al, Ba, and Ca in short-term tests (3 day MCC-1 and 7 day PCT-A) indicates that these elements are released from grain boundaries or from highly soluble phases. Results from long-term (28, 98, and 182 day) PCT-B show that the releases of Al, Ba, and Ca decrease with time, the releases of U and Zr increase with time, and that the releases of Cs, Gd, Mo, and Pu remain fairly constant. Formation of alteration phases may lead to the decrease of Ba and Ca in leachate solutions. Due to the heterogeneous nature of the material, the formation of alteration phases, and the inherently low solubility of several elements, no element(s) could be recommended as good markers for the overall corrosion of this ceramic. Our data show that, due to the complex nature of this material, the release of each element should be considered separately.

INTRODUCTION

Due to the ratification of several nuclear nonproliferation treaties, large quantities of weapons-grade Pu, contaminated Pu stock, and Pu scrap existing in the United States have been declared surplus and suitable for disposition. Several options are currently being considered by the US Department of Energy, Office of Materials Disposition, including immobilization. This option involves incorporating Pu into a glass or ceramic material [1]. As part of this effort, titanate-based ceramics are being developed at LLNL as materials for immobilizing Pu.

Studies of the corrosion of titanate ceramics and natural titanate minerals show that these materials are very resistant to aqueous corrosion [2-5]. Studies of SYNROC (a titanate ceramic designed to stabilize nuclear wastes) show that its corrosion is characterized by a relatively large initial release of some elements (Ba, Cs, and Mo), presumably from grain boundaries and amorphous material [5-7]. In this case, the corrosion rates observed in short-term tests (e.g. MCC-1) are not necessarily representative of longer-term corrosion rates of the same material. The corrosion rate might also be affected by the formation of a Ti-rich layer on the surface [8], which could retard the interdiffusion of water and Ca^{+2} [9].

The purpose of this study is to describe the corrosion behavior of a Pu-doped, zirconolite-rich ceramic material. Test results will be used to evaluate the resistance of the ceramic to aqueous corrosion, and to compare its corrosion behavior to other candidate immobilization materials. In particular, we are interested in the release of Pu and Gd. Since the goal of this program is to immobilize Pu, its release from the material is an important criterion for deciding on a final immobilization material. Gadolinium will be present in any Pu immobilization material as a neutron absorber to prevent a criticality event. The corrosion data presented here will be used, along with microcharacterization of the ceramic previously reported [10], to provide a comprehensive description of the corrosion of the materials.

EXPERIMENTAL

Preparation of the Pu-Doped Ceramic

The PuO_2 used to prepare the ceramic was made at LLNL from a low temperature oxidation of $PuH_{2.7}$ using $4\%O_2/Ar$. The temperature never exceeded 200°C during the oxidation process. The hydride was formed from actual pit material at about 100°C.

Samples of four ceramics were prepared at LLNL and sent to ANL for testing. Details of the preparation of these ceramics are presented elsewhere [10]. The target chemical compositions (as batched) of each ceramics is given in Table I. The target phase composition of these ceramic is 90% zirconolite ($CaZrTi_2O_7$) with the balance comprised of perovskite ($CaTiO_3$), hollandite $\{(Ba_xCs_y)[(TiAl)_{2x-y}]O_{16}\}$, and rutile ($TiO_2$).

Table I. The Compositions (As Mixed) of Ceramics Used in this Study

Oxide	Ceramic A	Ceramic B	Ceramic C	Ceramic D	PCT Mixture*
CaO	7.35	6.55	8.07	8.07	7.38
ZrO_2	16.2	14.4	17.7	17.7	16.2
TiO_2	38.6	34.4	40.4	40.4	40.0
Al_2O_3	10.9	9.71	4.71	4.71	7.99
BaO	2.99	2.67	3.37	3.37	3.04
PuO_2	14.4	19.3	16.9	16.9	17.1
Gd_2O_3	9.61	12.9	8.75	8.75	10.4

*A mixture of 26.4 mass % of ceramic A, 32.9 mass % of ceramic B, 20.2 mass % of ceramic C, and 20.5 mass % of ceramic D was used in PCT.

Corrosion Test Procedures

Several types of tests were performed to highlight different aspects of the corrosion process.

The MCC-1 test was originally developed to directly compare the relative durabilities of different materials. The test method has been standardized in ASTM C1220 [11]. Monoliths (1 cm in diameter, 1 mm thickness) were cut from ceramic B (Table I) and polished to a 240-grit finish. Tests were conducted by sealing a monolith in a stainless steel vessel with deionized water (18 g) for three days at 90°C. The leachate and acid strip solutions were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS). This test provides valuable information regarding the intrinsic corrosion behavior of the material under conditions in which feed-back effects of the solution are expected to be small.

