

ICEM05-1371

DURABILITY OF DEPLETED URANIUM AGGREGATES IN DUCRETE SHIELDING APPLICATIONS

Catherine H. Mattus
Oak Ridge National Laboratory
Oak Ridge, TN, USA 37831-6202
E-mail: mattusch@ornl.gov

Leslie R. Dole
Oak Ridge National Laboratory
Oak Ridge, TN, USA 37831-6166
E-mail: dolelr@ornl.gov

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. 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. Depleted uranium aggregate (DUAGG) is formed of DU dioxide (DUO₂) sintered with a synthetic-basalt-based binder. This study was designed to investigate possible deleterious interactions that could occur between the cement paste and the DUAGG.

We suspected the possibility of expansive alkali-aggregated reaction (ARR) between DUAGG and the cement paste because the fine DUO₂ grains are embedded in a basalt sintering phase that is close to the composition of a basaltic glass. Therefore, it is possible that alterations of this DUAGG sintering material with cement paste and the subsequent oxidation of the DUO₂ to DU₃O₈ could result in swelling that would mechanically disrupt the depleted-uranium concrete (DUCRETE) shielding. So, the accelerated corrosion of DUAGG pellets was studied for 27 months at three temperatures, 20, 67, and 150°C in DI water, 1 N NaOH solution. This is a conservative, more stringent modification of the ASTM C289-01 method to measure aggregate interactions with the cement pore liquids. The saturated

cement pore solutions were made from (a) ordinary Portland cement (OPC) and (b) a mix of OPC, blast furnace slag (BFS), and fly ash. The DUAGG and DUO₂ pellets were completely immersed in the solution with a 10 to 1 ratio of the volume of leachant to the surface area of the pellet and no change of the solution during the test (static cumulative test). There was no special handling of the pellet or the solutions to control the oxidation state. The analyses of the leachates were made, and the pellet was observed by scanning electron microscopy to identify the nature of the products formed during the cure. For comparison, the same tests were performed on pellets of high-fired DUO₂ for up to 9 months.

Several conclusions can be drawn:

- The total release of uranium is minimal under the conditions of our tests
- The release of uranium from DUAGG is lower than from a DUO₂ pellet: under most conditions, a difference of at least one order of magnitude exists between the DUAGG and DUO₂ release rates.
- The release of uranium is the worst in DI water, followed by the 1N NaOH solution.
- The cement pore solutions have a beneficial effect for both DUAGG and DUO₂ on the uranium release. For DUO₂, the maximum release was as much as 260 times lower in BFS and 750 times lower in OPC than in DI water. For DUAGG, the maximum release was as much as 600 times lower in BFS and 70 times lower in OPC than in DI water.

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 DU concrete (DUCRETE) [1]. The DUAGG material was developed at Idaho National Engineering and Environmental Laboratory (INEEL) and consists of DU dioxide (DUO_2) sintered with a synthetic-basalt-based binder that coats the sintered DUO_2 particles and retards their surface reactions [2,3]. 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 [4].

The uranium release from UO_2 and spent fuel has been studied by many researchers. Most of the studies agree on the steps that take place when spent fuel is dissolved under repository conditions. In a first stage, the oxidized layer at the surface of the matrix is released into the leaching solution. Then the oxidants attack the UO_2 surface, and more uranium is released and oxidized. The oxidized uranium precipitates as U(VI), and the reaction continues. Oxidizing conditions in a repository enhance the corrosion of UO_2 [5]; however, secondary uranyl alteration minerals can form and grow onto the surface, thus protecting the fuel material from further dissolution [6]. Uranyl oxide hydrates are the first to precipitate, but when the surrounding medium provides other species, uranyl silicates can be found [7,8]. The durability of basaltic glass, both synthetic in the laboratory and as a natural analog found in nature, has also been studied extensively, especially to determine the long-term durability of the high-level waste immobilized in glass.

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 \sim 12.6) and contains alkalis (sodium and potassium). The potential reaction products of the UO_2 and/or the constituents of the basalt-like binder could create deleterious expansive mineral growths, similar to alkali-aggregate (alkali-silica) reactions (AAR), which can disrupt normal concrete structures [9,10,11]. To assess the potential impacts of DUO_2 -DUAGG aggregates on the longevity and durability of DUCRETE casks, Oak Ridge National Laboratory (ORNL) used a modified standardized American Society for Testing and Materials (ASTM) exposure test that accelerates such surface interactions. Subsequent scanning electron microscopy (SEM) examination of the surface of the uranium aggregate showed the alteration products that were formed.

