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Processing of Non-PFP Plutonium Oxide in Hanford Plants

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CH Delegard

March 2011



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Processing of Non-PFP Plutonium Oxide in Hanford Plants

Processing of non-irradiated plutonium oxide, PuO_2 , at the Hanford Site has been done at the Plutonium Finishing Plant (PFP) and in recycle of PuO_2 -bearing fuels through Hanford reprocessing plants. Plutonium oxide is notoriously refractory and difficult to dissolve. As such, losses of PuO_2 residues from the PFP or from Hanford reprocessing plants can report to Hanford Site underground tank waste storage. Those stored wastes are destined to become feed to the Waste Treatment Plant, WTP. Information on the processing of non-PFP plutonium oxide in Hanford plants is provided in this brief report. To help gain perspective, information on PFP processing and plutonium additions to the tank farm system from other Hanford processing is also presented.

Processing of non-irradiated PuO_2 scrap for recovery of plutonium values occurred routinely at Hanford's PFP in glovebox line operations. Plutonium oxide is difficult to dissolve, particularly if it has been high-fired; i.e., calcined to temperatures above about 400°C and much of it was. Dissolution of the PuO_2 in the scrap typically was performed in PFP's Miscellaneous Treatment line using nitric acid (HNO_3) containing some source of fluoride ion, F^- , such as hydrofluoric acid (HF), sodium fluoride (NaF), or calcium fluoride (CaF_2). The HNO_3 concentration generally was 6 M or higher whereas the fluoride concentration was ~ 0.5 M or lower. At higher fluoride concentrations, plutonium fluoride (PuF_4) would precipitate, thus limiting the plutonium dissolution. Some plutonium-bearing scrap also contained PuF_4 and thus required no added fluoride. Once the plutonium scrap was dissolved, the excess fluoride was complexed with aluminum ion, Al^{3+} , added as aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, to limit collateral damage to the process equipment by the corrosive fluoride. Aluminum nitrate also was added in low quantities in processing PuF_4 .

The PuO_2 dissolution was not perfect, however, and some amount of PuO_2 survived the HNO_3/F^- treatment, continued as solids through the solvent extraction processes at the PFP, and reported to the waste that was sent to the Hanford tank farms. The process raffinate disposed from PFP to tank farms largely went to tank 241-SY-102. Identification and characterization of plutonium-bearing solids, including PuO_2 , has been done (Callaway 2004).

Not all PuO_2 dissolution for plutonium recovery at Hanford occurred at PFP, however. If the PuO_2 had been irradiated in a reactor, usually as part of a PuO_2/UO_2 (plutonium-uranium dioxide mixed oxide or MOX) fuel, the attendant high radiological doses precluded glovebox processing. Instead, the irradiated MOX with contained PuO_2 would enter a Hanford reprocessing plant for dissolution and recovery of plutonium and also uranium values.

According to an account of Hanford plutonium production history, processing of MOX fuel occurred at both REDOX and PUREX (Gerber 1996):

4.3.7 Processing of Other Materials at REDOX/PUREX

PUREX and REDOX processed small quantities of other irradiated fuels. In 1958, the PUREX facility began the recovery of neptunium 237 (Np-237) on an occasional batch basis from its normal product stream. Immediately, the plant became the AEC's prime supplier of this isotope. During 1962, both REDOX and PUREX were modified to permit the continuous recovery of Np-237 without interfering with normal plutonium recovery operations. The PUREX Np-237 equipment was placed in J Cell and Q Cell.¹¹⁶ During 1965-1966, the PUREX facility processed 664 tons of powdered thorium oxide fuel targets that had been irradiated for the production of uranium 233 (U-233), an isotope desired for its potential use in weaponry and because it could be made from plentiful, natural thorium. However, the processing campaign caused plugging and other equipment and contamination problems within PUREX. A more successful campaign in 1970 processed 820 kgs. of pelletized thorium oxide targets. Shortly afterward, for reasons unrelated to PUREX, thorium oxide fuel was ruled out for large scale development at HW.¹¹⁷ In the later years of REDOX operation (1963-1967), Plutonium Recycle Test Reactor (PRTR) and Shippingport (Pennsylvania) Reactor fuels were processed. PUREX also reprocessed some PRTR fuel in 1972, as well as some Southeast Experimental Fast Oxide Reactor (SEFOR) fuel. Core dissolving of these mixed oxide fuels involved the use of a highly corrosive mixture of nitric acid and hydrofluoric acid, with the dissolver solution then blended with recycled uranium to achieve criticality control.

Based on use of Hanford's Integrated Document Management System (IDMS) for technical records archiving and retrieval and internet searching, further investigation of the MOX processing for SEFOR (Southwest Experimental Fast Oxide Reactor; near Fayetteville, AR) and for PRTR (Plutonium Recycle Test Reactor; 300 Area, Hanford Site) was undertaken in preparation of the present report.

SEFOR

The SEFOR campaigns at PUREX in December 1966 and April-May 1967 separated plutonium to produce plutonium nitrate solutions that were shipped off-site for use in production of SEFOR MOX fuel (Duckworth and Ward 1966; Kison 1967). There were some SEFOR returns of irradiated fuel as waste to the 200 Area burial grounds. The bulk of the SEFOR fuel reprocessing appears to have been conducted at Savannah River between 7/84 and 12/84 (Kvarteck et al. 1994). The fuel may have been sent to Savannah River rather than Hanford because the Hanford PUREX plant shut down at about the same time the SEFOR reactor was deactivated.