The Product Consistency Test (PCT) was originally developed to monitor the consistency of high-level radioactive waste glasses. It has been standardized in ASTM C1285 [12]. The test is performed with crushed material (-100+200 mesh) and deionized water in stainless steel vessels. Due to the small amount of each of the four ceramic samples, we were unable to test each of them separately. Ceramics A, C and D, along with the portion of ceramic B remaining after monolith preparation were crushed and sieved to produce -100+200 mesh powder. The composition of the mixture used for the PCT is also given in Table I.

Tests were conducted under two sets of conditions: PCT-A, in which one gram of test material (ρ=4.5 g/cm^3) is sealed in the vessel with 10 g of water [giving a solid surface area to solution volume ratio (S/V) of about 1200 m^{-1}] for 7 days at 90°C; and PCT-B in which 5 g of test material is sealed in the vessel with 5 g of water (giving an S/V of about 12,000 m^{-1}) for various times at 90°C. The leachate and acid strip solutions were analyzed using ICP-MS. The behavior of a material in this type of test is expected to be dominated by the feed-back effects of the solution, which becomes highly concentrated as the material corrodes.

After completion of the MCC-1 and PCT, the stainless steel vessels were filled with dilute HNO_3 and placed in the 90°C oven for an additional 12-24 hours. This "acid strip" solution contains any material that was fixed on the vessel wall.

RESULTS AND DISCUSSION

Short-Term Test Results

Table II shows the amounts of several elements released from the ceramic during the 3 day MCC-1 and 7 day PCT-A. Six replicates of the MCC-1 and three replicates of the PCT-A were performed. The values presented in Table II are averages of the replicates ± the standard deviation and have been background-corrected. The amounts released are reported rather than the normalized loss

Table II. Results From Static Corrosion Tests. The amount of material released includes material in the leachate solution and material adsorbed onto the vessel wall.

	MCC-1		PCT-A	
	amount released, mg	% adsorbed*	amount released, mg	% adsorbed
Al	1.03±0.5	70	6.9±0.5	4
Ca	1.2±0.4	30	20±1	20
Ti	bdl**	-	0.31±0.07	90
Zr	0.39±0.49	50	bdl	-
Gd	0.65±0.35	80	0.43±0.13	90
Pu	0.46±0.66	90	0.40±0.04	90
Ba	1.5±0.5	1	170±0	3
U	0.18±0.34	90	8.4±0.5x10^{-3}	60
Cs	bdl	-	bdl	-
Mo	0.11±0.14	60	0.40±0.02	4

*Represents the amount of the element found in the acid strip solution as a percentage of the total.

**Below detection limit.

values because most of the elements are present in several phases, and therefore the surface area of each phase cannot be estimated. The background values for each element were calculated from results of a series of blank tests. Also included in Table II are the percentages of each element that were present in the acid strip solutions. Some of the elements found in the test solutions (U, Cs, and Mo) were not reported to ANL as added components. These elements are presumably contaminants from the feedstock material or from processing.

The results from these short-term tests (3 day MCC-1 and 7 day PCT-A, Table II) are used to compare the corrosion of ceramics and glasses in this program. In addition, the data can be used to understand the corrosion behavior of the ceramic material. The total surface area available in a PCT-A (1.2×10^{-2} m^2) is much larger than that available in a MCC-1 test (1.9×10^{-4} m^2) and the results of these tests must be interpreted with this in mind. The amount of Al, Ca and Ba released from the ceramic in PCT-A is much larger than is released in the MCC-1 tests. These elements are probably incorporated into grain boundaries or phases that are particularly susceptible to corrosion. Their release is dependent on the total solid surface area. The total release of Pu and Gd in PCT-A and MCC-1 are about the same.

Long-Term Results

Figure 1 shows the results of a series of PCT-B tests conducted at 90°C and an S/V of about 12,000 m^{-1}. The amount of an element released (y-axis in Figure 1) includes the material in the leachate and the acid strip solutions. The uncertainty in these concentrations is about ±15%, based on previous studies, and error bars in Figure 1 lie within the printed symbols. Trends in these data as a function of time can be interpreted in terms of processes affecting the corrosion of the ceramic.

Three of the elements (Al, Ca, and Ba) show decreasing release as a function of time. Such a decrease can be explained as a result of precipitation of solid phases. Small particles of BaO have been observed on the surface of glass particles reacted for 98 days. This explains the decrease in the amount of Ba released with time (Figure1a). Particles of $CaCO_3$ were detected with AEM in the leachate from 182 day PCT-B. A small amount of the leachate filtered through a carbon grid (pore size, 5 nm) was examined. Formation of these Ca-rich particles may explain the decrease in Ca concentrations during PCT-B (Figure 1a).

