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Impurity Effects**

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# CORROSION BEHAVIOR OF PYROCHLORE-RICH TITANATE CERAMICS FOR PLUTONIUM DISPOSITION; IMPURITY EFFECTS

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## ABSTRACT

The baseline ceramic contains Ti, U, Ca, Hf, Gd, and Ce, and is made up of only four phases, pyrochlore, zirconolite, rutile, and brannerite. The impurities present in the three other ceramics represent impurities expected in the feed, and result in different phase distributions. The results from 3 day, 90°C MCC-1 tests with impurity ceramics were significantly different than the results from tests with the baseline ceramic. Overall, the addition of impurities to these titanate ceramics alters the phase distributions, which in turn, affects the corrosion behavior.

## INTRODUCTION

Due to the dismantlement of nuclear weapons and the cleanup of weapons production sites, 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. Two options for the disposition of surplus Pu are currently being considered by the US Department of Energy: incorporation into mixed oxide fuel, and immobilization in a titanate ceramic. The four samples described and tested in this study are similar to the proposed immobilization material with Ce used as a surrogate for Pu.

The purpose of this study is to evaluate the effects of the impurities likely to be present in the feed on the corrosion of a titanate ceramic. Impurities are defined as any element other than Ti, U, Ca, Hf, Gd, and Ce. The baseline ceramic contains only the major elements (Table 1), and is made up of four phases, pyrochlore, zirconolite, rutile, and brannerite (Figure 1a). The presence of impurities in the other ceramics result in the formation of other phases. The impact of these new phases on the corrosion of the ceramic is the primary focus of this study.

## Test Method

Tests were conducted according to the standard MCC-1 procedure [ASTM-1992] (90°C, three day). 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 test samples were ultrasonically cleaned in 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 demineralized water (DIW), leading to a geometric surface area to leachant ratio (S/V) of about 10 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. This "acid strip" solution contains any material fixed on the vessel wall, and was analyzed with ICP-MS. The normalized mass loss [NL(i)] values shown represent the amount of the ceramic dissolved based on the amount of element i in the leachate and the acid strip solutions.

Table 1. Batch compositions of the ceramics tested, in elemental mass %

	Baseline	Low	Medium	High
Ca	7.2	7.2	7.2	7.6
Ti	22	21	21	19
Ce	6.2	6.1	5.9	5.3
Gd	6.2	6.1	6.6	6.0
Hf	9.1	9.0	8.6	7.8
U	21	21	20	18
O	28	29	28	28
B		0.049	0.050	0.11
F		0.060	0.22	0.63
Na		0.046	0.10	0.35
Mg		0.078	0.26	0.52
Al		0.17	0.27	0.84
Si		0.088	0.21	0.69
Cl		0.10	0.43	1.39
K		0.056	0.27	0.87
Cr		0.014	0.052	0.089
Fe		0.060	0.11	0.35
Ni		0.031	0.10	0.26
Zn		0.010	0.05	
Ga		0.10	0.43	
Mo		0.080	0.22	0.35
Ta		0.050	0.16	0.52
W		-	0.42	1.39
<b>Total Impurities</b>	<b>0.0</b>	<b>0.99</b>	<b>3.4</b>	<b>8.4</b>

\*-calculated by difference

## RESULTS AND DISCUSSION

### Phase Distribution

Four ceramics fabricated at Lawrence Livermore National Laboratory are included in this study (Table 1). One of the ceramics is the baseline composition. The other ceramics contain the impurity mixtures shown in Table 1. It should be noted that the "high" ceramic contains an amount of impurities in excess of that expected in the actual feed.

Each ceramic was examined with SEM and TEM to describe the phase distributions. Figure 1 shows SEM micrographs of each ceramic. Four major phases were observed in the baseline, pyrochlore  $[(Ca, Gd)(Hf, Pu)Ti_2O_7]$ , zirconolite  $[(Ca, Gd)(Hf, Pu)Ti_2O_7]$ , brannerite  $[(U, Pu)Ti_2O_6]$ , and rutile  $[(Ti, Hf)O_2]$ . While the chemical formulae of pyrochlore and zirconolite are identical, their crystal structures are distinct [MAZZI-1983]. In these ceramics, the morphology and the U/Hf ratio are useful for distinguishing these two phases. The impurity ceramics also contain a small amount of a silicate. This silicate phase contains Al, Si, Ca, Ti, Ga, and Mo and is amorphous. Calcium and cerium phosphate crystals are often present within the silicate. The "high" ceramic also contains perovskite  $(CaTiO_3)$ , which has been shown to be a particularly soluble phase in titanate ceramics [SMITH-1997].

