

**Testing the Durability of Shielding Concrete Containing  
Depleted Uranium Dioxide Aggregate**

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# Testing the Durability of Shielding Concrete Containing Depleted Uranium Dioxide Aggregate

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**Abstract**—The depleted uranium (DU) inventory in the United States exceeds 500,000 metric tonnes. To evaluate the possibilities for reuse of this stockpile of DU, the U.S. Department of Energy (DOE) has created a research and development program to address the disposition of its DU<sup>1</sup>. One potential use for this stockpile material is in the fabrication of nuclear shielding casks for the storage, transport, and disposal of spent nuclear fuels. The use of the DU-based shielding would reduce the size and weight of the casks while allowing a level of protection from neutrons and gamma rays comparable to that afforded by steel and concrete. DUAGG (depleted uranium aggregate) is formed of depleted uranium dioxide (DUO<sub>2</sub>) sintered with a synthetic-basalt-based binder. This study was designed to investigate possible deleterious reaction that could occur between the cement paste and the DUAGG. After 6 months of exposure to a cement pore solution, no deleterious expansive mineral phases were observed to form either with the DUO<sub>2</sub> or with the simulated-basalt sintering phases. In the early stages of these exposure tests, Oak Ridge National Laboratory preliminary results confirm that the surface reactions of this aggregate are much less than expected. This finding may indicate that DUAGG/ DUCRETE casks can be expected to experience service lives sufficient to meet the projected needs of DOE and the commercial nuclear power industry.

## 1. INTRODUCTION

In 1993, the DOE Office of Environmental Management began investigating the potential use of depleted uranium (DU) in heavy concretes, or DUCRETE (depleted uranium concrete).<sup>2,3</sup> This concrete consists of depleted uranium ceramic or DUAGG (depleted uranium aggregate), which replaces the coarser aggregate that is mixed with Portland cement, sand, and water for use in normal concrete. The DUAGG material was developed at Idaho National Engineering and Environmental Laboratory (INEEL) and consists of depleted uranium dioxide (DUO<sub>2</sub>) sintered with a synthetic-basalt-based binder that ultimately coats the sintered DUO<sub>2</sub> particles and retards their surface reactions. The preliminary work on DUAGG and DUCRETE properties has been performed at INEEL. However, more information is required to fully evaluate the long-term stability and durability of these materials.

Under oxidizing conditions and with the pore-water chemistry of Portland cement-based concretes, dense DUO<sub>2</sub> aggregates (DUAGG) are expected to react to form expansive, less-dense oxides that could affect the strengths, thermal conductivities, and competence of the shielding made from the DUCRETE™ in proposed storage and transport casks.<sup>4</sup> For the expected service conditions of

DUCRETE in spent fuel casks, the rates and extent of these potential aggregate/cement-paste interactions are unknown. The principal area of concern regarding the stability of DUAGG pellets in concrete is the possible reactions between the sintered DUO<sub>2</sub> particles and the cement pore solution, which is a very basic medium (pH ~12.6) that contains large quantities of alkalis (sodium and potassium). The potential reaction products of the uranium oxide and/or the constituents of the basalt-like binder could create deleterious expansive mineral growths. These reactions could be similar to the alkali-aggregate (alkali-silica) reactions, which can disrupt normal concrete structures, generating cracks and spalling.

Therefore, in an attempt to assess the potential impacts of DUO<sub>2</sub> aggregates on the longevity and durability of DUCRETE casks, Oak Ridge National Laboratory (ORNL) is using standardized American Society for Testing and Materials (ASTM) exposure tests that accelerate the onset and progress of such surface interactions.

## 2. EXPERIMENTAL

Current testing at ORNL measures the extent and rates of surface reactions of the DUAGG under the expected service temperatures and the simulated chemical

environments of cement pastes. Using DUAGG samples obtained from the Starmet CMI (formerly Carolina Metals, Inc.), the DUO<sub>2</sub>/basalt aggregates were cleaned in an ultrasonic bath with distilled/deionized (DI) water to remove surface residuals from the preparation. These intact aggregates of DUAGG were then tested for reactivity using a modified ASTM C289-01<sup>5</sup> method to measure interactions with the pore liquids that are expected to occur in concrete pastes.