The amount of U and Zr released from the ceramic continues to increase in tests with durations up to 182 days (Figure 1b). This shows that these elements are still being released into solution after 182 days.

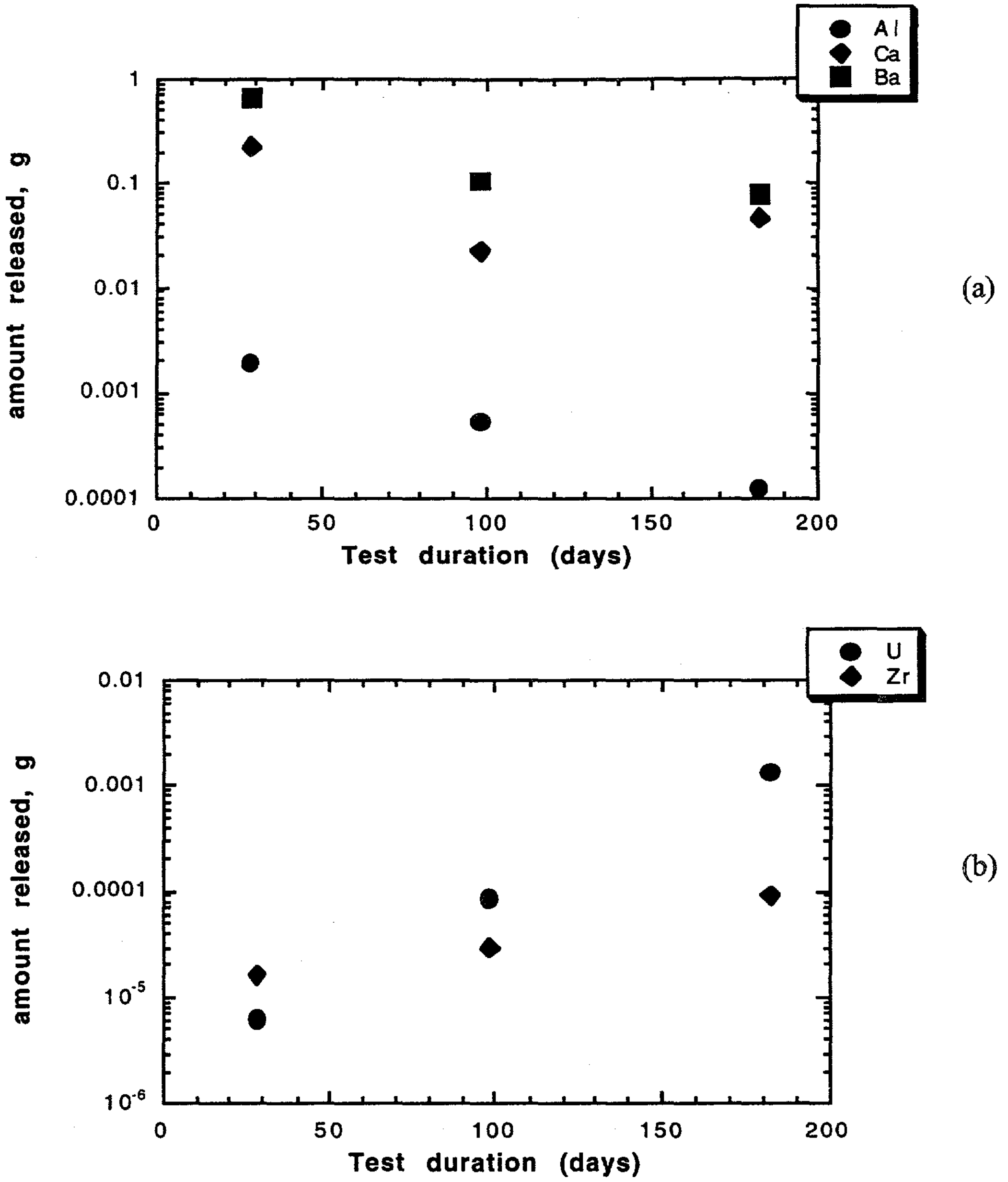
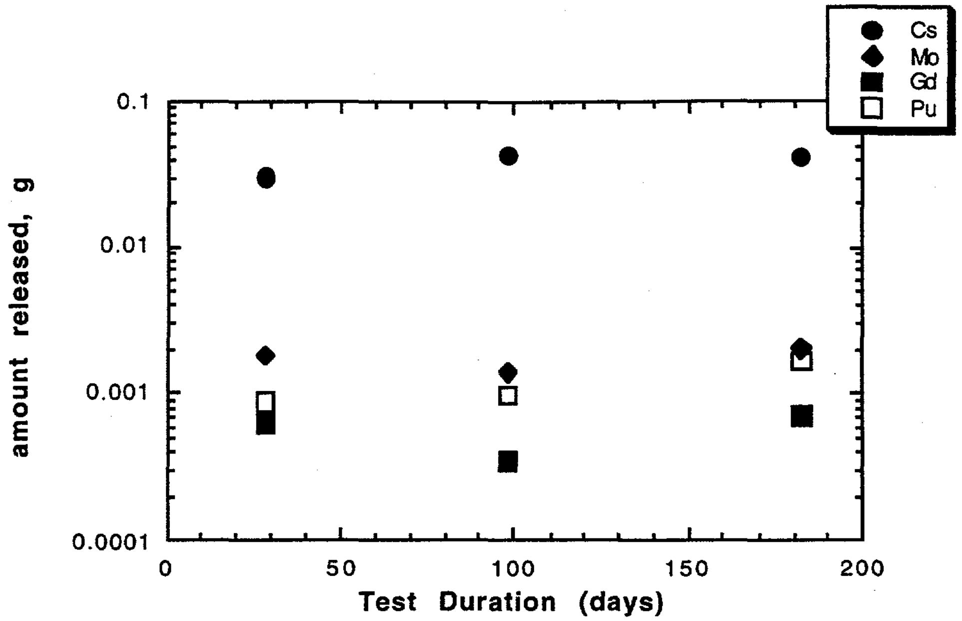