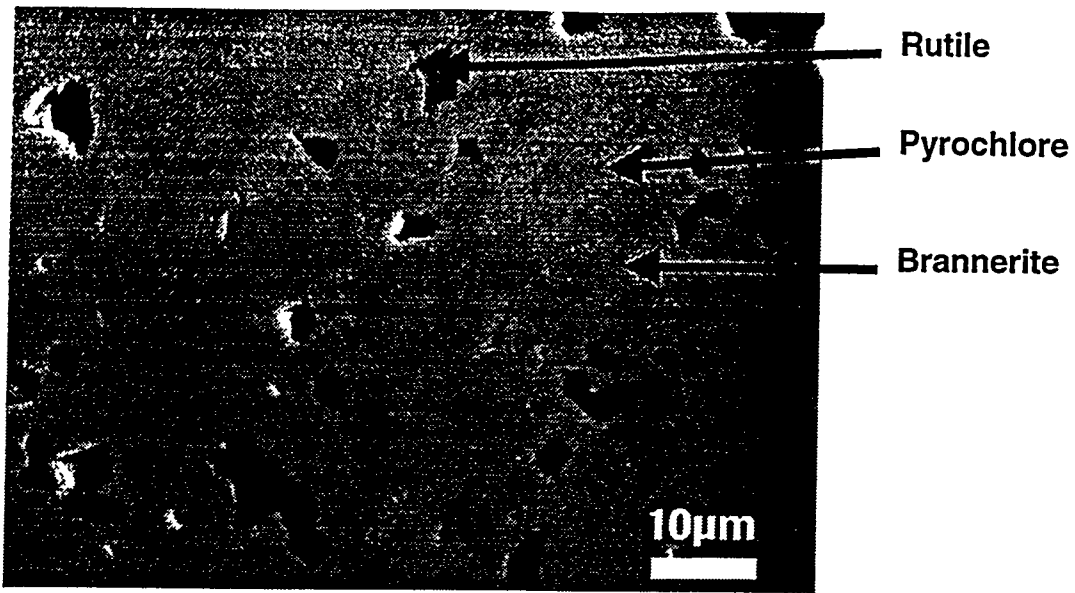


Figure 1a. SEM photomicrograph (100x, back scatter emission) of a surface of the baseline ceramic.

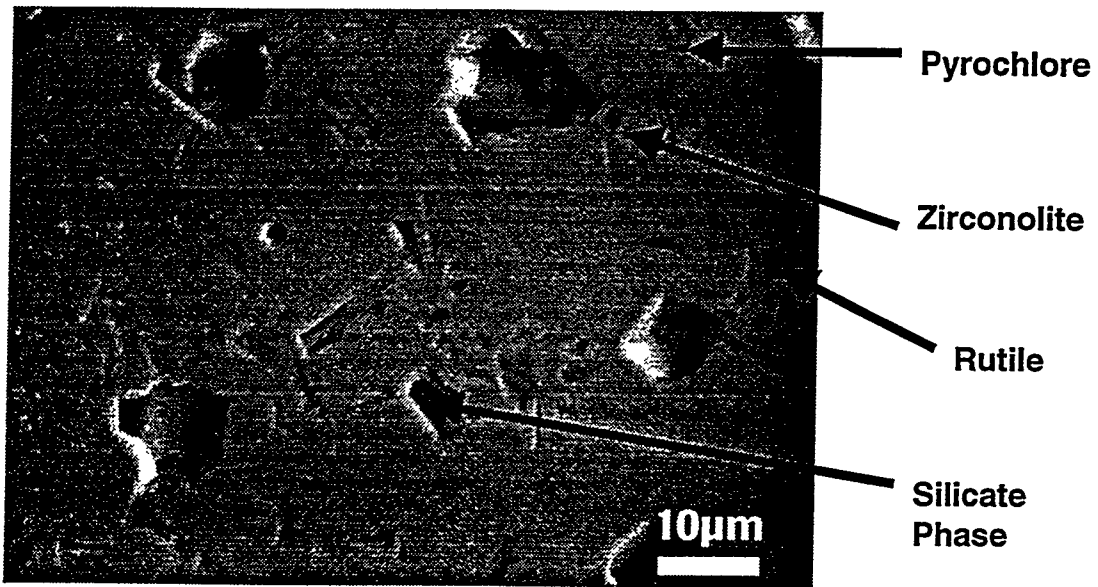


Figure 1b. SEM photomicrograph (1000x, back scatter emission) of a surface of the "low" ceramic.

