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DURABILITY OF DEPLETED URANIUM AGGREGATES (DUAGG) IN DUCRETE SHIELDING APPLICATIONS

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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(1). 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_2) sintered with a synthetic-basalt-based binder. This study was designed to investigate possible deleterious reactions that could occur between the cement paste and the DUAGG. After 13 months of exposure to a cement pore solution, no deleterious expansive mineral phases were observed to form either with the DUO_2 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 proceed more slowly than expected. This finding may indicate that DUAGG/ DUCRETE (depleted uranium concrete) casks could have service lives sufficient to meet the projected needs of DOE and the commercial nuclear power industry.

INTRODUCTION

In 1993, the U.S. Department of Energy (DOE) Office of Environmental Management began investigating the potential use of depleted uranium (DU) in heavy concretes, or DUCRETE (depleted uranium concrete). 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_2) sintered with a synthetic-basalt-based binder that ultimately coats the sintered DUO_2 particles and retards their surface reactions.(2,3) The preliminary work on DUAGG and DUCRETE properties has been performed at INEEL.(4,5) The DUCRETE material would be of beneficial use in the fabrication of casks for the transport and storage of spent nuclear fuels because of the additional shielding it provides.(6) 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_2 aggregates (DUAGG) were postulated, based on a review of the literature, as generating a possible failure mechanism 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. 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 reaction between the sintered DUO_2 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

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the constituents of the basalt-like binder could create deleterious expansive mineral growths. These reactions could be similar to alkali–aggregate (alkali–silica) reactions, which can disrupt normal concrete structures, generating cracks and spalling.(7,8,9)

Therefore, in an attempt to assess the potential impacts of DUO₂ 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.

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 Starmet CMI (formerly Carolina Metals, Inc.), the DUO₂/basalt aggregates were cleaned in an ultrasonic bath with distilled/deionized (DI) water to remove surface residuals. These intact aggregates of DUAGG were then tested for reactivity using a modified ASTM C289-01(10) 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- μ 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. A test sponsored by the Electric Power Research Institute (EPRI) (11) indicates that while the outside of the cask would remain at ambient temperature, the side adjacent to the fuel could reach temperatures varying from 50 to 140EC. The higher temperature was obtained for off-normal conditions when the ventilation channels in the cask were blocked. Therefore, we chose to conduct studies at three temperatures: ambient, 66EC, and 150EC.

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), 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 (~1 kg), which would not permit us to generate enough of a selected fraction size of the material. Therefore, we decided to use a whole pellet of DUAGG for the test. The pellets were exposed to the solutions for different lengths of time to allow ongoing monitoring of the reaction. 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 volume/surface ratio of 10. This ratio is often used in leaching tests such as American Nuclear Society (ANS) 16-1 and appeared to be a better choice for our experiment. A ratio of 10 is much higher than that found in the “real” conditions in a concrete, where the amount of interstitial liquid is very low — especially when the concrete is aging and the liquid is used to form cement hydrates. Using a higher liquid/solid ratio is a way to accelerate the reactions taking place in the experiment.(12,13)

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 ± 0.01 cm². The average weight was found to be 6.39

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± 0.01 g, and the average volume was 0.784 ± 0.002 cm³. The measured density of these DUAGG pellets was 8.15 g/cm³. With a pellet surface area of 5.8 cm² and a leachate surface/volume ratio of 1:10, 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 ~300 g of a type I-II Portland cement with ~ 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- μ m filter. The inductively coupled plasma (ICP) analysis showed that the solution contained ~ 3 mg/L of barium, ~1800 mg/L of potassium, ~300 mg/L of sodium, and ~ 50 mg/L of strontium. The resulting pH of the solution was ~ 12.6.

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. These vessels can withstand high temperatures as well as pressures up to 220 psi. After the sample was introduced with its curing solution into the Teflon liner, the vessel was closed tightly to prevent any leakage. The preparation of the vessels and the static corrosion test were performed in aerated conditions.

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 time intervals were 30 days, 60 days, 90 days, 180 days, 360 days, and 2 years. One vessel was prepared for each time interval chosen, and the solutions were not changed at any time during the experiment. Thus the concentration at any given time is a measure of cumulative extraction rather than incremental extractions. 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- μ m filter for analysis of aluminum, silicon, uranium, alkalies, and other measurable elements by inductively coupled plasma & atomic emission 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 I) to determine the degree of corrosion of the aggregate surfaces.

Consistent with the guidelines of ASTM C295-98,(14) 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.

