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PERFORMANCE ASSESSMENT MODEL FOR DEGRADATION OF TRISTRUCTURAL-ISOTROPIC (TRISO) COATED PARTICLE SPENT FUEL

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The U.S. Department of Energy is conducting research and development on generic concepts for disposal of spent nuclear fuel and high-level radioactive waste in multiple lithologies, including salt, crystalline (granite/metamorphic), and argillaceous (clay/shale) host rock. These investigations benefit greatly from international experience gained in disposal programs in many countries around the world. The focus of this study is the post-closure degradation and radionuclide-release rates for tristructural-isotropic (TRISO) coated particle spent fuels for various generic geologic repository environments.[1,2,3]

The TRISO particle coatings provide safety features during and after reactor operations, with the SiC layer representing the primary barrier. Three mechanisms that may lead to release of radionuclides from the TRISO particles are: (1) helium pressure buildup[4] *that may eventually rupture the SiC layer, (2) diffusive transport through the layers (solid-state diffusion in reactor, aqueous diffusion in porous media at repository conditions), and (3) corrosion*[5] *of the layers in groundwater/brine. For TRISO particles in a graphite fuel element, the degradation in an oxidizing geologic repository was concluded to be directly dependent on the oxidative corrosion rate of the graphite matrix*[4]*, which was analyzed as much slower than SiC layer corrosion processes. However, accumulated physical damage to the graphite fuel element may decrease its post-closure barrier capability more rapidly.*

Our initial performance model focuses on the TRISO particles and includes SiC failure from pressure increase via alpha-decay helium, as exacerbated by SiC layer corrosion[5]*. This corrosion mechanism is found to be much faster than solid-state diffusion at repository temperatures but includes no benefit of protection by the other outer layers, which may prolong lifetime. Our current model enhancements include constraining the material properties of the layers for porous media diffusion analyses. In addition to evaluating the SiC layer porosity structure, this work focuses on the pyrolytic carbon layers (inner/outer-IPyC/OPyC) layers, and the graphite compact, which are to be analyzed with the SiC layer in two modes: (a) intact SiC barrier until corrosion failure and (b) SiC with porous media transport. Our detailed performance analyses will consider these processes together with uncertainties in the properties of the layers to assess radionuclide release from TRISO particles and their graphite compacts.*

I. INTRODUCTION

The TRISO particle fuels consist of numerous coated fuel particles, slightly less than 1 mm in diameter, that are embedded in graphite cylinders (i.e., compacts, which are then loaded into hexagon-columns of graphite fuel elements), or graphite spheres[5] called pebbles. Ref. 4 indicates about 5,580 TRISO particles are embedded in graphite compacts (graphite cylinders 4.928 cm long and 1.245 cm in diameter). The TRISO particles themselves consist of a micro spherical fuel kernel (U-Th-Ox) ~500-600 μm in diameter, surrounded by four layers/coatings (Figure 1). These layers[6] are: (1) an innermost porous pyrolytic carbon layer; (2) a dense inner pyrolytic carbon (IPyC) layer; (3) a silicon carbide (SiC) layer; and (4) a dense outer pyrolytic carbon (OPyC) layer. These particles show potential long lifetimes as waste forms[4,5] and there has been recent increased interest in the U.S. in high-temperature gas reactors that utilize TRISO particle fuel, and which have high efficiency due to the high temperatures and high fuel burnup (i.e., the fraction of uranium that fissions).

Two recent studies[4,5] have evaluated the potential releases from TRISO spent fuel in geologic repository environments. Ref. 5 conducted experiments to measure hydrologic properties (i.e., porous media diffusivities) and corrosion rates for the various materials of the TRISO fuel pebbles/particles in a number of fluid compositions at relevant temperatures. The measurements were made on separated materials rather than intact pebbles or particles. The diffusive transport behavior was measured for the graphite matrix (i.e., from the pebble) using isotopes of hydrogen, chlorine, strontium, and cesium. Corrosion rates were measured for the graphite matrix, the SiC (non-irradiated and irradiated), and the pyrocarbon. Ref. 5 also

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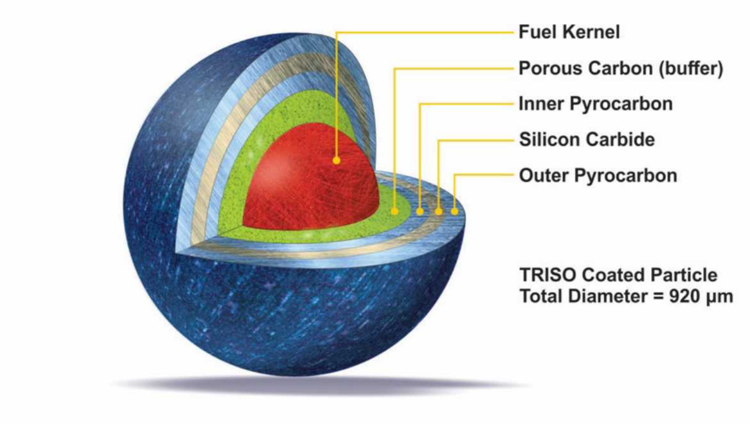
measured leaching rates of ThO_2, UO_2, and (Th-U) mixed oxide (MOX) fuel kernels in various fluids over a range of redox conditions.