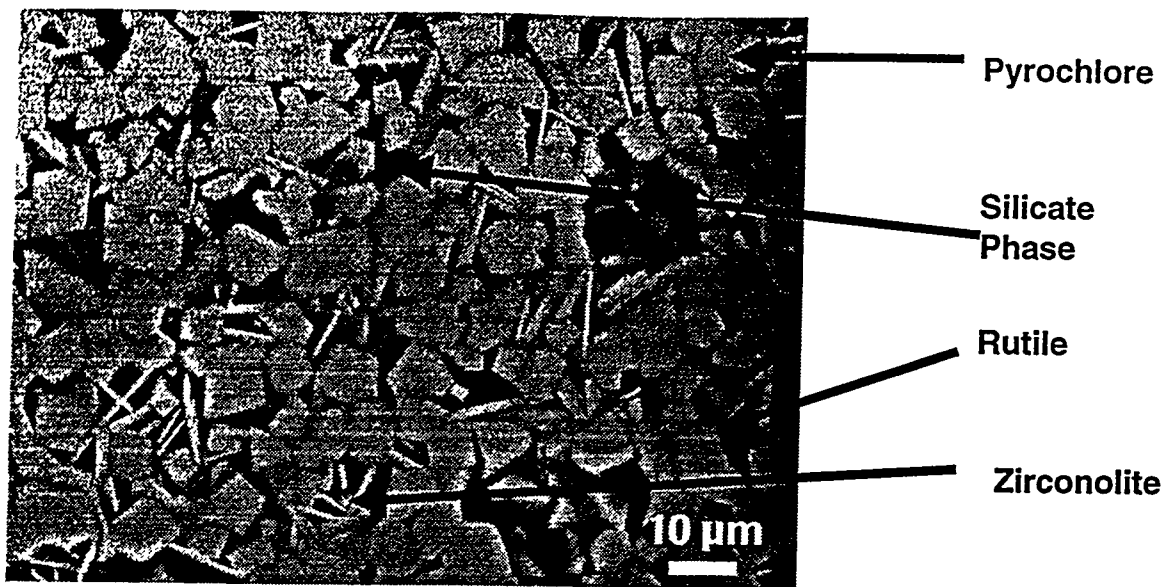


Figure 1c. SEM photomicrograph (1000x, back scatter emission) of a surface of the "medium".