In short, aside from the account in the brief processing overview (Gerber 1996), no written evidence for the processing of SEFOR MOX at Hanford was found in the technical literature. Instead, it seems that the supporting documents (Duckworth and Ward 1966; Kison 1967), which described reprocessing campaigns to recover plutonium from relatively high burn-up (ca. 8% ²⁴⁰Pu) Hanford fuel for use in preparing SEFOR MOX, were misinterpreted to draw the conclusion that the reprocessing of irradiated SEFOR fuel occurred at Hanford. The dates of the processing reports (1966-1967) alone indicate that reprocessing of irradiated SEFOR fuel did not occur at Hanford because SEFOR did not go critical until April 1969 (Johnson 1972).

PRTR

The PRTR fuel is nominally 2% PuO₂ in uranium dioxide (UO₂) of natural or depleted enrichment (Lini and Rodgers 2002) but other fuel compositions were made at PRTR. The brief account in excerpted earlier (Gerber 1996) describes processing PRTR fuel at PUREX and REDOX.

At PUREX

PRTR fuel was dissolved in PUREX in 1972 for reprocessing and recovery of the plutonium values. The total quantity of PRTR fuel reprocessed at PUREX was not stated, but planning documents indicated PRTR fuel would account for 0.3% of the PUREX processing capacity (Ehrlich 1963). In PPD-493-5-DEL, the following was reported:

For the period of this report, the dissolution of the PRTR materials was very successful, achieving excellent material balances across the dissolvers.

This statement would indicate the PRTR fuel dissolution would not have produced significant plutonium solids in the waste from PUREX.

At REDOX

At REDOX, PRTR containing 0.48% PuO₂-UO₂ was processed in 1965 along with zircalloy-clad UO₂, PuAl, and aluminum-clad depleted uranium (Goodwin 1965). From RHO-CD-505 RD (Synopsis of REDOX Plant Operations), the following was gathered regarding PRTR:

- 1963 Feb, Mar, Zr-clad Pu-Al fuel processed (1st PRTR batch); Oct (2nd batch; UO₂ fuel, no contained Pu)
- 1964 PRTR processed (March-April; 3rd batch no info on type; 100.1% Pu recover, 6.3 kg Pu)
- 1965 Zr-clad 0.48% PuO₂-UO₂ processed in June & July tests (June report gives process specs); other processing followed
- 1966 PRTR processed in Nov, fuel type not stated, 5th and last batch, no waste rework required

There is a hard-to-read chart on page 35 of the Synopsis that has some throughput data. The annual totals for PRTR appear to be:

- 1963 1.7 tons U; Pu not reported
- 1964 1.6 tons U; 8.0 kg Pu
- 1965 0.5 tons U; 16.4 kg Pu
- 1966 1.5 tons U; 9 kg Pu

If so, the total PRTR Pu processed was >33.4 kg (estimate ~42 kg if Pu loading in 1963 the same as in 1964 fuel). The Pu loss from dissolution of Pu-Al metal fuel in 1963 is probably small and the Pu recovery in 1964 was excellent. The oxide fuel (1965 and probably 1966) contained 25.4 kg Pu. A 1% process loss would be a high amount to lose; this would translate to only about 0.25 kg Pu lost.

Plutonium from Other Hanford Processing Plant Operations

Based on examination of monthly waste loss data, PUREX and REDOX waste losses from 1957 to 1966 listed below represent about 0.5% waste losses for PUREX and about 0.3% for REDOX (McDonald 1964). The amounts are cumulative totals for each year. A similar record was not located for PFP. These are total losses in all forms of material based on input/output differences.

Reprocessing Plant Waste Losses, kg Pu		
Year	REDOX	PUREX
1957	5.386	17.74
1958	2.613	7.468
1959	7.772	2.692
1960	1.912	18.195
1961	1.586	11.513
1962	2.183	14.546
1963	2.805	13.556
1964	3.74	12.75
1965	5.52	12.83
1966	6.218	10.459
Sum	39.735	121.749

In the monthly operating report PPD-493-6-DEL, dissolution of some (presumably non-irradiated) MOX scrap from 234-5 resulted in undissolved solids due to low heating efficiency in the plate coil. A special flush with HF-HNO₃ was used to dissolve the fines. In this case, material balance differences lead to an investigation that identified undissolved solids and the system was adjusted to recover from this upset.

At PFP, a scrubber was used on the off-gas from the incinerator. Filtration testing on the incinerator scrubber before the system went "hot" found that a size analysis of the fly ash in the off-gas showed 10 percent greater than 6 microns, 30 percent between 6 and 2.5 microns, 30 percent between 2.5 and 0.5 microns, and 30 percent less than 0.5 microns (Conner and Crocker 1961). No evidence was found that significant quantities of PuO₂ were transferred as waste through this route.

In the final months of PUREX operations before shutdown in 1972, processing of bulk MOX that had come from the PFP was done. Some descriptions of the dissolution success are given in the Chemical Processing Department monthly reports from that period (e.g., PPD-493-5-DEL 1972; PPD-493-6-DEL 1972).

Conclusions

Based on published Hanford process report, PuO₂ could have been introduced to the Hanford Site waste tank farm system from not only PFP but also from processing of PRTR fuel at REDOX and PUREX reprocessing plants. Not published estimates of the quantities of PuO₂ reporting to the tank farms as PRTR fuel processing losses were reported. However, projected losses from this source are estimated to be less than 0.25 kg. Processing of irradiated SEFOR MOX fuel, described in a general Hanford historical account (Gerber 1996), could not be substantiated by examination of other more specific Hanford processing records. Contributions of plutonium (though not as oxide) to the tank waste system through process losses at REDOX and PUREX also were summarized.

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