The ASTM test called for the reaction of crushed material (150- to 300- $\mu$ m fraction) with 1 *N* sodium hydroxide (NaOH) solution at 80EC for 24 h, followed by the analysis of the solution for silicon. We modified the temperature to cover the range of temperatures the DUAGG would be exposed to in a cask with spent nuclear fuel. It was determined that while the outside of the cask would be at ambient temperature, the side adjacent to the fuel would reach a maximum temperature of 150EC and that for the center of the cask would likely be  $\sim$  66EC. Therefore, we chose to study these three temperatures.

The exposure to 1 *N* NaOH represents an extreme situation that does not accurately characterize the cement pore solution to which the DUAGG would actually be exposed. Therefore, we decided to study three media: DI water (to represent a better-case scenario situation), a cement pore solution (the actual scenario), and a 1 *N* NaOH solution (the worse-case scenario).

Because we wanted to examine the surface of the DUAGG after exposure, the use of a fine fraction size was not practical. Furthermore, we had a limited quantity of DUAGG material ( $\sim$ 1 kg) which would not permit us to generate enough of a selected fraction size of the material. Therefore, we decided to use one whole pellet of DUAGG for the test. The time of exposure of the pellet to the solutions was modified to allow for better reactions, and the selected times were 30 days, 60 days, 90 days, 180 days, 360 days, and 2 years.

The ASTM method called for 25 g of crushed material to be tested with 25 mL of 1 *N* NaOH solution. Because we were using a whole pellet, we chose to use a liquid/surface ratio of 10. This ratio is often used in leaching tests like ANS 16-1 and appeared to be a better choice for our experiment.

The almond-shaped DUAGG aggregates are approximately 1.59 cm long, 0.95 cm wide, and 0.64 cm thick, with a measured average surface area of  $5.77 \pm 0.01$  cm<sup>2</sup>. The average weight was found to be  $6.39 \pm 0.01$  g, and the average volume was  $0.784 \pm 0.002$  cm<sup>3</sup>. The measured density of these DUAGG pellets was 8.15 g/cm<sup>3</sup>. With a pellet surface area of 5.8 cm<sup>2</sup> and a leachate volume/surface

ratio of 10, the volume of liquid used in the sealed leach vessels was 58 mL for each DUAGG pellet.

The cement pore solution was prepared by mixing  $\sim$ 300 g of a type I-II Portland cement with  $\sim$  0.8 to 1 L of DI water. The mixture was tumbled for 7 days, allowed to settle, and then filtered through a 0.45- $\mu$ m filter. The inductively coupled plasma (ICP) analysis showed that the solution contained  $\sim$  3 mg/L of barium,  $\sim$ 1800 mg/L of potassium,  $\sim$ 300 mg/L of sodium, and  $\sim$  50 mg/L of strontium.

The containers used for the test were vessels from a microwave digestion system. These vessels are made of an outer shell of Ultem; a thick inner shell of tetrafluoroethylene (TFE) Teflon; and, finally, a 20-mil clear perfluoroalkoxy (PFA) liner. They can withstand high temperatures as well as pressures up to 220 psi.

At a consistent surface-to-liquid ratio of 1:10, the sintered DUAGG samples were exposed to (1) DI water, (2) a 1 *N* NaOH standard solution, and (3) a saturated water extract of high-alkali cement. The three exposure temperatures were 20, 66, and 150°C, and the six times intervals were 30 days, 60 days, 90 days, 180 days, 360 days, and 2 years. At the end of each exposure period, the vessels in which the samples were exposed were cooled to room temperature and opened. The liquid phase was then separated and filtered through a 0.45- $\mu$ m filter for analysis of aluminum, silicon, uranium, alkalies, and other measurable elements by inductively-coupled plasma spectroscopy (ICP-AES) using a Thermo Jarrell Ash model 61E trace analyzer. The quantities leached were compared with the initial content of a DUAGG pellet (see Table 1 below) to determine the degree of corrosion of the aggregate surfaces.

Consistent with the guidelines of ASTM C295-98,<sup>6</sup> the surfaces of the exposed aggregates were subsequently examined and compared by scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence (EDX) analyses using a Phillips XL30FEG from the Shared Research Equipment (SHaRE) Collaborative Research Center and Program at ORNL.