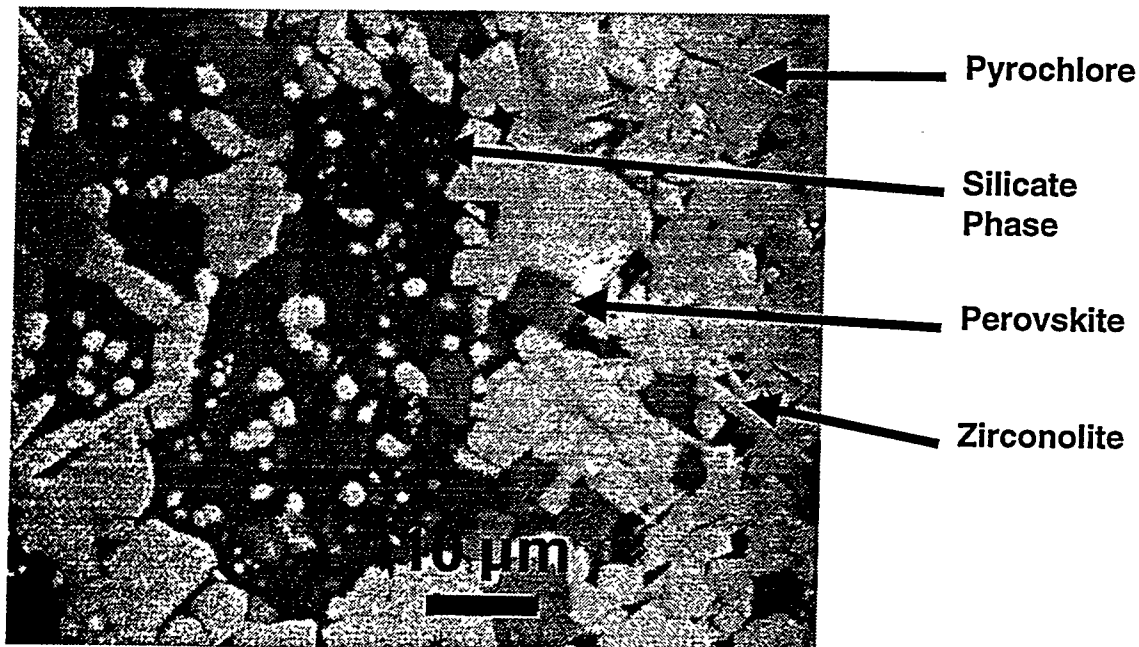


Figure 1d. SEM photomicrograph (1000x, back scatter emission) of a surface of the "high" ceramic.

### Normalized Mass Losses

The NL(i) values based on Ca, Ti, Ce, Gd, Hf, and U for these ceramics vary by several orders of magnitude (Table 2, and Figure 2). In tests with the baseline ceramic for example, the NL(Ca) is relatively high ( $1.0 \text{ g/m}^2$ ). High NL(Ca) values in corrosion tests have been observed during leach testing of similar materials [RINGWOOD-1988]. The NL(i) values for baseline ceramic based on other major elements are lower than NL(Ca). The NL(Ce) ( $0.015 \text{ g/m}^2$ ), NL(Gd) ( $0.015 \text{ g/m}^2$ ), and NL(U) ( $0.012 \text{ g/m}^2$ ) are similar, while NL(Ti) ( $<0.0004 \text{ g/m}^2$ ) and NL(Hf) ( $<0.0001 \text{ g/m}^2$ ) are much lower.

Table 2. Normalized mass loss values ( $\text{g/m}^2$ ) based on each element for MCC-1 tests and average measured pH values from the same tests.

	Baseline	Low	Medium	High
Ca	$1.0 \pm 0.6$	$5 \pm 2$	$6 \pm 3$	$14 \pm 5$
Ti	<sup>1</sup> $<0.0004$	$0.0006 \pm 0.0001$	$0.0014 \pm 0.0001$	$0.0020 \pm 0.0008$
Ce	$0.015 \pm 0.008$	$0.044 \pm 0.003$	$0.07 \pm 0.04$	$0.01 \pm 0.01$
Gd	$0.015 \pm 0.005$	$0.011 \pm 0.005$	$0.007 \pm 0.002$	$0.002 \pm 0.003$
Hf	$<0.0001$	$<0.0001$	$<0.0001$	$<0.0001$
U	$0.012 \pm 0.003$	$0.0049 \pm 0.0007$	$0.0031 \pm 0.0005$	$0.0013 \pm 0.0007$
B			$30 \pm 20$	$18 \pm 7$
Mg		$1.4 \pm 0.2$	$1.9 \pm 0.6$	$6 \pm 2$
Al		$8 \pm 3$	$10 \pm 6$	$8 \pm 3$
Si		$26 \pm 5$	$27 \pm 9$	$10 \pm 4$
Ni		$300 \pm 200$	$50 \pm 30$	$20 \pm 30$
Zn		$400 \pm 500$	$6 \pm 1$	
Ga		$0.57 \pm 0.09$	$0.8 \pm 0.3$	
Mo		$0.4 \pm 0.2$	$0.4 \pm 0.3$	$1.5 \pm 0.9$
pH	$5.1 \pm 0.4$	$5.5 \pm 0.2$	$5.3 \pm 0.2$	$6.7 \pm 0.6$

<sup>1</sup> – value derived from limit of quantitation.

