



Sequestration of radioactive iodine in silver-palladium phases in commercial spent nuclear fuel



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HIGHLIGHTS

- A Pd-Ag halide phase has been observed in a high burn-up UO_2 reactor fuel.
- The phases contains iodine and bromine.
- Iodine release in high burnup fuels may be reduced through the formation of recalcitrant phases.

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ABSTRACT

Radioactive iodine is the Achilles' heel in the design for the safe geological disposal of spent uranium oxide (UO_2) nuclear fuel. Furthermore, iodine's high volatility and aqueous solubility were mainly responsible for the high early doses released during the accident at Fukushima Daiichi in 2011. Studies Kienzler et al., however, have indicated that the instant release fraction (IRF) of radioiodine ($^{131/129}\text{I}$) does not correlate directly with increasing fuel burn-up. In fact, there is a peak in the release of iodine at around 50–60 MW d/kgU, and with increasing burn-up, the IRF of $^{131/129}\text{I}$ decreases. The reasons for this decrease have not fully been understood. We have performed microscopic analysis of chemically processed high burn-up UO_2 fuel (80 MW d/kgU) and have found recalcitrant nano-particles containing, Pd, Ag, I, and Br, possibly consistent with a high pressure phase of silver iodide in the undissolved residue. It is likely that increased levels of Ag and Pd from ^{239}Pu fission in high burnup fuels leads to the formation of these metal halides. The occurrence of these phases in UO_2 nuclear fuels may reduce the impact of long-lived ^{129}I on the repository performance assessment calculations.

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1. Introduction

Light water nuclear reactor fuels used in commercial power plants consist of uranium oxide (UO_2) and/or mixed oxide (U,Pu) O_2 ceramic pellets contained within zirconium alloy cladding [1–6]. Once irradiated to burn-ups exceeding 50–60 MWd/kgU, the spent nuclear fuel (SNF) undergoes significant chemical and microstructural changes [1]. Fission products, such as Zr, Sr, and the lanthanides, as well as the neutron capture products; Pu, Np, and Am, are retained in the UO_2 (uraninite) fluorite-type structure. The fission gases, Xe and Kr, are trapped as gas bubbles and the transition metals (Mo, Tc, Ru, Rh, and Pd) are partitioned into metallic phases

that are found embedded in the fuel grains, grain boundaries, defects, and triple points [4–8]. Smaller amounts of Ag, Te, and Se are also thought to be associated with these phases, although Ag is almost completely immiscible in Ru metal [9]. Iodine has been assumed to form CsI, the most favorable sites being at fission-gas bubbles, grain boundaries, and cracks in the matrix. At low burn-ups (<5 MWd/kgU), CsI is not expected to form; however, at higher burnups, the radiation-induced bubble microstructure is thought to serve as reaction sites for thermodynamically favorable CsI formation [2,10]. As the Cs/I molar ratio is ~10, excess cesium forms Cs_2MoO_4 . Thomas et al. [4] reported the occurrence of Ag-Pd precipitates in SNF using Auger spectroscopy.

Knowledge of the distribution of radionuclides partitioning between the fuel matrix and other discrete phases within or outside the fuel grains is necessary to make predictions about potential release if the fuel bundle is compromised in some manner.

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For instance, a fraction of the inventory of fission gases and some of the more volatile radioelements (e.g., Cs, I) may migrate out of the UO_2 matrix during in-reactor operations and accumulate in locations, collectively referred to as the “gap region” (e.g., the interface between the pellets and the cladding, the rod plenum regions, and pellet fracture surfaces) [1–3].

Nuclear accidents that have resulted in melting or partial melting of the reactor core have led to the rapid release of these volatile radionuclides, many of which have short half-lives and contribute to hazardous dose levels [10,11]. Radioactive iodine-131 ($t_{1/2} = 8$ d) is one of the most harmful radionuclides because it has the highest activity among radionuclides that could be released after an accident. During the Chernobyl accident in 1986, 30–40% of the ^{131}I was released, contributing to approximately 17–45 MCi; and during the Fukushima Daiichi accident in 2011, ~0.03 MCi of ^{131}I was released. There is interest in understanding the release of this radionuclide, as such information may provide insight into the fuel condition at the time of the accident [12–16].

Iodine (^{131}I) is the radioisotope of concern for accident scenarios but it is not an issue for either long-term storage or fuel recycling, owing to its rapid decay. However, another iodine radioisotope, ^{129}I ($t_{1/2} = 15.5$ Ma), becomes a concern at the time-scale of potential reprocessing (or recycling) operations, storage, and final geologic disposal. A nuclear fuel reprocessing facility, such as La Hague in France that is capable of handling ~1400 t of SNF per year, might process ~320 kg of ^{129}I each year. The difficulty of retaining ^{129}I during recycle is one of the major factors that hinders the development of fuel recycling world-wide [17]. Because ^{129}I is assumed to be released instantly from a compromised SNF waste package, it plays a significant role in performance assessment calculations for geologic disposal under all repository designs. Data from Gray [18] and Finn and coworkers [19] have illustrated a clear relationship between fission gas release (FGR) and the release of several radionuclides, including radioiodine; although, it should be noted that the FGR does not necessarily correlate with fuel burnup. At higher burn-ups, there has been tentative evidence of radioiodine retention during fuel dissolution. Kienzler and González-Robles have pointed out that linear power is a much better predictor of iodine release than burnup [20].