EXPERIMENTAL

Description of the Durability/Leaching Test

The intact aggregate pellets of DUAGG were tested for reactivity according to a modified ASTM C289-01[12]

method to measure interactions with the cement pore liquids. This test simulated the expected service temperatures and the chemical environment for a cask made of concrete containing spent nuclear fuel (SNF).

This method had to be modified to better match the conditions that would exist in a cask. The ASTM test called for the reaction of crushed material with a 1 N sodium hydroxide (NaOH) solution at 80°C for 24 h, followed by the analysis of the solution for silicon.

In our test, the temperatures were modified to cover the temperatures that could be seen in SNF casks, as reported by the Electric Power Research Institute (EPRI) [13]. Three temperatures were selected for the test: ambient, 67°C, and 150°C. Three leaching media were chosen for the testing: DI water (reference), two cement pore solutions (actual scenario), and a 1 N NaOH solution (worst-case scenario). The volume (leachate, cm^3) to surface (pellet, cm^2) ratio of 10 cm was selected. Because we wanted to examine the surfaces of the samples after exposure, one pellet of DUAGG and two pellets of high-fired DUO_2 were used in the test series. The pellets were exposed to the solutions for different lengths of time to allow ongoing monitoring of the reaction. The exposure times were 30 days, 60 days, 90 days, 180 days, 360 days, and 24 and 27 months. The tests were run under atmospheric conditions in a closed system, and the solutions were not changed during the experiment.

DUO_2 Materials Tested

The almond-shaped DUAGG aggregates were obtained from Starmet CMI (formerly Carolina Metals, Inc.). They were \sim 1.59 cm long, 0.95 cm wide, and 0.64 cm thick, with a measured average surface area of $5.77 \pm 0.01 \text{ cm}^2$. The average weight was found to be $6.39 \pm 0.01 \text{ g}$, and the average volume was $0.784 \pm 0.002 \text{ cm}^3$. The measured density of the DUAGG pellets was 8.15 g/cm^3 . With a pellet surface area of 5.8 cm^2 and a leachate surface to volume ratio of 1:10, the volume of liquid used in the sealed leach vessels was 58 mL for each DUAGG pellet. Some of the pellets had surface defects, and the most regular ones were selected. However, the irregularity and roughness of the surfaces (as was later seen using electron microscopy) probably induced a large error in the surface measurement.

The high-fired DUO_2 pressurized water reactor (PWR) pellets were available at ORNL. They were cylindrically shaped with a diameter of 0.685 cm and height of 1.39 cm. The weight of one pellet was 5.355 g and the density 10.52 g/cm^3 . Two pellets were used for each test to obtain enough solution for analysis. The outside surfaces of the pellets presented fewer defects than the DUAGG pellet.

Leaching Solutions

Type II DI water was used, as well as a commercial 1 N NaOH solution. The cement pore solutions were obtained by mixing a combination of dry blend additives with a stoichiometric excess of DI water. The ordinary Portland cement (OPC) pore solutions were prepared using a Type I-II Portland cement. The pH of the solution was ~12.6. The blast furnace slag (BFS) solution was prepared by mixing a blend of 40% of BFS and 60% of the same OPC. The BFS-DUO₂ solution resulted from a mixture containing 40% OPC, 30% Class F fly ash (Southeastern Fly Ash Co., Inc.), and 30% BFS. Both OPC and BFS were from Lone Star Industries, Inc.

Experimental Setup

The containers used for the tests at elevated temperatures were armored Teflon vessels from a microwave digestion system. One vessel was prepared for each time interval, test specimen, and leachate chosen. The solutions were not changed at any time during the experiment. Thus the concentration at any given time was a measure of cumulative extraction. The preparation and curing of the samples were performed under atmospheric conditions with no control for CO₂ or O₂ interaction with the uranium pellets or solutions. Both the DUAGG and DUO₂ pellets were rinsed with DI water, dried, and then introduced into the selected solution. The vessels were sealed tightly to prevent any leakage.

