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Editorial: Plutonium legacy storage and degradation

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Editorial on the Research Topic
Plutonium legacy storage and degradation

The safe and secure management of special nuclear materials (SNM) is a matter of international importance. Of these SNM materials, plutonium is of special importance given its radiotoxicity and use in nuclear weapons. However, plutonium also can be used as a nuclear fuel for power generation in both current generation (thermal) and future generation (fast) reactors to generate large amounts of low carbon energy. It is produced in significant quantities during the irradiation of uranium fuels in thermal reactors and can be recovered for recycling into new fuels by nuclear fuel reprocessing technologies such as the PUREX process. Reprocessing and recycling plutonium in this "closed" fuel cycle can substantially enhance the sustainability of nuclear power. However, from historic civilian and defense programs substantial quantities of separated plutonium exist across the world. The largest stockpile (estimated at over 140 tonnes) (Nuclear Decommissioning Authority, 2022) is in the United Kingdom but the United States, France, Japan and other countries also have significant quantities of plutonium in interim storage or contained within wastes, weapons or new fuels. These separated, unirradiated, plutonium materials pose specific challenges related to their radiological hazards, proliferation risks and physical security as well as the logistics and economics of ensuring their safe and secure storage. Furthermore, depending on their form, these materials may present chemical hazards resulting from chemical and physical processes such as radiolysis and radioactive decay, radiogenic heating, corrosion, etc. This can lead to changes in the plutonium materials, evolution of gases (which may be flammable such as hydrogen or like helium from alpha decay cause pressurization of containers), degradation of packaging materials or other deleterious effects. Due to the challenges of working with plutonium, many of these processes remain poorly understood at the fundamental level such that safe storage is commonly ensured by application of sound engineering principles, careful monitoring, and the accumulation of operational experience. To address these issues and share knowledge and experience in the management of plutonium this Research Topic was initiated.

The first three papers in this Research Topic address the issues of radiolysis and long-term storage. Plutonium materials are typically stored as oxides, either in a pure form or as mixed U-Pu oxides. Radiolysis can lead to the degradation of the oxide material and to pressurization through the formation of radiolytic gases. Sims and Orr provide a primer on radiolysis and describe why accurate models are needed that can assess the H_2 generation rate from a radioactive material exposed to water or water vapor. This requires an understanding of the phenomena-controlling H_2 creation and destruction, and interactions at solid-water interfaces. The simplest models have used conservative estimates for G-H_2 and generally ignore chemical kinetics and recombination reactions. Such models are based primarily on the energy deposition into the solution. For instance, the Three-Mile Island (TMI) model is based on energy deposition (Henrie and Fischer, 1987; Vinson et al., 2002). These conservative approaches have been used during SNM storage and transportation as they are straightforward, and the chemistry of the system can be ignored. The argument that these models are conservative is based on the assessment that G-H_2 tends to drop rapidly in most experiments from 0.45 molecules/100 eV for gamma and 1.3 molecules/100 eV for alpha-radiation within a short period. However, it is possible that these models could become non-conservative, particularly if •OH scavenging agents are present, such as halides, or if air is in the package, enabling the buildup of HNO_3 or HCl, and leading to corrosion of packages. Hirooka et al. describe the effect Cl radiolytic species, derived from polyvinyl chloride (PVC) bags commonly used to contain radioactive materials, have on the degradation of mixed U-Pu oxides. They point out that not only is the interfacial alpha-radiolysis important but also the surrounding materials that can increase the local gamma dose and accelerate degradation. It has long been known that anomalous H_2 production during irradiation is enhanced at metal oxide interfaces (Petrik et al., 2001). Webb et al. delved into the factors that impact H_2 generation from water radiolysis with PuO_2, a question that remains unclear. Their experiments on a wide range of PuO_2 materials, produced from the oxalate under different process conditions, provide a comprehensive data set covering ranges of surface area, relative humidity and overlying atmosphere. The connection between oxalate and oxide, and the original processing conditions, is linked to the preservation of the overall morphology of the Pu solid during calcination.

The last two papers in the Research Topic by Buck et al. and Ausdemore et al. address the conversion of Pu oxalate to oxide. Questions remain regarding the exact nature of the process (Orr et al., 2015). Buck et al. endeavor to improve understanding by using advanced electron microscopy to study the structural and compositional changes in calcined Pu oxalate. Precipitation of plutonium from an acid solution most often involved reaction with oxalic acid in a continuous precipitator to obtain Pu-oxalate (Facer and Harmon, 1954; Nash, 2015). Operators established the chemical conditions under which plutonium nitrate and oxalic acid needed to be reacted to control the quantity and particle size of the resulting plutonium oxalate. The key parameters were the acidity, oxalic acid concentration, rate of agitation, residence time, and temperature that impacted the Pu oxalate morphology which, in turn, impacted the filterability of this solid. When the acid concentration was below 1.5 M, the precipitate was too fine and did not settle and if the acid concentration was above 4.5 M, the Pu(IV) oxalate was high and the precipitate became thixotropic (Facer and Harmon, 1954; Miller et al., 1977). This product was then calcined to the oxide that altered the surface area both internal and external. Linking processing conditions to Pu oxide morphology could provide additional methods for nuclear forensics. Ausdemore et al., have developed a Bayesian Adaptive Spline Surface model to address this inverse problem. This method does not require any physical or chemical understanding of the system but can, nevertheless, accurately predict the starting conditions from the fully calcined product.

The subject of nuclear forensics is becoming increasingly important to ensure control of SNM. However, it still relies heavily on radio-analytical and mass spectroscopy data. Morphological analysis provides another approach. The objective of this evolving approach, exemplified by papers in this Research Topic, is to provide the forensic scientist with yet another signature that help identify SNM that are out of regulatory control. Morphology also controls the surface area of these nuclear materials and is an important parameter in models that are being used to predict radiolytic H_2 production associated with the long-term storage of SNM.

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