RESULTS AND DISCUSSION

The 30-, 60-, 90-, 180-, and 390-day (1-, 2-, 3-, 6- and 13-month) tests have been 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 I.

The ICP analyses of the leachate solutions at 1, 2, 3, 6, and 13 months showed that the total mass leached from the DUAGG pellet was low even after 13 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 I), is illustrated in Figs. 1 to 3. The figures show the results for three leachates (DI water, NaOH solution, and cement pore solution) at five time intervals (1, 2, 3, 6, and 13 months) for three temperatures (20, 66, and 150°C).

**Table I. 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

The low leachability of uranium in alkaline solutions, as shown in Fig. 2, indicates that the dissolution 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. However, at 13 months in DI water, the amount of uranium leached was found to be 0.15% at higher temperatures (66 and 150EC). The SEM observations of the surface for this time interval are not available, and this sudden rise cannot yet be explained. One possible hypothesis is that the basaltic binder on the surface became completely eroded, thus providing no more protection against the dissolution of the UO_2 phase.

The amount of titanium leached varied from 0 to 0.15%, with higher concentrations released in NaOH solution at higher temperature. The release of zirconium was found to be between 0.02 and 0.10%, with higher concentrations found in both of the alkaline solutions. Unlike all the other elements, the release of zirconium does not appear to be influenced by temperature. Zirconium exhibits a very atypical behavior; the amount released is low ($\sim 0.04\%$) and is the same regardless of the temperature, the time of exposure, or even the leaching medium (as long as the solution is alkaline). However, at 13 months in cement pore solution, the amount released doubled to reach 0.1%. This finding indicates that the zirconium is probably not part of the glassy basalt phase but instead resides in separate crystals that resist the corrosiveness of the alkali solutions.