In this paper, we show, for the first time, in high burn-up SNF, that iodine is sequestered into a solid phase. This phase could limit the subsequent release of iodine under geologic disposal in an engineered repository, during fuel recycle operations (depending on the chemical processes used), or possibly, during a nuclear accident event.

Initial characterization of Approved Testing Material (ATM)-109, a spent fuel from a Boiling Water Reactor from the Quad Cities I reactor (Quad Cities Generating Station, Cordova, Illinois, USA) was performed by Wolf et al. [21]. This fuel was irradiated from February 1979 to September 1987, and again from November 1989 to September 1992. The original uranium oxide (UO_2) fuel was fabricated by the General Electric Company. The UO_2 had an initial 3.0% ^{235}U enrichment and an initial grain size of ~30 μm . The specimens received a maximum burn-up of 70–80 MWd/kgU. This higher burn-up resulted in more ^{239}Pu fission and the SNF possessed higher levels of Ag than lower burn-up fuels. We have previously reported on the nature of the metallic epsilon particles from these fuels and aspects of their chemistry [22,23]. Palomares and co-workers [24] reported on the composition of undissolved residues from the dissolution of ATM-109 fuel using concentrated nitric acid (CNA) and ammonium carbonate-peroxide (ACP) dissolution methods. These ACP and CNA dissolution processes have been described elsewhere in detail [25–27]. The neutron activation results reported by Palomares and co-workers indicated that the CNA dissolved fuel had a slightly lower Mo and Ru concentration

than the ACP dissolved material and that the residue material from the ACP process contained far more radioiodine (700% more) than the CNA dissolved material [24]. Results for Br, Ag and Pd were not reported in the neutron activation study.

In this paper, we report the direct observation of iodine associated with Ag and Pd in SNF. The object of this paper is to provide evidence for the occurrence of this material in the undissolved solids and then to discuss its origin as either in the original SNF or whether this material formed during the CNA and ACP dissolution processes.

2. Experimental section

As of July 2014, the ATM-109 fuel had been cooling for approximately 22 years. The material was dissolved using two dissolution solutions; hot concentrated nitric acid (termed CNA) and ammonium carbonate-peroxide (ACP). The dissolution process that produced the samples examined in this paper is described in detail in Refs. [25,26]. However, in summary, the fuel was dissolved using the following process: 12.0536 g of raw UO_2 fuel, crushed to pass through a 212- μm screen, was dissolved in a saturated solution of ammonium carbonate with about one fifth its volume of 30% H_2O_2 , at room temperature and atmospheric pressure. The reaction was continued for four days, leaving the noble metal phase as a fine black suspension. The black suspension was filtered out of solution using a 0.45- μm membrane filter. The filtrate was clear yellow. The black suspension was then treated with more ammonium carbonate, hydrogen peroxide solution to assure that the UO_2 had completely dissolved. No further yellow color appeared in the solution, indicating that no more uranium was going into solution. The black insoluble matter was washed with 0.5 M HNO_3 to dissolve the soluble carbonates (expected BaCO_3 and SrCO_3), then centrifuged. The washed black solids were dried and weighed. Final dry weight of black insoluble matter (consisted largely of noble metal phase) was 0.2320 g.

Each of these treatments dissolved the UO_2 and nearly all of the fission products and transuranic elements, leaving an undissolved residue of fine, black material that consisted largely of the metals; Mo, Tc, Ru, Rh, and Pd, and with smaller amounts of other elements. Approximately 13 g of fuel was used for each dissolution. The black undissolved residue was centrifuged out of solution, washed to remove the dissolved fuel, and then removed from the hot cell for analysis.

2.1. Sampling

The undissolved solids recovered from these treatments of the ATM-109 were slurried in water and placed in polyethylene vials. Aliquots were pipetted from these slurries onto carbon coated TEM grids and SEM mounts.

2.2. Microanalysis with SEM and TEM

Specimens of the undissolved SNF residues were carefully removed from the parent sample under radiologically protected environments (i.e. radioactive materials glove box) and transferred to smaller vials. For scanning electron microscopy (SEM) analysis, these vials were opened in a contained chamber and a few particles were placed on a clean glass slide. A pipette containing a small amount of methanol was used to extract a few particles. These were then deposited on a sticky carbon tape, coated with conductive carbon and analyzed with an FEI (Hillsboro, OR, USA) Quanta250™ field emission gun SEM equipped with an EDAX (EDAX Inc., Mahwah, NJ) compositional analysis system. Images were obtained under backscattered electron (BSE) imaging conditions and

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