At the end of each exposure period, after cooling, the pellets were removed and were rinsed with DI water to eliminate the salts left by the solution prior to being dried for further SEM examination. The liquid phase was sampled, and the volume was measured. The solution was acidified with concentrated nitric acid to bring the solution to a pH of <2. The leachate was then analyzed for total composition by ICP-AES. The empty containers were rinsed with a solution of 10% nitric acid to dissolve and analyze the deposits that may have formed on the surfaces of the Teflon liners. The quantities of each element leached were compared with the initial content of a DUAGG pellet to determine the degree of corrosion of the aggregate surfaces. In the case of the high-fired DUO₂, the theoretical composition of 88.148 wt % of uranium was used instead of the analyzed value found during the analysis (80 ± 14 wt %). Consistent with the guidelines of ASTM C295-98 [14], the surfaces of the exposed aggregates were subsequently examined and compared by SEM and energy dispersive X-ray fluorescence (EDX) analyses using a Phillips XL30FEG.

RESULTS AND DISCUSSION

Chemical Analyses of the Leachates

The ICP analysis of the DUAGG revealed that the most abundant elements in the pellet are uranium, silicon, and titanium. For calculating the percentage of uranium

released from the DUO₂ pellets, the theoretical value was used instead of the one measured by ICP. The maximum "normalized" leaching, which is the amount leached relative to the initial amount of the specific element in the DUAGG or DUO₂, is calculated as shown in Eq. (1). The results are presented in Table 1.

$$\% \text{ Amount leached} = \frac{((C_{Li} \cdot V_{Li}) + (C_{Ri} \cdot V_{Ri})) - (C_{Bi} \cdot V_{Bi})}{A_i} \quad (1)$$

where C_{Li} and V_{Li} are the measured concentrations (mg/L) of the specific element (i) and the volume of leachate (L) at the time interval considered, C_{Ri} and V_{Ri} are the measured concentrations (mg/L) in the rinse of the vessel for that element and the volume (L) of acid used to rinse, C_{Bi} and V_{Bi} are the measured concentrations (mg/L) for (i) and the volume (L) of the blank, and A_i is the amount (mg) of the element (i) in the initial DUAGG pellet.

Release of Uranium from the DUO₂ Aggregates

Even though the tests with DUO₂ did not last as long as those with DUAGG, the results allow some definitive conclusions:

1. The most important one is that the release of uranium is lower from DUAGG than from the DUO₂ pellet. Under most conditions, a difference of an order of magnitude difference exists between DUAGG and DUO₂ release rates.
2. The release of uranium increases when the temperature increases, in almost all cases.
3. DI water is the worst solution in terms of the inhibition of the release of uranium. It is followed by the NaOH solution, then by the OPC and BFS cement pore solutions.
4. Cement pore solutions have a beneficial effect for both DUAGG and DUO₂ on the reduction of uranium release. For DUO₂, the maximum release was as much as 260 times lower in BFS and 750 times lower in OPC than in DI water. For DUAGG, the maximum release was as much as 600 times lower in BFS and 70 times lower in OPC than in DI water.

The release rates of uranium from DUAGG and high-fired UO₂ have been compared with data found in the literature for release rates of uranium from UO₂ or simulated nuclear fuel. The results for the release rates of uranium from the DUAGG pellet are presented in Table 1. The release rate was calculated as follows:

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

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.

Wronkiewicz et al. [7] have published results of UO_2 leaching over a long-term period (2 to 8 years) at 90EC, but a very small amount of flowing leachant (0.075 mL/3 days) was used. They found that the overall release of uranium varied from 0.1 to 15 $mg \cdot m^{-2} \cdot day^{-1}$, depending upon the conditions. The work of Thomas and Till [15] was very similar to our project, except that the duration of their tests was limited to 8 days. They found a release rate of 5 $mg \cdot m^{-2} \cdot day^{-1}$ for uranium when UO_2 was kept in DI water at 70EC. In our work, after 1 month of exposure at 67EC in DI water, the amount of uranium released from the DUAGG was found to be only 0.25 $mg \cdot m^{-2} \cdot day^{-1}$, 20 times less. Jégou [16] studied the alteration of clad spent fuel in groundwater at room temperature and calculated a rate of fuel dissolution in the range of 1 to 2 $mg \cdot m^{-2} \cdot d^{-1}$.

Our work with DUO_2 pellets at 20EC in DI water was also falling in the range of 1 to 2 $mg \cdot m^{-2} \cdot d^{-1}$. Very interestingly, the results obtained with DUAGG under the same conditions were at least two orders of magnitude lower. The combination of uranium and basalt release resulted in a competition between the different species (uranium, aluminum, silicon, iron, titanium, and zirconium) for interaction with the solution species. This comparison provided strong evidence that the basalt phase effectively protects the UO_2 .