### 3. RESULTS AND DISCUSSION

Measurements at ORNL began in September 2001. The 30-, 60-, 90-, and 180-days (1-, 2-, 3-, and 6-month) tests are completed. The ICP analysis of the DUAGG revealed that the most abundant elements in the pellet are uranium, silicon, and titanium, as shown in table 1.

The ICP analyses of the leachate solutions at 1, 2, 3, and 6 months showed that the leaching from the DUAGG

Table 1. Composition of a DUAGG pellet

Element	wt %
Aluminum	0.61
Copper	0.04
Iron	0.42
Potassium	0.14
Magnesium	0.15
Silicon	2.16
Strontium	0.01
Titanium	1.35
Uranium	93.71
Zirconium	0.85

pellet was minimal even after 6 months of exposure. The maximum "normalized" leaching, which is the amount leached relative to the initial amount of the specific element in the DUAGG (from Table 1), was found to be 0.008% for uranium, 0.15% for titanium, and 0.10% for zirconium. However, much worse results were obtained for aluminum and silicon, with 50 and 43% leached, respectively. The ICP results are illustrated in Figs. 1 to 4. Each figure shows the results for three leachates (DI water, NaOH solution, and cement pore solution) at four time intervals (1, 2, 3, and 6 months) for three temperatures (20, 66, and 150EC). The consistently low leachability of uranium in Fig. 3 indicates that the surface reactions of the  $DUO_2$  particles in the DUAGG matrix are relatively slow, confirming that the postulated protection by the "basalt phase" may be true. The larger extractions obtained for aluminum and silicon point to the fragility of the basalt phase when exposed to alkaline solutions. It is noteworthy to point out that the cement pore solution was found to be much less corrosive to the DUAGG surface than the 1 N NaOH solution was.

In order to determine if any deleterious phases were formed, the surfaces of the samples at 2, 3, and 6 months of exposure were examined by SEM equipped with EDX. The observations made indicate that except for the samples kept in distilled DI water (Fig. 5), the surface of the DUAGG is covered by crystals that mask the initial morphology of the sample. The images at the surface of the sample made with back-scattered electrons (BSE) allow the average atomic number of each particle to be determined: the DU particles that have a high average Z will be seen as white on a BSE image. Using this feature, one can see that in the sample

kept in DI water, the repartition of  $UO_2$  particles is identical to that of the original unexposed DUAGG pellet. However, for the samples cured in NaOH or in cement pore solution, the BSE images do not show as many white areas, confirming that the surface is covered by crystal growth. The samples kept in DI water show some erosion of the surface, with a crystalline phase containing large amounts of titanium. This titanium phase, probably resembling rutile, is more resistant to leaching than the other basalt phases and appeared unaltered even after the other basalt phases were leached out.

Because of the chemical composition of the synthetic basalt used for fabricating the DUAGG pellets, the possibility of an alkali-aggregate reaction of the DUAGG with the cement pore solution was envisioned.<sup>7,8,9</sup> This possibility was the driver for our study. Because we had only a small quantity of pellets available (less than 1 kg), we had to design a test that could produce the necessary information with this limited amount of material. Although ASTM C289 was used as a baseline for our test design, we decided to test the noncrushed material to assess the reactivity of the surface of the aggregate as it would be used in concrete in a cask. We used a ratio of volume of leachant to surface of the pellet of 10, the same ratio that is used in leaching test ANS16.1. The three temperatures studied were chosen to represent the maximum that could be found near the spent nuclear fuel in a cask (150EC), that in the center of the cask (67EC), and the temperature on the outside of the cask (20EC).

Of the chemicals that produce the basalt phase, aluminum and silicon are the elements that leach the most in the cement pore water and even more strikingly in the 1 N NaOH solution. Both of these solutions are very basic, with pH above 12.6; at these high pHs, both alumina and silica are extremely soluble. The amount leached is higher for NaOH and also increased with the temperature and time of exposure. This indicates that the dissolution of the basalt phase is progressive and does not produce a protective layer that would slow down the dissolution process. Observation using the SEM showed the presence of crystallized phases that contained Na, Al, Ti, Ca, and some Si and that resembled the crystals found in alkali-aggregate reaction (rosette type), as illustrated in Fig. 6.