Figure 1. Results from PCT-B (90°C, 12,000 m^{-1}) for the indicated elements as a function of time. The amount of each element released includes what is present in the leachates and what is adsorbed on the vessel walls. Note that the y-axis is logarithmic.



(c)

Figure 1 - cont'd

The amounts of Cs, Gd, Mo, and Pu released into solution remain quite constant between 28 and 182 days (Figure 1c). This pattern would result if a highly soluble minor phase(s), containing these elements dissolved in the first 28 days of reaction. Alternatively, such a pattern would result if the release of these elements from the ceramic, under these conditions, is solubility controlled and that the maximum solubilites was reached before 28 days. This seems unlikely given the high solubility of Cs and Mo. Calculations are underway to estimate the solubility limits of these elements in these solutions. In either case, the data show that the release of these elements is quite slow after 28 days.

Possible Marker Elements

It is often desirable to define a marker element that accurately describes the extent of corrosion of a material. Such a marker element must be released from the material at a maximum rate and must not be incorporated into any alteration phases. Previous studies have used Ca as a marker element for the corrosion of titanate ceramics in short-term static tests [2-5]. Our data show that Ca is incorporated into alteration phases in long-term PCT (182-day, 90°C, 12,000 m^{-1}), and that the release of Ca from the ceramic decreases with time between 28 and 182 days. In addition, previous characterization studies have shown that Ca is present in several distinct phases in the ceramic [10]. Based on these observations, we view Ca as a poor marker element. The relatively low solubility of Ti and Zr compounds [13] makes them likely to be involved in precipitation reactions, particularly during long-term or accelerated tests. This presents a serious difficulty for using either of these elements as markers. Therefore, the major elements present in the ceramic are all inappropriate for use as corrosion marker elements. The presence of most of the minor constituents in multiple phases within the ceramic makes them inappropriate as well. A highly soluble element, which is rarely incorporated into alteration phases (such as B) might be incorporated into the zirconolite structure to serve specifically as a marker element.

CONCLUSIONS

Data from this ongoing study show that interpretation of static test results are complicated by the heterogeneous nature of the ceramic material. The release of each element should be considered separately. We believe that the corrosion behavior of any one element depends on the phases in which it occurs, and the solubility of the element in the leachate solution. In addition, the release of Ba, and Ca in some long-term tests appears to be affected by the formation of alteration phases.

The corrosion behavior of this material observed in this study is consistent with previous studies. A relatively large amount of material, primarily Ba, Ca, and Al, is initially released from grain boundaries and from highly soluble phases. These processes are reflected in the results of short-term tests (MCC-1 and PCT-A).

Data presented here shows that the corrosion of this ceramic in short- and long-term static tests releases only small amounts of Gd and Pu. Therefore, based on the limited data presented in this study, this ceramic appears to be an effective immobilization material for Pu.

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