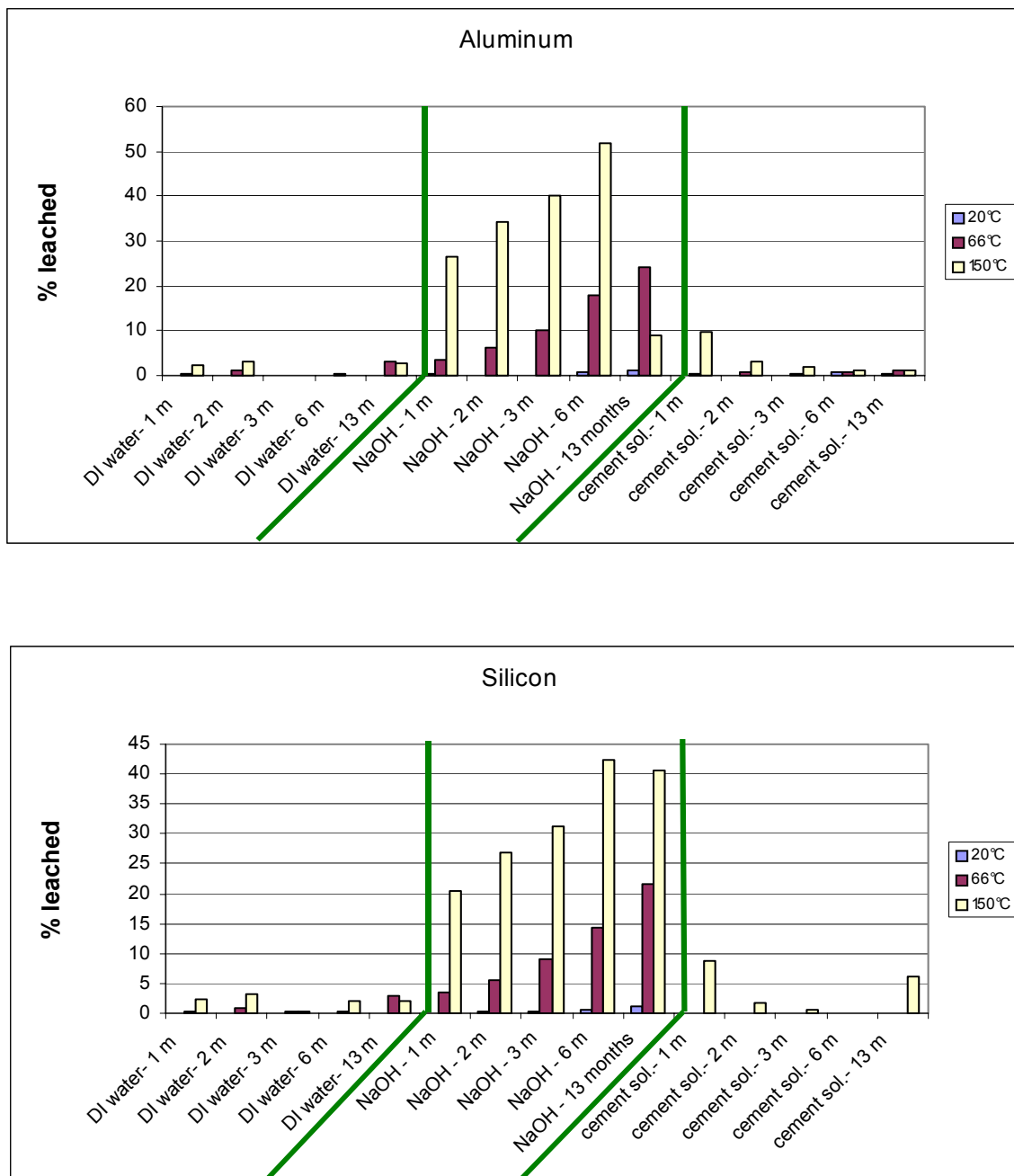


Fig. 1. Normalized leaching of aluminum and silicon.