Figure 1. Schematic drawing of a TRISO fuel particle (not to scale) with four protective layers (pyrocarbon = pyrolytic carbon).[3]



The conclusions of Ref 5 included (a) the graphite matrix of the pebble serves as a porous medium that reduces water contact with the TRISO particles, (b) porous media diffusion is the primary transport mechanism through the graphite matrix of the pebble, (c) pyrolytic carbon and SiC layers have lifetimes from 1000's to 100,000's years depending on conditions (temperature, fluid composition, radiation dose), and (d) fuel kernels may have relatively long lifetimes (≥100,000's years) depending on conditions. Their study[5] also recommended further work evaluating (a) the porous media behavior of the graphite matrix and how it changes due to graphite corrosion, (b) the effect of internal pressure build-up on the layer lifetime, (c) mass transport through the graphite matrix, and (d) development of an integrated model of the total set of processes.

In the second study, Ref 4 constructed a performance assessment of hexagonal graphite fuel elements (with TRISO particles in graphite compacts) degrading within an unsaturated (oxidizing) geologic repository system. The primary waste form barrier in that work was the graphite matrix of the fuel element (or the compact graphite matrix in a second scenario without the fuel element), which slowly oxidatively corrodes to release radionuclides uniformly over tens of millions of years. Ref 4 evaluated stochastic failure (rupture) of the SiC layer of the TRISO particle due to combined effects of SiC corrosion and internal pressure build-up from helium generation. Their analyses included statistical variability of the SiC strength, and concluded that, if protection by the OPyC layer is ignored, then lifetimes on the order of thousands to hundreds of thousands of years were expected.[4] Although Ref. 4 estimated that protection by the OPyC layer could extend SiC layer lifetime to millions of years, they made the simplifying assumption that the particle lifetime was short compared to graphite matrix corrosion (of either the fuel element or the compact). Hence for their model Ref 4 assumed the TRISO particles had released all radionuclides uniformly distributed throughout their spherical approximations (of either the entire fuel element or just of a single graphite compact) of corroding graphite. The oxidative corrosion rate of the graphite sphere was then used to assess radionuclide releases from the TRISO fuel directly to the host rock. Given the very low shear strength of graphite and the axial cylindrical channels traversing the hexagonal elements, we do not view the fuel elements as being likely physical barriers to advective flow/transport.

As recommended by Ref 5, we have begun the construction of a quantitative integrated model on the scale of a fuel compact.[1,2,3] Our integrated model considers major features, events, and processes to evaluate stochastically the release of radionuclides under varying repository conditions through time. In this initial work, we present our analyses of the primary coupled process considerations for the SiC layer of the TRISO particles. The analyses assess the relative relevance of these processes at repository conditions. The next stage considers material properties for constraining their porous media transport processes. This includes assessment of the uncorroded *in situ* SiC layer porosity and its connectivity (or lack thereof). The SiC layer may remain effectively impermeable until after corrosion breach, or fracture. If it does, the initial analyses here represent the first stage of degradation and radionuclide release from the particles. We are currently compiling material properties for each of the TRISO particle layers and the graphite compact. These data will be included in our performance model for quantitative stochastic analyses.

II. MODEL DESCRIPTION AND RESULTS

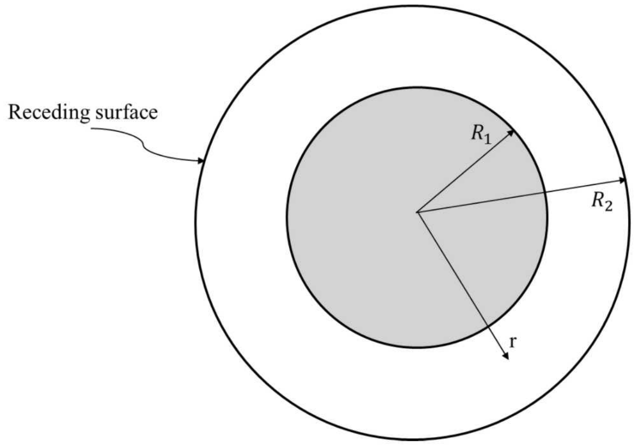
Numerous studies have been reported on measuring radionuclide releases from TRISO fuel under reactor conditions[7,8,9,10] and modeling[11,12,13] these processes. For these studies the fuel may attain an operating temperature of 1200°C. However, under geological repository conditions the temperatures are much lower, and the fuel will evolve over much longer time than operations in the reactor.