Release of the Basalt Components from DUAGG

The basalt phase in DUAGG represents only a minor part of the aggregate, about 9 wt % of the mass of the pellet. The release of each of these basalt components was very different, depending upon the leaching solution they were exposed to. As much as ~54 wt % silicon was released from a DUAGG pellet, while the release of zirconium did not exceed 0.30 wt %. For aluminum and silicon, the most aggressive media were the 1N NaOH solution and the DI water. The release was also more pronounced at higher temperatures for these two solutions. In cement pore solutions, the release of silicon and aluminum was completely different and much lower. This soluble Si, Al, and Fe later forms a precipitant that protects the surface of the DUAGG. The mixture of OPC and BFS gave even better results; the releases measured at 67 and 150EC were $\leq 5\%$. The release of iron was found to be moderate with a maximum leached of ~6% in DI water at 150EC. Titanium and zirconium appeared to be quite stable under all the conditions tested, and only very small amounts were leached (<0.3% was measured). This could indicate that the basalt glass was not really homogeneous and that some crystalline compounds were present within the glassy phase.

Table 1: Uranium release rates ($mgGm^{-2}Cd^{-1}$) obtained for DUAGG and high-fired DUO_2

Time in months	TEC	DI Water		NaOH		OPC		BFS	
		DUAGG	DUO_2	DUAGG	DUO_2	DUAGG	DUO_2	DUAGG	DUO_2
1	20	0.065	2.9	0	68	0.10	0.12	-	0.35
	67	0.14	47	0	51	0.10	0.32	-	0.16
	150	3.7	208	9.4	20	1.50	0.64	-	0.30
2	20	0.012	1.9	0	54	0	0	-	0
	67	0.23	17	0.92	15	0.10	0	-	0
	150	2.4	106	6.6	16	0.09	0	-	0
3	20	0	1.1	0	59	0	0.05	-	0.11
	67	0	30	1.08	15	0.06	0.05	-	0.05
	150	0.044	75	4.6	9	0.10	0.13	-	0.12
6	20	0	1.8	0.02	34	0.03	0.54	-	0.17
	67	0	48	1.30	3.7	0.06	1.05	-	0.59
	150	0.006	274	2.7	12	0	0.56	-	2.84
9	20	-	1.3	-	16	-	0.06	-	0.09
	67	-	12	-	2.5	-	0.20	-	0.23
	150	-	526	-	29	-	0.31	-	2.05
13	20	0.046	-	0.12	-	0.01	-	0	-
	67	30	-	0.70	-	0.02	-	0.004	-
	150	34	-	3.2	-	0.08	-	0.03	-
20	20	-	-	-	-	-	-	0.10	-
	67	-	-	-	-	-	-	0	-
	150	-	-	-	-	-	-	0	-
24	20	0.005	-	0.02	-	0.69	-	0.01/0.03	-
	67	0.9	-	0.27	-	0.01	-	0.03/0.03	-
	150	12	-	1.0	-	0	-	0.05/0.02	-
27	20	3.8	-	0.01	-	0	-	-	-
	67	1.3	-	0.17	-	0.01	-	-	-
	150	44	-	8.1	-	0.07	-	-	-

The topic of basaltic glass alteration had been studied extensively since basalt is a natural analogue for nuclear waste glass. All the papers reviewed showed that, after the initial release, the dissolved elements from the basalt increased in the solution and started precipitating. The alteration products formed a film around the surface of the sample that slowed the release rate considerably. Techer [17] reported a release rate four orders of magnitude below the initial maximum rate. In the case of DUAGG, we can see that the release rate of uranium was also reduced, as was expected by the developers of this material. The presence of such a protective film on DUAGG was observed by SEM.

SEM Examinations of Surface and Fractures

In order to determine if any deleterious phases were formed, the surfaces of the DUAGG samples at 27 months of exposure were examined by SEM equipped with EDX. For the high-fired DUO₂ pellets, the samples collected after 9 months of exposure were examined. Each pellet of DUAGG or DUO₂ was cut at the center into two pieces, one piece including the outside surface of the pellet and a fractured piece allowing a view of the profile from the outside surface to the center of the pellet. These two fragments were coated with a film of carbon to render the surface conductive to electrons and then examined by SEM.