In the cement pore solution, the release of aluminum and silicon was elevated at the beginning of the test and at high temperature (about 10% for aluminum and silicon each). However, for all temperatures, the amount decreased with time, with less than 1% aluminum released at 6 months and less than 0.1% silicon released. This decrease can be explained by the formation of a protective layer of cement hydration products covering the surface of the DUAGG pellet. SEM examination of the pellets at 6

months of exposure confirmed that the grains of  $\text{DUO}_2$  are

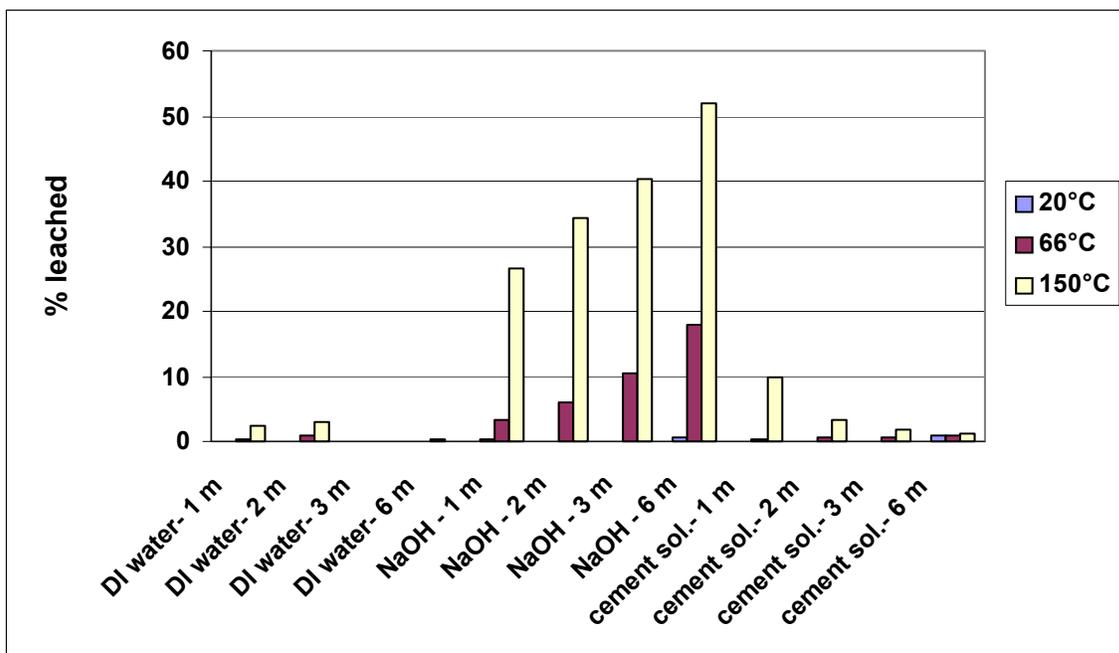