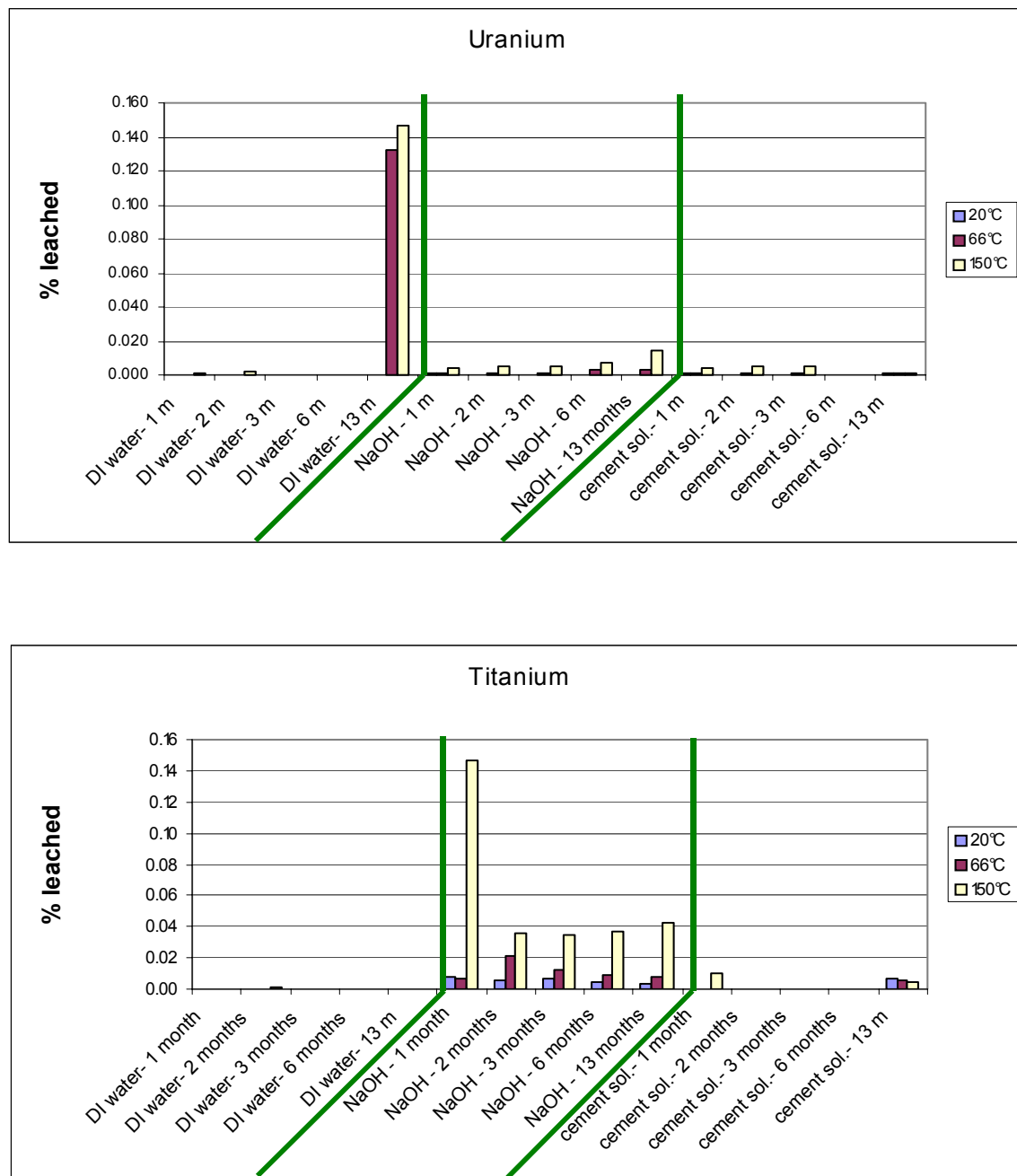


Fig. 2. Normalized leaching of uranium and titanium.

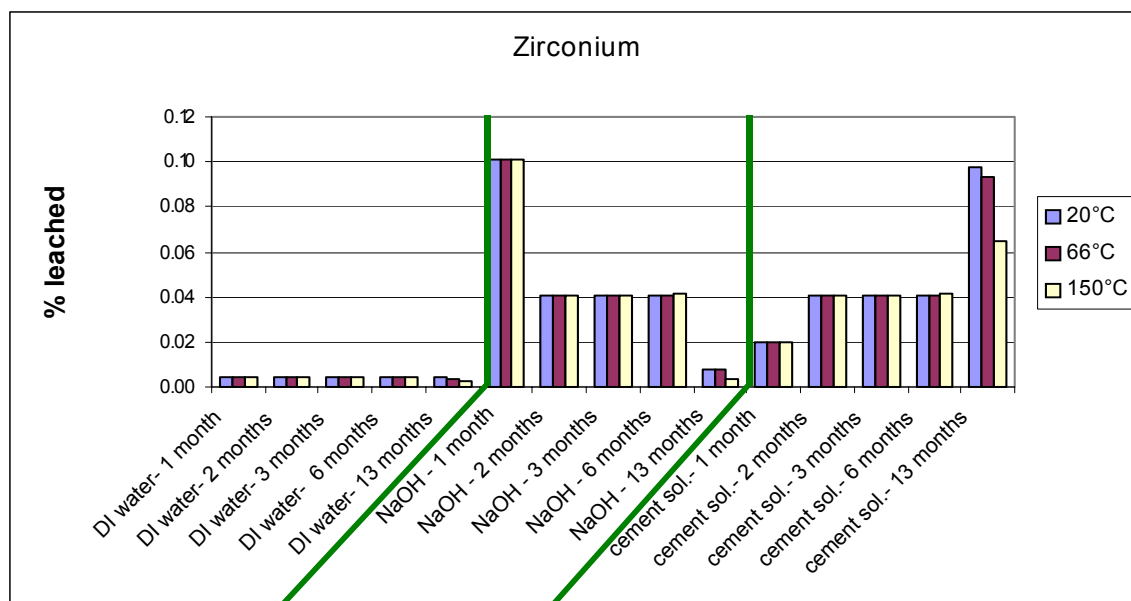


Fig. 3. Normalized leaching of zirconium.

The leaching of iron was low, with a maximum of ~ 2% in NaOH at 150EC after 6 months of exposure. 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&0.5 %, regardless of the temperature or the time of exposure.

Much worse results were obtained for aluminum and silicon, with 53 and 43% maximum leached, respectively, in the sample kept in the 1 N NaOH solution after 6 months of exposure. The NaOH solution is the most corrosive medium in terms of DUAGG stability, and elevations in temperature increase the amount of material released. The larger extractions obtained for aluminum and silicon point to the fragility of the basalt phase when it is 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. 4A), 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 appear white on a BSE image. Using this feature, one can see that in the sample kept in DI water, the repartition of UO₂ 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

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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.

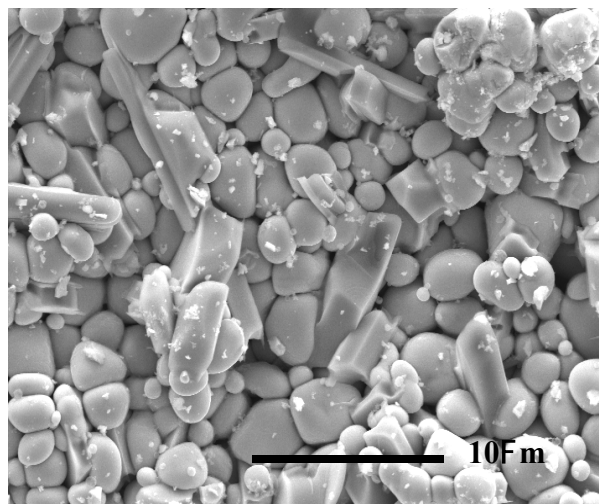
Of the chemicals that produce the basalt phase, aluminum and silicon are the elements that leach the most in the cement pore water and even more strikingly in the 1 *N* NaOH solution. Both of these solutions are very basic, with pH above 12.6; at these high pHs, both alumina and silica are extremely soluble. The amount leached was higher for NaOH and also increased with the temperature and time of exposure. This indicates that the dissolution of the basalt/glass phase is progressive in NaOH solution. 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 the alkali–aggregate reaction (rosette type), as illustrated in Fig. 4B. These crystals could also have originated from the recrystallization of the glass constituents that had been dissolved.