High-fired DUO₂ Pellets

After 9 months in DI water at 20EC, the outside surface of the pellet was corroded and the DUO₂ grains appeared pitted. The corrosion increased with temperature and, at 67EC, most of the UO₂ grains appeared to be cracked, altered and pitted. In Fig. 1 at 150EC, the grain corrosion was extreme (pitting, cracking). Locally some crystals of dehydrated schoepite [(UO₂)₈O₂(OH)₁₂·12H₂O] were visible. The fractured sample showed individual grains that were ready to detach from the pellet.

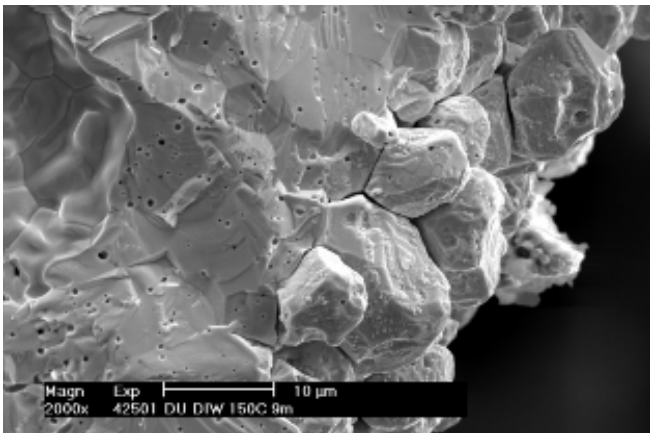


Fig. 1. Fracture surface of high-fired DUO₂ after 9 months at 150EC in DI water.

This illustrates the progression of the corrosion process: the areas around the grains are attacked by the solution. The grains are detached from the material, and then the solution can have access to new grains further inside of the pellet and continue the corrosion.

In NaOH solution kept at 20EC, the outside of the pellet did not show any change from the original morphology. The fracture revealed the presence of an alteration zone that was marked by the breakage of the uranium grains along the grain sides while the non-attacked zone showed uranium grains broken inside the grain itself. At 67EC, the alteration was more pronounced, with the outside surface of the pellet showing recrystallization of DUO₂, probably schoepite, in an outside layer ~1 μm thick. The corrosion was also visible by the appearance of grain contours. The grain corrosion was even worse at 150EC, with the recrystallized dehydrated schoepite forming a layer (~5 μm thick) on the outside of the pellet (Fig 2).

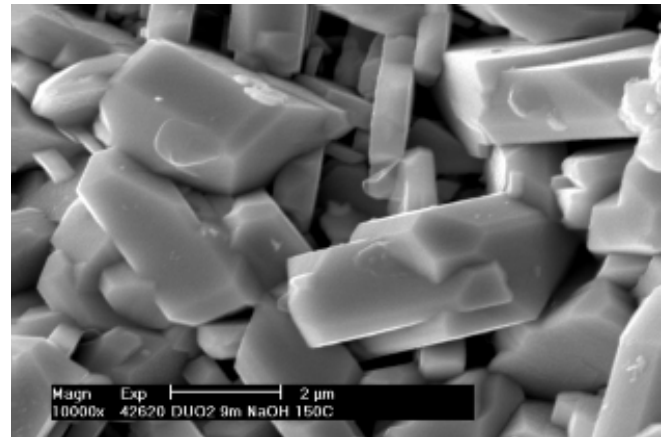


Fig. 2. Schoepite crystals formed on the surface after 9 months at 150EC in a 1N NaOH solution.

The SEM observations were very similar for both cement pore solutions. After 9 months at 20EC, the outside of the cylinder showed recrystallization of calcium carbonates or calcite. These crystals of calcite did not form a continuous layer for BFS, but for OPC the layer was estimated to be ~5 μm thick. The fracture of the pellet revealed that the uranium grains were not corroded and the grains, boundaries were not visible. The amount of calcite visible increased with temperature; and, for the OPC, the crystallization of the calcium carbonates showed another morphology at 67EC. The fracture of the cylinder showed that the pellet was not damaged at all. Some etching on the surface of grains was observed at 150EC. The outside surface of the pellet showed that the UO₂ had been attacked, with some recrystallized uranium phases being formed. The

fractured sample showed more cracks than at lower temperatures, and some calcite was visible locally. Some rare pockets of altered grain were also found within the pellet near the surface for the BFS pellet; however, the uranium grains appeared intact without pitting or cracking in the fractured cylinders kept in both cement pore solutions.