As a first step in our analyses, we consider that the SiC barrier layer of the TRISO particle is unfractured, and its porosity is minor and unconnected (like a metallic barrier layer). For radionuclide release from the TRISO particle, our model includes the effects of SiC barrier layer corrosion while radionuclides simultaneously decay and diffuse through the barrier layer. Barrier corrosion creates a moving-boundary diffusion problem.

Transport within a domain with a moving boundary is a well-studied problem,[14,15] but we have not found such analysis for TRISO particles. In this work we apply the analysis techniques developed for heat conduction with an ablating surface to a corroding diffusion barrier. In our case, this problem is simpler because the corrosion rate is independent of the radionuclide concentration. This results in a linear system of equations for each time step that does not require an iterative solution.

The TRISO model is simplified with a core region that has a uniform radionuclide concentration, enclosed within a barrier of SiC that provides a diffusion barrier for radionuclides as shown in Figure 2. The core corresponds to the region $0 \leq r \leq R_1$. For TRISO fuel the core consists of the fuel (e.g., UO_2) kernel, the porous pyrolytic carbon layer, and the IPyC layer. The core is not discretized in this simplification as each layer has a diffusivity that is much, much higher than for the SiC layer. In this case, the core radionuclide concentration is well approximated as spatially uniform. Because of corrosion, the SiC barrier thickness decreases with time, thus resulting in a moving-boundary problem. The moving-boundary problem is reduced to a fixed-boundary problem using two transformations.[2] To maximize the release, the concentration at R_2 is taken to be zero (i.e., a rapid radionuclide removal at the boundary). For convenience, the initial concentration in the barrier is taken as zero also, but the analysis can use an initial concentration profile when available.

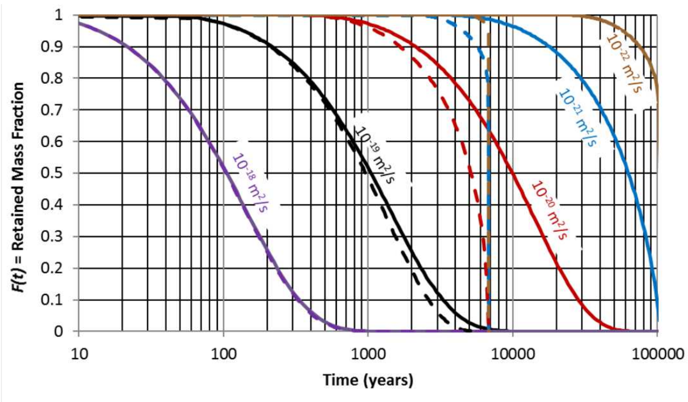
Figure 2. Schematic of spherical shell silicon carbide barrier with inner and outer radii of R_1 and R_2, respectively, and surrounding a core (light gray) with a spatially uniform radionuclide concentration. The outer radius decreases with time due to corrosion.[2]



The mass fraction of released radionuclide (from the core, or conversely the retained mass fraction in the core) is analyzed for a broad range of diffusivities in SiC. This evaluation was performed because diffusivity data in SiC have not been found for the temperature conditions of interest (25°C to ~90°C), and so this large parametric range was analyzed to identify threshold values where radionuclide release transitions between diffusion to corrosion dominated processes. Note that radionuclide decay occurs concurrently, and the decay rates of specific radionuclides are taken into account in the analyses.[2]

Figure 3 shows the fraction of radionuclide mass remaining within the core and corroding SiC barrier as a function of the diffusivity in the barrier and the SiC corrosion rate. Corrosion rates from Ref. 5 of 4.5×10^{-5} and 2.9×10^{-6} g/m^2/day (at 90°C and 25°C, respectively), correspond to corrosion lifetimes of ~7,000 years (dashed lines) and ~100,000 years (solid lines), respectively. The retained radionuclide mass fraction is shown in Figure 3 for diffusivities of 10^{-18}, 10^{-19}, 10^{-20}, 10^{-21}, and 10^{-22} m^2/s. For diffusivities of 10^{-18} and 10^{-19} m^2/s, the diffusion time-scales are 39 and 390 years, respectively, much shorter than the shortest corrosion time-scale of 7,000 years. Therefore, for these diffusivities the radionuclide would diffuse out of the SiC barrier layer before corrosion would remove this layer. There is little difference between the solid and dashed lines for these diffusivities, indicating that diffusive release dominates corrosion release (i.e., insensitive to the rate of SiC layer corrosion).