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 each of the two elements). However, for all temperatures, the amount that was released decreased with time. At 13 months, ~ 1% aluminum and less than 0.1% silicon were released (with the exception of the 6.2% release of silicon at 150EC). This decrease can be explained by the formation of a protective layer of cement hydration products and/or minerals containing calcium, aluminum, and silicon covering the surface of the DUAGG pellet. SEM examination of the pellets at 6 months of exposure confirmed that the grains of DUO_2 are almost invisible (Figs. 4C and 4D). This finding has been previously explained in corrosion studies of natural basalt rocks. (8,9)

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 ~ 0.15% was leached in the worst-case conditions, in DI water at temperatures of 66 and 150EC after 13 months of exposure. Except for these two conditions, the amount released was found to be less than 0.01% after 13 months of exposure. 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. In the cement pore solution, the amount of uranium leached increased slightly during the first 6 months and then started to decrease, indicating probably that recrystallization of the dissolved uranium has occurred.

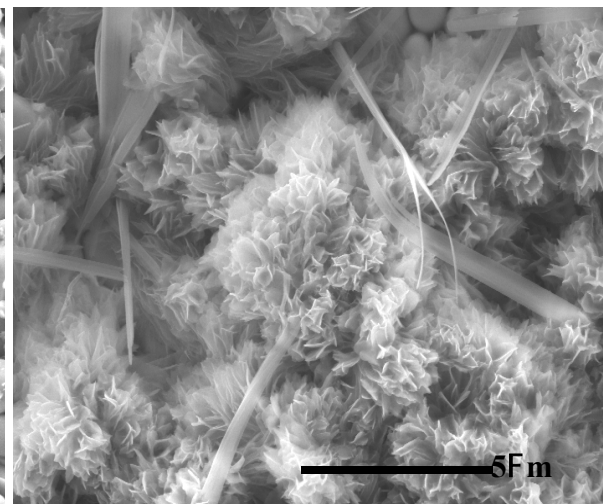
The release of uranium is of great importance and has been compared with data found in the literature on release rates of uranium from UO_2 . Wronkiewicz et al.(15) have published results of UO_2 leaching over a long-term period (2 to 8 years) at 90EC but using a very small amount of flowing leachant (0.075 mL/3 days). They found that the overall release of uranium (i.e., that comprised of the uranium in the leachant plus the uranium attached to the walls of the vessel but excluding the uranium in secondary crystals on the surface of the aggregate) varied from 0.1 to 15 mg/(m²•day), depending upon the conditions.

The work of Thomas and Till (16) was very similar to our project except that the duration of the tests they performed was limited to 8 days. They found a release rate of 5 mg/(m²•day) for uranium when UO_2 was kept in DI water at 70EC. In our work, after 1 month of exposure at 66EC in DI water, the amount of uranium released from the DUAGG was found to be only 0.25 mg/(m²•day), 20 times less than in the



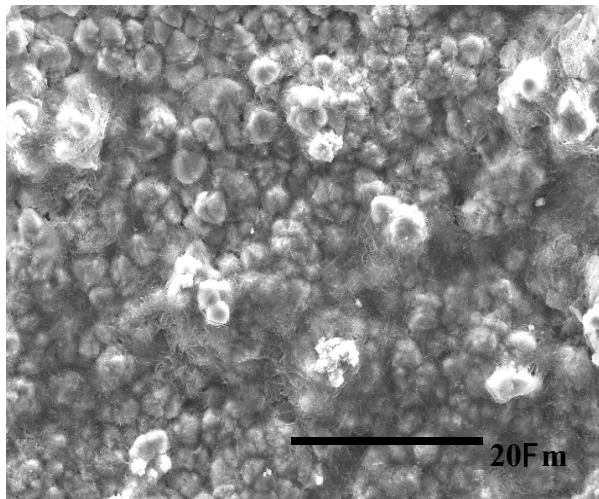
4A DI water

The oblong particles contain Ti and some Mg, while the rounded ones are made of DU.