DUAGG Pellet

After 27 months, the outside surface of the pellet kept at 20°C in DI water showed little alteration. Locally, small crystals made from the basalt components were covering the DUO₂ grains as shown in Fig. 3. The fractured sample showed that the recrystallization products from the basalt had penetrated the pellet for <10 μm and that there was no continuous layer of secondary products on the outside of the pellet. At 67°C, rhombohedral crystals were visible on the outside surface of the pellet. They were mixed with submicron crystals that resembled those seen at 20°C. The hexagonal crystals contained aluminum and titanium only and could be a form of aluminum titanate. No outside layer surrounding the pellet was seen.

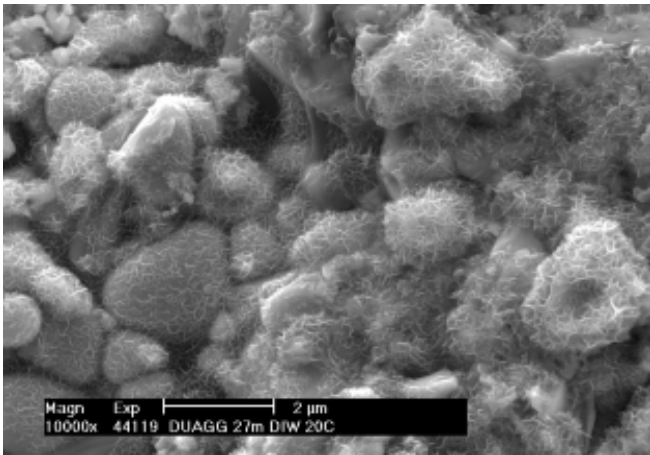


Fig. 3. DUAGG pellet with recrystallization products from the basalt phase after 27 months at 20°C in DI water.

The alteration of the basalt increased with temperature, and at 150°C, the outside surface of the pellet showed only the round grains of DUO₂. The basalt was completely gone, and only small amounts of recrystallization products were visible. On the fractured sample, it could be seen that the zone where the basalt was attacked was about 100 μm thick. The grains of UO₂ were also being attacked.

The outside surface of the pellet kept at 20°C in NaOH solution was covered with very finely crystallized

deposits made of small plates (~1 μm or less) that contained uranium, magnesium, titanium, and iron. Others contained mostly iron and magnesium. Observation of the fractured pellet indicated that no outside layer was formed and that the basalt was not damaged. At 67°C, the outside surface was completely covered by needle-like crystals containing sodium, silicon, and calcium. The fractured pellet showed that these needles were deposited above a dense layer surrounding the pellet that contained mostly aluminum, silicon, and calcium with some sodium. Next to the border, the basalt phase appeared locally to be like a gel with lots of cracks. This gel-like phase contained aluminum, silicon, sodium, calcium, and uranium. Locally on the outside, some very large crystals were found that sometimes contained only sodium and other times sodium with silicon and uranium or sodium and uranium. Titanium and calcium could also be found locally in addition to the other elements. Some of the needle-like crystals were also seen within a depth of 50 μm of the surface inside of the pellet. The uranium grains next to the border were rounded, meaning that the fracture took place within the basalt phase, not within the DUO₂ grains. Except on the very border, the uranium grains were not attacked or pitted.

At 150°C, the outside surface of the pellet looked like an oursinite [(H₃O)₂ (Co, Ni, Mg) (UO₂)₂(SiO₂)₂·2.3H₂O] with a dense layer of needles made of uranium, titanium, sodium, and silicon. Locally on the surface, some large agglomerations of crystals containing sodium, aluminum, and silicon were visible. Other recrystallization products were spherical and contained silicon, calcium, titanium, and iron. The fractured sample showed a dense layer surrounding the pellet that was between 5 and 10 μm thick. The uranium grains were not fractured but appeared rounded and damaged. The protective layer contained some crystals in which uranium was mixed with the basalt components.

The pellets exposed to OPC cement pore solution at 20°C appeared unchanged from the original morphology. On the outside surface, some crystals resulting from the basalt recrystallization were sporadically present. Underneath, the uranium oxide grains were visible, but the basalt appeared slightly eroded. The fracture showed the DUO₂ grains fractured through the grain, indicating that the basalt was in good condition. No outside products were visible along the border. This sample appeared to have sustained little or almost no corrosion. At 67°C, the outside surface of the sample was covered with large needle-like crystals containing calcium, silicon, and some titanium. Locally within the needles, orthorhombic pseudo-cubic crystals of perovskite-like crystals (calcium and titanium oxide) were visible. The fracture showed the presence of a dense layer of needles on the surface, as thick as 20 to 30 μm. The basalt appeared to be altered within a depth of ~50 μm inside the pellet. At 150°C, the surface of the sample was also covered with recrystallization products

containing calcium, silicon, aluminum, and titanium. Instead of needles, the crystals were in the form of plates. The fractured sample showed the thickness of this layer to be $<5 \mu\text{m}$. Next to the outside surface, the DUO_2 grains appeared rounded, indicating that the fracture occurred in the basalt phase.