Fig. 1 Normalized leaching of aluminum

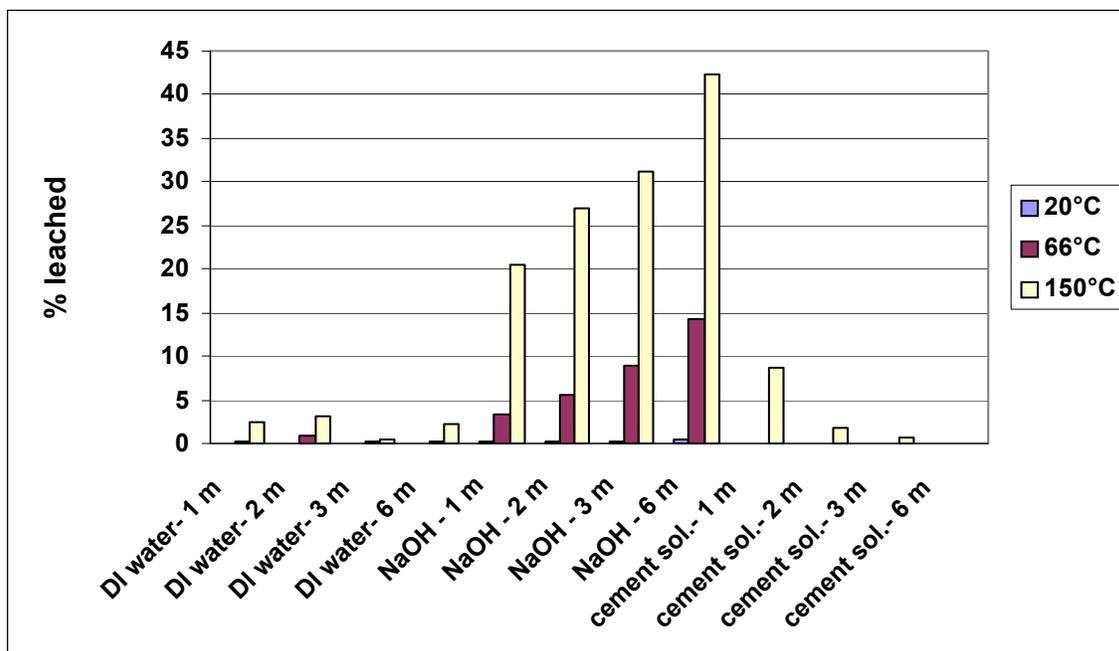


Fig. 2 Normalized leaching of silicon

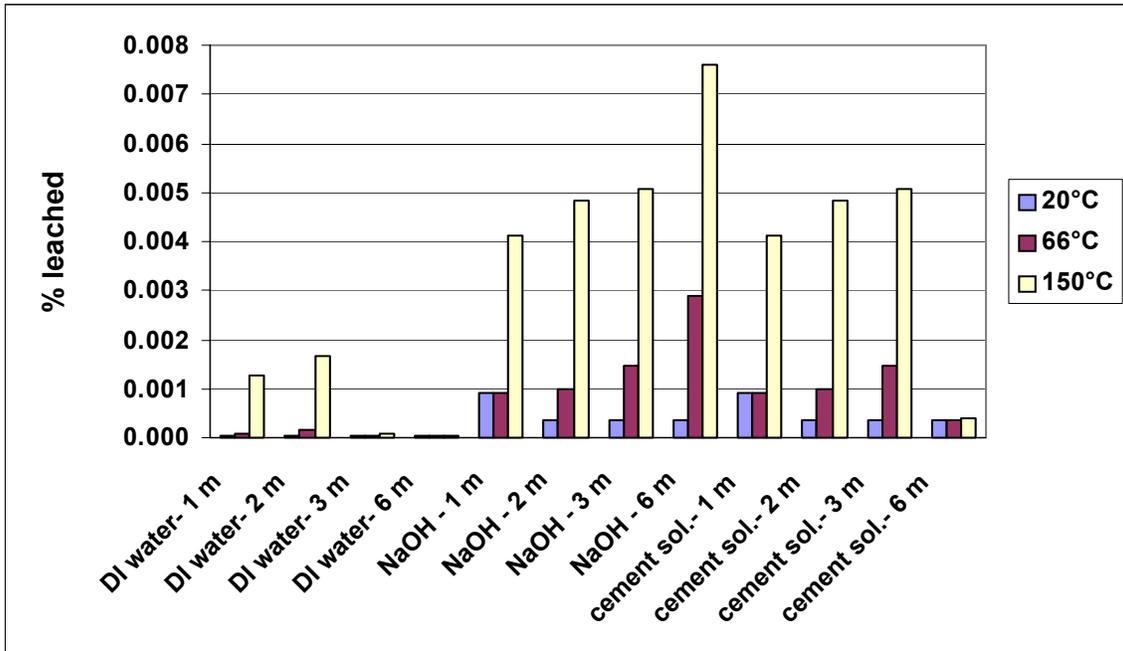


Fig. 3 Normalized leaching of uranium

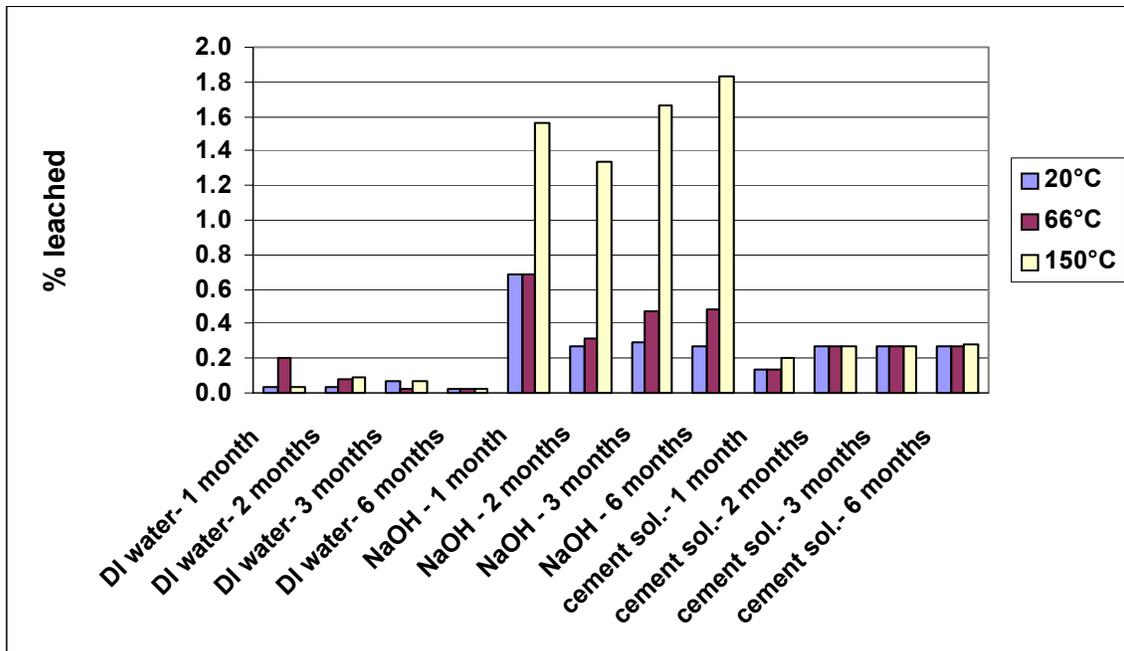
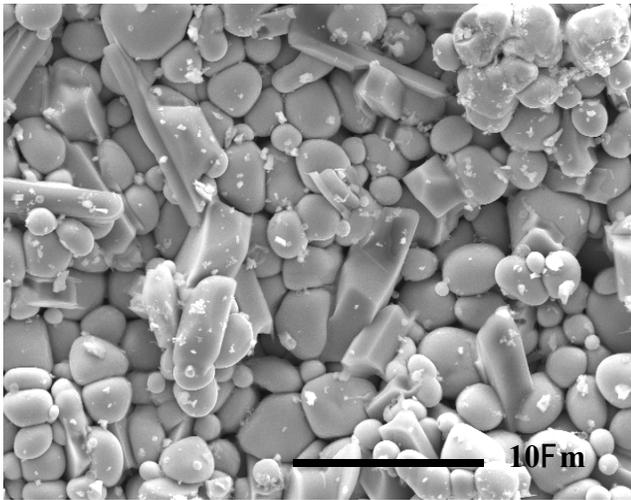
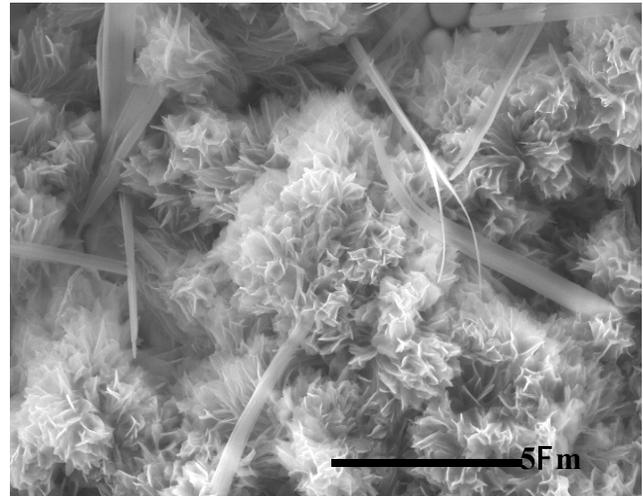