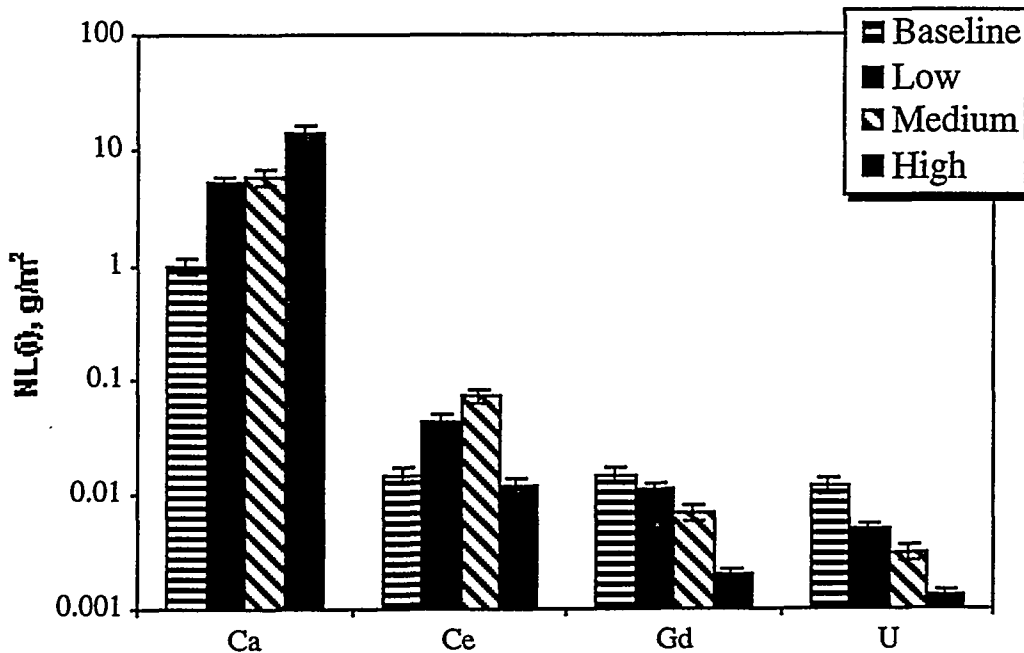


Figure 2. Bar plot of NL(i) values based on the major elements, for each ceramic tested. The error bars are  $\pm 15\%$  based on analytical uncertainty.

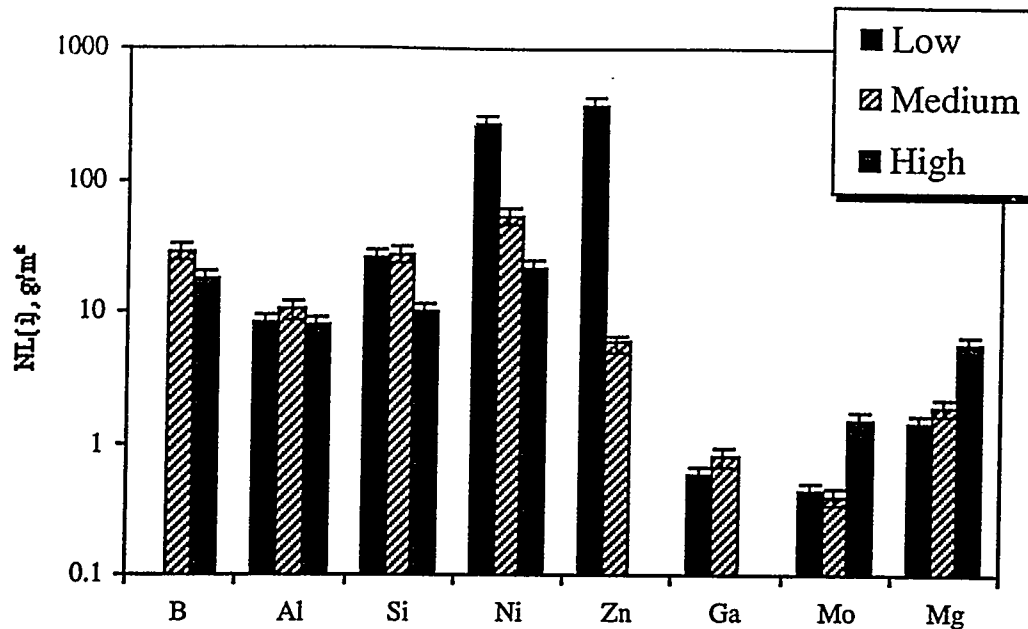


Figure 3. Bar plot of NL(i) values based on the impurity elements, for each ceramic tested. The error bars are  $\pm 15\%$  based on analytical uncertainty.