Like the surface of a pellet in the OPC solution, at 20°C the surface of the pellet exposed to BFS cement pore solution was covered with recrystallization products containing calcium and titanium. These crystals appeared as agglomerations of needles deposited on top of the pellet. The fracture of the sample showed that there was not a continuous layer around the pellet. Also, the basalt was intact, even next to the border. At 67°C the surface was covered with recrystallization products that were not as well crystallized as at 20°C . Locally, some of the products resembled hydrated calcium silicates (CSH) as seen in cement paste. The fractured sample showed the basalt to be altered within a depth of $\sim 200 \mu\text{m}$. At 150°C , the surface of the pellet was covered with a thick layer of crystal agglomerations (Fig. 4) with mainly two types of crystals: massive prisms containing aluminum, silicon, and potassium, and others that appeared more as plates and contained aluminum, silicon, potassium, and calcium. Locally, some needle-like crystals containing mostly silicon and calcium were visible.

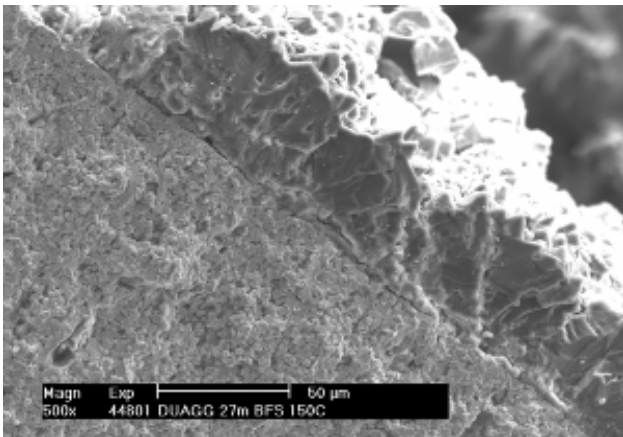


Fig. 4. Fracture surface of the DUAGG pellet, showing an outside layer of about $50 \mu\text{m}$ thickness, after 27 months in BFS pore solution at 150°C .

CONCLUSIONS

The corrosion of DUAGG pellets was studied for as long as 27 months at three temperatures, 20 , 67 , and 150°C , in DI water, in 1 N NaOH solution; and in two saturated cement pore solutions, one of OPC and one of a mix of OPC, BFS, and fly ash. The pellets were completely immersed in the solution with a 10 to 1 ratio of volume of leachant to surface area of the pellet. The solution was not changed during the test (static

cumulative test). There was no special handling of the pellet or the solutions to control the oxidation state. The leachates were analyzed, and the pellets were observed by SEM to identify the nature of the products formed during the exposure. For comparison, the same conditions and testing were performed on pellets of high-fired DUO_2 for 9 months. Several conclusions can be drawn from the results gathered:

- The total release of uranium was minimal under the conditions of our tests: after 27 months at 150°C , maxima ranging from 0.40% to 0.0003% uranium (amount leached divided by the total amount of uranium present in the pellet before testing) were released from DUAGG and from 0.90 to 0.0005% from high-fired DUO_2 after 9 months at 150°C .
- The release of uranium from DUAGG was lower than from a DUO_2 pellet; under most conditions, there was a difference of at least one order of magnitude between DUAGG and DUO_2 .
- The release of uranium was worse in DI water than in the 1 N NaOH solution.
- The cement pore solutions had a beneficial effect for both DUAGG and DUO_2 on uranium release. For DUO_2 , the maximum release was as much as 260 times lower in BFS and 750 times lower in OPC than in DI water. For DUAGG, the maximum release was as much as 600 times lower in BFS and 70 times lower in OPC than in DI water.
- The release rate of uranium has been compared with data found in the literature for release rates of uranium from UO_2 or simulated nuclear fuel, and it was lower for DUAGG. It was comparable for DUO_2 in the presence of DI water, but the contact of pure uranium pellets with cement pore solutions decreased the release rate.

