

PuO₂ – A Powerful Oxidizing Agent? C.E. Whiting¹, D. P. Kramer¹, D. Cairns-Gallimore², and C. D. Barklay¹,
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Introduction: Since the inception of using pressed and sintered PuO₂ fuel as the thermal source for radioisotope based thermoelectric power systems for space exploration applications, there have been a number of unexplained chemical phenomena, such as: reaction of PuO₂ with the graphite dies used to press the pellets; outgassing of CO and CO₂ from fueled General Purpose Heat Sources (GPHS) [1,2]; and the pervasiveness of superstoichiometric plutonium oxides (PuO_{2+x}) [3-6]. Chemical thermodynamic modeling, coupled with an in-depth literature review, suggests the presence of either OH [7] or atomic O [6] in the PuO₂ crystalline structure as a single root source for many of these phenomena. While there has been no work to conclusively determine whether OH or O is the species present in the PuO_{2+x} crystal, it is the opinion of these authors that a stronger case is made for OH at this point in time.

This interstitial OH/O has a tendency to outgas under high temperatures (>1200 °C) and/or very low pressures [4,5,8]. While these temperatures and pressures may seem extreme for laboratory conditions, they closely mimic the conditions that PuO₂ is exposed to during fuel pellet processing, storage, and when in outer space. Additionally, PuO₂ will readily uptake OH/O, even in the presence of extremely small quantities of water vapor (>6 torr), making it very difficult to obtain and maintain pure PuO₂. Both OH free radicals and atomic O are extremely powerful oxidizing agents, and their release from the PuO₂ lattice structure could induce oxidative corrosion in nearby materials.

PuO₂ is expected to first encounter conditions that can induce outgassing during the hot-pressing of the PuO₂ powder in graphite dies into a fuel pellet. Oxidative erosion of the dies is expected to occur as a result of outgassed OH/O.

PuO₂ is also expected to encounter conditions that induce outgassing during storage and flight. Outgassing at this stage is likely to cause oxidative erosion of surrounding materials as well as ingrowth of potentially detrimental gaseous byproducts.

In this paper the authors will review the mechanisms governing the uptake and outgassing of the OH/O in the PuO_{2+x} crystal, and using thermodynamic modeling, provide mechanisms suggesting how PuO_{2+x} interacts with the materials and equipment commonly found in PuO₂ processing and fuel pellet applications.

Potential implications of these mechanisms on system performance are also discussed.

Review: In 2000 [6] Haschke published a seminal report describing a mechanism for the generation of the superstoichiometric oxide of plutonium, which has been a nagging question hanging over the heads of the actinide chemists since the 1950s [3-5]. In this report, Haschke published the following reaction:



which shows how water, adsorbed to the PuO₂ surface reacts to create the superstoichiometric oxide with hydrogen gas as a byproduct. Additionally, Haschke showed that PuO_{2+x} can be formed in a dry atmosphere containing only O_{2(g)} and H_{2(g)} [9]. They hypothesized that the generation of PuO_{2+x} under these conditions was due to the formation of H₂O at the PuO₂ surface, which could then undergo the reaction presented in equation 1.

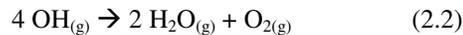
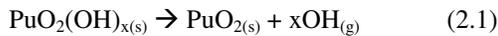
Later, Penneman and Paffett hypothesized that the PuO_{2+x} interstitial species was OH [7] based on bond length/strength calculations using Zachariasen's formulations [10], though no new experimental evidence was provided. Since a quantitative determination of H_{2(g)} produced was not provided in Haschke's report, there is no conclusive experimental evidence regarding the identity of the interstitial species.