The NL values based on some of the impurity elements (B, Al, Si, Ni, and Zn) are significantly greater than  $1 \text{ g/m}^2$  (Table 2, Figure 3). Normalized mass loss values based on the other impurities (Ga, Mo, and Mg) are similar to the values for NL(Ca). The preferential release of B, Al, Si, Ni, and Zn might result from any of several factors. For example, B, Al, and Si are probably incorporated into soluble silicate and/or perovskite. Some of the impurity elements may also be present at grain boundaries [COOPER-1986, BUCK-1997], and are therefore particularly susceptible to leaching.

The NL(Ca) value for the baseline ceramic is about  $1.0 \text{ g/m}^2$ . The NL(Ca) value for the “high” ceramic, which contains the silicate and perovskite, is  $14 \text{ g/m}^2$ . The NL(Ca) values for the ceramics containing the silicate (“low” and “medium”) are  $5.1$  and  $5.9 \text{ g/m}^2$ . These observations show that the presence of the silicate increases the release of Ca, and the presence of perovskite increases the release of Ca a great deal.

The NL(Ce) values are higher for the “low” and “medium” ceramics than for the baseline, suggesting that Ce is released from the silicate (or the Ca, Ce phosphate crystals) at a higher rate than it is released from Ce-bearing major phases. The NL(Ce) values for the “high” ceramic are lower than those for the other ceramics containing the silicate phase (Table 2). This observation is difficult to explain, although the NL(Ce) value might result from the higher pH in tests with the “high” ceramic (Table 2).

Data in Table 2 and Figure 2 show that corrosion of the baseline ceramic releases more U than corrosion of the impurity ceramics. Brannerite is present in the baseline ceramic, but not in any of the impurity ceramics (see Figure 1). We believe that the corrosion of brannerite is responsible for the observed NL(U) values. The conclusion that brannerite is relatively soluble is particularly important, because brannerite in the Pu-

bearing baseline ceramic contains both U and Pu. Therefore the corrosion of brannerite might be an important Pu release process.

Therefore, our data show that the presence of silicate leads to increased release of both Ca and Ce. The presence of perovskite leads to relatively high leachate pH and a significant increase in the release of Ca. Finally, the presence of brannerite leads to increased release of U.

## Conclusions

The primary purpose of this study is to evaluate the effects of impurities on the corrosion behavior of these titanate ceramics. Microscopic phase characterization shows that the presence of impurities alters the phase distribution. Results from corrosion tests further show that the changes in phase distribution affect the corrosion behavior of the ceramic.

The baseline ceramic contains, pyrochlore [(Ca, Gd)(Hf, Pu)Ti<sub>2</sub>O<sub>7</sub>], zirconolite [(Ca, Gd)(Hf, Pu)Ti<sub>2</sub>O<sub>7</sub>], brannerite [(U, Pu)Ti<sub>2</sub>O<sub>6</sub>], and rutile [(Ti, Hf)O<sub>2</sub>]. The addition of impurities apparently suppresses the formation of brannerite in these ceramics. All of the impurity ceramics include a silicate containing Al, Si, Ca, Ti, Ga, and Mo. In addition, the ceramic containing the highest level of impurities (about 8.4 mass % total impurities) includes perovskite (CaTiO<sub>3</sub>). This is a particularly important observation since perovskite has been shown to be more soluble than the other titanate phases in these ceramics.

The results from 3 day, 90°C MCC-1 tests with impurity ceramics were significantly different than the results from tests with the baseline ceramic. The presence of brannerite in the baseline ceramic results in a relatively high NL(U) value. In the absence of brannerite, the U is probably partitioned into less soluble pyrochlore and zirconolite phases. The presence of the silicate in the impurity ceramics results in relatively high NL(Ca), and NL(Ce) values. These results are explained by the corrosion of both silicate and the included phosphate. The presence of perovskite leads to high pH and a particularly high NL(Ca) value, resulting from the relatively rapid corrosion of this phase. Overall, the addition of impurities to these titanate ceramics alters the phase distributions, which in turn, affects the corrosion behavior.

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