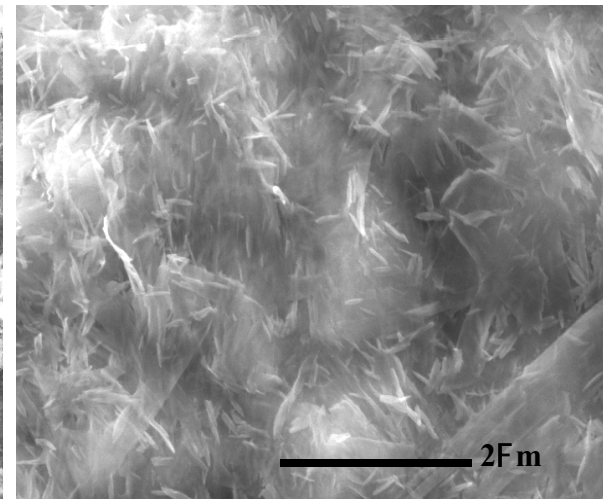
4B NaOH

Alkali-reaction products contain Na, Al, Si, Ca, and Ti.



4C Cement pore solution

Cement hydration products cover the DU particles.



4D Cement pore solution

Cement hydration products contain Ca, Si, and Al.

Fig. 4. SEM images (secondary electrons) obtained after 6 months of exposure at 150EC

work of Thomas. This comparison provides strong evidence that the basalt phase effectively protects the

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UO₂. The results of the release rates of uranium from the DUAGG pellet are presented in Table II. The release rate was calculated as follows:

$$R(mg \bullet m^{-2} \bullet day^{-1}) = \frac{U(mg \bullet L^{-1}) \bullet V(L)}{SA(m^2) \bullet D(day)} \quad (Eq. 1)$$

where U is the concentration of uranium in the leachate, V is the volume of leachant, SA is the surface area of the DUAGG pellet, and D is the duration of the leach period.

The temperature dependance of the release of ionic species was shown to conform to an Arrhenius diffusion over the range of temperature studied.

**Table II. Release Rate of Uranium [mg/(m²•day)]
from DUAGG under Different Conditions**

		20EC	66EC	150EC
DI water	1 month	0.17	0.25	3.78
	2 months	0.07	0.29	2.48
	3 months	0.04	0.04	0.04
	6 months	0.04	0.02	0.02
	13 months	0.06	29.98	33.89
1 N NaOH	1 month	2.69	2.69	12.11
	2 months	0.54	1.46	7.10
	3 months	0.36	1.43	4.95
	6 months	0.18	1.46	2.82
	13 months	0.06	0.08	0.09
Cement solution	1 month	0.66	0.66	2.06
	2 months	0.54	0.65	0.64
	3 months	0.36	0.43	0.47
	6 months	0.20	0.23	0.13
	13 months	0.36	0.39	0.40

CONCLUSIONS

The corrosion of the DUAGG surface after 13 months at 150°C in saturated cement water appears to be minimal under the conditions of our tests with a 10 to 1 ratio of the volume of leachant to the surface area of DUAGG. This ratio represents a worse-case scenario, in which the time is artificially accelerated by allowing more dissolution/reactions to occur via the use of a larger volume of leachant. In concrete, the

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interstitial liquid phase decreases with time as liquid is used to form hydrated cement reaction products. This interstitial liquid phase becomes rapidly saturated, and the kinetics of the reactions would be slowed compared with those of our experiment.

A protective coating of cement hydration and/or recrystallization of glass dissolution products covers the DU particles as well as the interstitial basalt in the alkaline solutions. Thus far, no deleterious crystals have resulted from alkali–aggregate reactions when the samples were kept in cement pore solution. From the ICP results, the amount of uranium leached from the DUAGG pellet appears to be very small, except when the pellet was kept in DI water for 13 months. Because the SEM observations have not yet been performed, a conclusive explanation for this sudden rise is not possible. It is important to remember that the “real” conditions under which the DUAGG would be used is with cement pore solution; the two other media studied are extreme situations that will not be found in a transport/storage cask.

When compared with other studies, the release rate of uranium from the DUAGG is much lower than for UO_2 alone. These results show that the stability of the DUAGG pellets is very good in cement pastes, at least after 13 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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