Regardless of the identity of the species, outgassing of either powerful oxidizing agent would lead to significant oxidative corrosion of materials in close proximity to the PuO_{2+x}. It has been known for quite some time that PuO_{2+x} can be reduced to the stoichiometric oxide, PuO₂, by heating the PuO_{2+x} up to 800 °C in an inert (e.g. He) or reducing (e.g. H₂) atmosphere or by heating up to 1200 °C in air [3-5]. More recently, however, it was shown that PuO_{2+x} begins to undergo significant structural change in temperatures as low as 100 °C when also placed in ultra-high vacuum [8]. Combined, the data from these reports suggest that a gaseous oxidizing agent is being released from the PuO_{2+x} lattice.

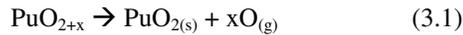
Results: PuO₂ fuel pellets are likely to experience conditions that will induce outgassing (i.e. T > 1200 °C) during the hot-pressing operation, storage, and flight. Therefore, in order to model the behavior of the outgassed species, we chose to use 1200 °C as our

operating temperature for all theoretical calculations.

Since we cannot conclusively identify which species is being outgassed, we propose that the outgassing occurs by one of the following sets of reactions:

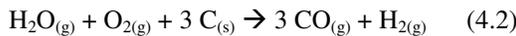


or

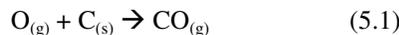


Since OH and O are unstable even at 1200 °C, we expect that the products from equations 2.2 and 3.2 likely represent a vast majority of the final outgassed products from PuO_{2+x} , if given adequate conditions to reach equilibrium. However, given the limited space observed in the hot-press process and within GPHS units, it is possible that some OH free radicals or atomic O are able to react with nearby materials before the reactions listed in equations 2.2 and 3.2 can occur. Using these outgassing products, we then modeled the behavior of these products with materials used during processing and in the GPHS.

The reactions between PuO_2 and the graphite dies used during the fuel pellet processing can be explained by a reaction of the outgassed OH/O with the graphite die. If OH is used as the interstitial species, the following reactions are thermodynamically predicted:



With O as the interstitial species:



In both cases, an erosion of the graphite is expected as the C reacts to form carbon monoxide gas.

A similar set of reactions is expected to be observed in a fueled GPHS kept in storage or in flight. The first material that the outgassed products would encounter is the cladding, which is made of a material that was chosen, in part, because it is chemically inert. After escaping the cladding, the outgassed products would encounter the graphite shell used to house the fuel pellets, producing the same reactions observed with the graphite dies used in the fuel pellet processing. One of the key products of these reactions is CO, which explains why spontaneous generation of CO is observed in a GPHS.

Clearly, the superstoichiometric oxide is capable of producing strong oxidizing agents when it is placed under high temperatures and low pressures, and these agents can cause detrimental effects to materials found

near the PuO_2 .

Consequences: Erosion of the graphite dies used during fuel processing is likely to cause significant damage to this equipment since the dimensional tolerances on the dies are very small.

Erosion of the graphite found in GPHS leads to 2 concerns: structural integrity of the components and ingrowth of undesirable gaseous products. Regarding structural integrity of the graphite components, their primary purpose is to act as a safety measure and prevent the release of the fuel. In a worst case scenario, 1 kg of fuel is calculated to erode just over 10 g of C. Considering the over-engineering generally involved in fuel safety, this is not expected to be a significant factor in component integrity.

Ingrowth of undesirable gaseous products, on the other hand, can be a more significant concern. Some of the outgassed products could escape and be available to induce oxidative corrosion to other, more sensitive components (e.g. some designs would allow these gaseous products to interact with the solid state thermoelectrics). The truly ironic twist to this scenario is that the CO released from the graphite reaction is a fairly strong reducing agent, making reductive corrosion a concern as well [1]. Finally, the ingrowth of other gases, such as CO, will decrease the thermal conductivity of the unit, leading to a decrease in the overall power output. For missions that are evacuated to space, the ingrowth of other gases is not typically a point of concern [1,2], however, for missions that require planetary protection, the sealed nature of the unit makes gaseous ingrowth a factor that should be considered.

References:

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