Catalyzed Corrosion of Plutonium: Hazards and Applications

John M. Haschke and Joseph C. Martz

Catalyzed corrosion reactions of plutonium metal are not laboratory curiosities produced by careful manipulation of chemical reactants. Several incidents involving the corrosion of plutonium metal, failure of storage containers, and localized release of plutonium-containing particles into the work environment were attributed to catalyzed corrosion reactions (Haschke and Martz 1998b) and led to redesigning the storage package. In addition, catalyzed corrosion reactions have become the basis of efficient methods for converting plutonium metal from classified weapons configurations into simple ingots.

In 1993, a worker at the Los Alamos Plutonium Facility became contaminated with plutonium-containing particles while handling a standard storage package containing a 2.5-kilogram plutonium casting. The packaging configuration was similar to that used world-wide. It consisted of an inner cylindrical steel container to hold the casting, two layers of sealed "bag-out" plastic to contain radioactive contamination, and an outer slip-lid can. The incident occurred after the package had been stored for 11 years. As the outer can was flexed during handling, a puff of air carrying plutonium-containing particles

escaped through a break in the taped seal of the can and contaminated the worker. The package was placed in a reduced-oxygen (less than 3 percent O_2) glove box, and the inner cylinder was left there for 3 hours after having been removed from the package. The accompanying photographs were taken during the disassembly. As the plastic-wrapped inner

container was lifted out, its end ruptured because of pressure from the continuing rapid formation of plutonium oxides and other low-density corrosion products. A typical plutonium casting would form about 10 grams of PuO_2 per year from normal oxidation in air. Instead, the observed extent of the reaction was many orders of magnitude greater. Also, the inner vessel, which still contained unreacted metal, had become hot, and its diameter had increased by about 50 percent. The vessel was transferred to an argon-filled glove box, where the reaction ceased at once.

Evaluation of this incident shows that hydride catalysis caused by a complex set of physico-chemical processes led to rapid corrosion of
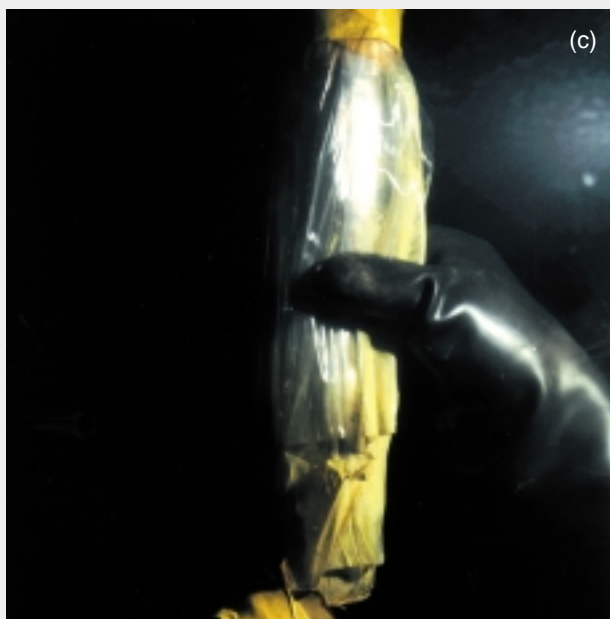
the metal casting during storage and to very rapid corrosion during the 3-hour waiting period in the reduced-oxygen glove box. The weld at the ruptured end of the inner vessel had evidently been defective from the start, allowing gases to be continually pumped in and out of that vessel, as atmospheric pressure changes compressed and expanded the sealed plastic bagging. Plutonium oxide particles were entrained by thermal currents in the vessel, transported through openings in the weld, and deposited on the plastic over several years. During that period, the bagging isolated the metal casting from any external oxygen source, and the normal surface PuO_2 was apparently autoreduced to Pu_2O_3. Over time, the plastic bagging became discolored near the weld, as well as embrittled from the radiolytic decomposition induced by α-particles emitted from the deposited plutonium oxide particles. The molecular hydrogen produced during the radiolysis of the plastic entered the inner vessel and formed hydride on the Pu_2O_3-activated surface of the casting. During these processes, the storage package did not change its mass, and therefore the problem was not detected. When the embrittled plastic failed during storage, air reached the inner vessel, and a hydride-catalyzed reaction of the oxygen and nitrogen with the hydride-coated plutonium ensued at a throttled rate determined by access of air to the reaction zone. The resulting expansion of the solid led to the complete failure of the defective weld.

The corrosion rate became rapid during exposure to the glove box atmosphere and was estimated from the dramatic increase in the the vessel's volume during the 3-hour period, the bulk density of the corrosion product, and the approximate surface area of the metal. The result (0.3 g Pu/cm^2 min) is in excellent agreement with the value measured during studies of hydride-catalyzed corrosion (0.7 ± 0.1 g Pu/cm^2 min).

The experience and knowledge we gained from evaluating this incident and from studying catalyzed corrosion reactions find broad application in reducing the nuclear danger. The safe storage of plutonium requires using two metal containers with certified seals and ensuring that organic materials are excluded from the package. These two safety criteria are incorporated in the plutonium storage standards adopted by the U.S. Department of Energy and the International Atomic Energy Agency.

Knowledge of plutonium corrosion kinetics and particle-size distributions for a whole range of conditions enables realistic hazard assessments of plutonium dispersal during accidents. Catalyzed hydriding is also the key reaction in the hydride-dehydride recycle process for destroying weapon configurations and recovering plutonium metal—both done in a single step. Hydride-dehydride recycling generates no mixed or liquid waste of any

kind. The recovered plutonium is a storage-ready ingot, and the hydrogen gas, which is both created and recycled in a uranium hydride storage system, is never released and does not present an explosion hazard. This process was recognized by the *R&D Magazine* as one of the best 100 technical innovations of the year and is the foundation technology of the Automated Retirement and Integrated Extraction System (ARIES) for separating plutonium from weapon components. The hydride-catalyzed oxidation of plutonium holds potential for development as a parallel single-step process in the rapid recovery of plutonium as oxide rather than metal.

Failed Storage Container for Plutonium Metal

Each photo shows a step in the disassembly of the container for a 2.5-kg casting of plutonium metal. (a) The outer container is placed in a glove box; (b) when the lid is removed, the plastic bagging shows; (c) when the plastic bagging and inner cylinder are lifted out of the container, discolored, embrittled plastic decomposed by radiolysis is revealed; (d) a rupture in the inner container is visible; (e) the corrosion product pours out of the ruptured end; and (f) an increase in the inner vessel's diameter near the ruptured end shows the extent of hydride-catalyzed corrosion during a 3-hour period.

(e)

(f)