Figure 3. Fraction of radionuclide mass remaining within the core and corroding SiC barrier as a function of the diffusivity in the barrier and corrosion rate. The diffusivity values are shown in the same color as the lines. Solid lines and dashed lines correspond to corrosion lifetimes of 100,000 years and 7,000 years, respectively.[2]



However, for a diffusivity of 10^{-20} m^2/s, the diffusion time-scale is 3,900 years. As shown in Figure 3, for this diffusivity (and smaller values), there are significant differences in the retained radionuclide mass fraction depending on the corrosion rate (dashed vs. solid curves). For a corrosion time-scale of 100,000 years (solid curves), which is much longer than the diffusion time-scale, diffusion can release nearly all the radionuclide before the SiC layer is fully removed by corrosion (compare the red solid curve to the 100,000 years corrosion lifetime). However, for corrosion time-scales of 7,000 years, both diffusion and corrosion contribute. Complete release occurs essentially when the SiC layer is fully removed by corrosion (note the red dashed curve).

For diffusivities of 10^{-21} m^2/s or smaller, the diffusion time-scale is 39,000 years or longer. Therefore, for a corrosion time-scale of 7,000 years, most of the radionuclide is released by corrosion as shown by the blue dashed curve truncated at ~7000 yrs. Similarly, for a diffusivity of 10^{-22} m^2/s the diffusion time-scale is 390,000 years, and radionuclide release is dominated by corrosion for the ~100,000 years corrosion time-scale.

Diffusivities larger than the bounding value indicate that if brine contacts the SiC barrier, diffusion may release radionuclides before the barrier has corroded. However, for diffusivities that are smaller than the bounding value, then diffusive releases will be minimal until the barrier is removed/breached by corrosion. This conclusion may be different if the physical properties of SiC (e.g., connected porosity) allow porous media transport to occur prior to corrosion breach at expected repository temperatures. Therefore, the SiC layer may act as a barrier for up to ~100,000 years, if the diffusivities remain lower than about 10^{-22} m^2/s. The SiC lifetime could be longer if the OPyC layer provides corrosion protection by reducing surface area contacted by brine and providing additional strength to withstand internal pressure increase.

III. CONCLUSIONS

In this work we analyzed the combined simultaneous effects of bulk (e.g., solid-state) diffusion of a radionuclide through the SiC barrier, barrier corrosion, and radioactive decay for TRISO particles. The analysis is general for a single corroding barrier with specified radionuclide bulk diffusivity and decay rate. From the time-scales for bulk diffusion, corrosion, and decay, estimates were obtained on how each process would affect the radionuclide release. Because we did not find the bulk diffusivities in SiC of interest at repository temperatures, a broad range of diffusivities was used in the analysis. Release may occur predominantly via diffusion before the SiC barrier has corroded if the bulk diffusivity is more than about 10^{-20} m^2/s. For bulk diffusivity less than 10^{-21} m^2/s significant diffusional release should not occur prior to SiC corrosion removal.

In the next stage of this work, the physical characteristics and porous media properties of the TRISO particle layers and of the encapsulating compact graphite matrix (or pebble graphite matrix), are to be constrained for integration into a stochastic model degradation/release from the graphite compact containing TRISO particles. Graphite oxidative corrosion, as analyzed previously,[4] appears to be the slowest process of all and can be ignored to a first approximation relative to aqueous diffusion through a saturated graphite pore structure.

Based on the analysis in this work, TRISO fuel is a very robust design for retaining radionuclides if the protective SiC layer remains intact and precludes radionuclide transport by advection or aqueous-phase diffusion. Measurements have shown that if the layers composed of pyrolytic carbon and silicon carbide are contacted by brine, corrosion of these layers may occur.[5] Even if the corrosion rate for the OPyC layer measured at 90°C by Ref. 5 is assumed to be applicable over geological time-scales, the OPyC layer should last more than about 10^6 years. The long lasting OPyC layer would provide at least some corrosion protection to the silicon carbide (SiC) layer that is covered by the OPyC layer.

The measurements of Ref. 5 show that SiC corrodes much faster in brine than does the pyrolytic carbon. Therefore, if the OPyC layer is damaged such that brine contacts the SiC layer surface uniformly, then there is the potential for the corrosion of SiC with concurrent radionuclide release as analyzed here. Regardless how rapidly the SiC layer corrodes, there is potential radionuclide release by bulk diffusion through SiC. Protecting the SiC layer from corrosion increases the time needed for diffusion through this barrier. Slow release through the SiC layer provides a barrier. Quantitative evaluation of diffusive transport in porous media (the compact graphite matrix and TRISO layers) at repository conditions is our next major model development.

In our future work, we will evaluate the uncertainty range of potential radionuclide release via aqueous diffusive pathways in a coupled performance degradation/release model that integrates quantitatively porous media behavior of the TRISO particle layers and the surrounding compact matrix graphite.

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