The combination of uranium and basalt in DUAGG resulted in a competition between the different species (uranium, aluminum, silicon, iron, titanium, and zirconium) for interaction with the solution species. The examination of the samples after more than 2 years of cure provided strong evidence that the basalt phase effectively protected the UO_2 . A protective coating of recrystallization of basalt dissolution products covered the DU particles and formed a very dense layer that slowed or stopped the exchange of species between the pellet and the solution. The examination showed no deleterious crystals that may have resulted from AAR when the samples were kept in cement pore solution. The nature of the compounds formed after curing for the high-fired DUO_2 was similar to the nature of those reported in the literature for SNF or surrogate SIMFUEL, with observation of crystals such as schoepite. For the DUAGG pellets, such products were not visible; and the protective crystals such as those found in alteration of

nuclear glasses were observed. The results obtained tended to prove that DUAGG behaves as a nuclear glass. Such glasses are currently used for the long-term storage of high nuclear wastes. They have been studied extensively during the years and are approved as being safe for storage of long-lived radionuclides.

REFERENCES

1. R. R. Price, M. J. Haire and A. G. Croff, "Depleted Uranium Uses Research and Development Program," Proc. Waste Management 2001 Symposium, Tucson, Arizona (February 25-March 1, 2001).
2. W. J. Quapp and P. A. Lessing, "Radiation Shielding Composition," U.S. Patent No. 5,786,611 (July 28, 1998).
3. W. J. Quapp and P. A. Lessing, "Radiation Shielding Composition," U.S. Patent No. 6,166,390 (December 26, 2000).
4. L. R. Dole and W. J. Quapp, "Radiation Shielding Using Depleted Uranium Oxide in Nonmetallic Matrices," ORNL/TM-2002/111, Oak Ridge National Laboratory (August 2002).
5. D. W. Shoesmith, "Fuel Corrosion Processes Under Waste Disposal Conditions," *J. Nucl. Mater.* **282**, 1–31 (2000).
6. P. Trocellier, C. Cachoir, and S. Guilbert, "A Simple Thermodynamical Model to Describe the Control of the Dissolution of Uranium Dioxide in Granitic Groundwater by Secondary Phase Formation," *J. Nucl. Mater.* **256**, 197–206 (1998).
7. D. J. Wronkiewicz, et al., "Uranium Release and Secondary Phase Formation during Unsaturated Testing of UO₂ at 90°C," *J. Nucl. Mater.* **190**, 107-127 (1992).
8. P. C. Burns, R. C. Ewing, and M. L. Miller, "Incorporation Mechanisms of Actinides Elements into the Structures of U⁶⁺ Phases Formed during the Oxidation of Spent Nuclear Fuel," *J. Nucl. Mater.* **245**, 1–9 (1997).
9. S. A. Marfil et al., "Relationship Between SiO₂, Al₂O₃, CaO, K₂O, and Expansion in the Determination of the Alkali Reactivity of Basaltic Rocks," *Cement Concrete Res.* **28**(2), 189–196 (1998).
10. W. A. Tasong et al., "Aggregate-Cement Chemical Interactions," *Cement Concrete Res.* **28**(7), 1037-1048 (1998).
11. W. Prince et al., "Similarity Between Alkali-Aggregate Reaction and the Natural Alteration of Rocks," *Cement Concrete Res.* **31**(2), 271–276 (2001).
12. ASTM C289-01, "Standard Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method)," American Society for Testing and Materials, 2001.
13. "Performance Testing and Analyses of the VSC-17 Ventilated Concrete Cask," EPRI report TR-100305, Project 3073-1, PNL-7831, UC-85, final report 1992, Pacific Northwest Laboratory and Idaho National Engineering Laboratory (1992).
14. ASTM C295-98, "Standard Guide for Petrographic Examination of Aggregates for Concrete," American Society for Testing and Materials, 1998.
15. G. F. Thomas and G. Till, "The Dissolution of Unirradiated UO₂ Fuel Pellets under Simulated Disposal Conditions," *Nucl. Chem. Waste Manage.* **5**, 141–147 (1984).
16. C. Jegou et al., "Identification of the Mechanisms Limiting the Alteration of Clad Fuel Segments in Aerated Carbonated Groundwater," *J. Nucl. Mater.* **326**, 144–155 (2004).
17. I. Techer et al., "Dissolution Kinetics of Basaltic Glasses: Control by Solution Chemistry and Protective Effect of the Alteration Film," *Geological Geology* **176**, 235–263 (2001).