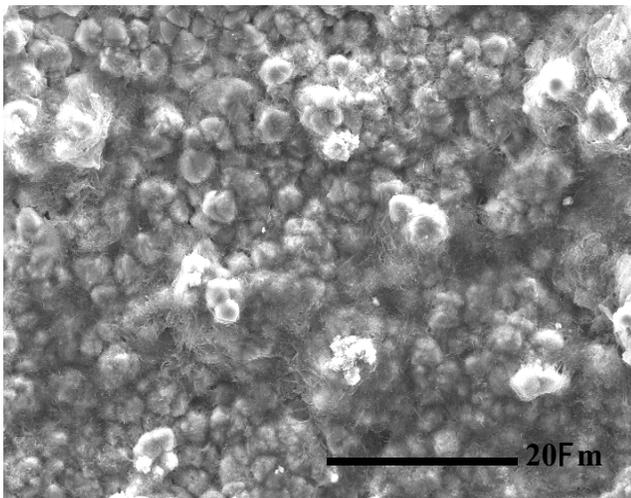
Fig. 4 Normalized leaching of iron



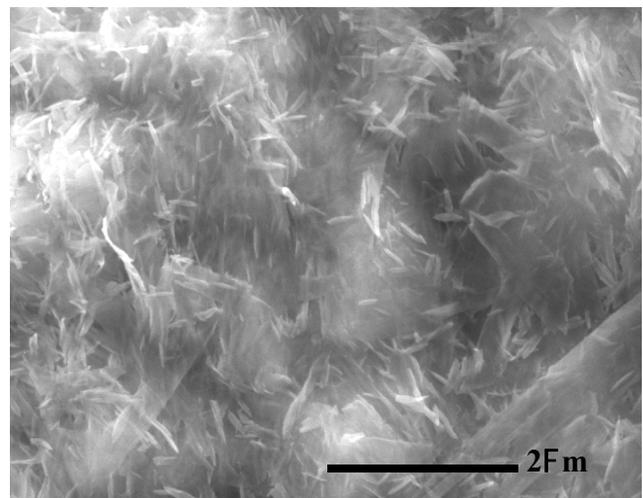
**Fig. 5 Secondary electron image of DI water at 150EC and 6 months exposure.** The oblong particles contain titanium and some magnesium, while the rounded ones are made of DU



**Fig. 6 Secondary electron image of NaOH at 150EC and 6 months exposure.** The alkali reaction particles contain Na, Al, Si, Ca, and Ti.



**Fig. 7 Secondary electron image of cement pore solution at 150EC and 6 months exposure, showing cement hydration particles covering the DU particles.**



**Fig. 8 Secondary electron image of cement pore solution at 150EC and 6 months exposure.** The cement hydration particles contain Ca, Si, and Al.

almost invisible any longer (Figs. 7 and 8). This finding has been previously explained in studies of natural basalt rocks.<sup>7,8</sup>

The leaching of other basalt constituents such as titanium and iron is not as pronounced. Of the two, iron is the element that is leached more (with ~ 2 % in NaOH at 150°C). At lower temperatures, the release is found to be less pronounced (between 0.25 and 0.7 %). In the cement pore solution, the release of iron in solution is quasi-constant at 0.3 %, regardless of the temperature or the time of exposure. Titanium shows the same pattern as iron, but its release is less abundant, with the maximum found at 0.15 %.

Zirconium exhibits a very atypical behavior; the amount released is low (~ 0.04%) and is the same regardless of the temperature, the time of exposure, or even the leaching medium (as long as the solution is alkaline). This finding indicates that the zirconium is probably not part of the glassy basalt phase but instead resides in separate crystals that are resisting the corrosiveness of the alkali solutions.

Uranium is not found to be leached in large amounts from the DUAGG pellet. Even though the pellet is composed of more than 90% uranium, a maximum of only 0.008% was leached. The NaOH solution is slightly more corrosive to the uranium than the cement pore solution is. As noted for almost all the other elements, the higher exposure temperatures are associated with greater releases of material. At 6 months, the results for the cement pore solution do not follow the trend developed in the previous periods of exposure. Because only one sample is obtained for each time interval, it will be interesting to see the 1-year results to determine see if a change in the reaction is actually occurring.

#### 4. CONCLUSIONS

The corrosion of the DUAGG surface after 6 months at 150°C in saturated cement water appears to be minimal. A protective coating of cement hydration crystals covers the DU particles as well as the interstitial basalt. Thus far, no deleterious crystals have resulted from alkali–aggregate reactions. From the ICP results, the amount of uranium leached from the DUAGG pellet appears to be very low. These results show that the stability of the DUAGG pellets is very good in cement pastes, at least after 6 months of exposure. Therefore, concretes containing DUAGG aggregates should be stable. However, more time is needed to interpret these test results and extended-exposure tests are continuing.

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