Appendix G

Supplemental Information on the UO_3 Plant

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APPENDIX G
Supplemental Information On The UO_3 Plant

G.1 Operating History Uranium Trioxide (UO_3) Plant [Gerber 1993]

The original Uranium Trioxide (UO_3) Plant was located in a World War II facility known as the 224-U Bulk Reduction Building. This three-story, frame and concrete block structure had just under 12,000 square feet, and had been constructed to house a part of the plutonium separation and concentration process used at Hanford in the 1940s. However, process improvements as early as 1945 demonstrated that the 224-U Building was not needed. Rather than contaminate it with plutonium, Hanford management decided to utilize the building as a training facility until another use was found. The 224-U Building was modified in 1951 to accomplish conversion of Uranyl Nitrate Hexahydrate (UNH) to UO_3. This facility subsequently became known as the UO_3 Plant.

The facility began test runs in January 1952, and full operations the following month. The first UO_3 calciners simply were large pots that heated the UNH in batches. An early difficulty concerned the UNH feed from REDOX, which contained impurities sufficient that much of Hanford's UO_3 product "proved to be inadequate for successful processing in the continuous UF_6 conversion process at Oak Ridge." Process improvements in the REDOX Plant were made during 1952-1953, to correct this situation. The first feed supplies of UNH received from the U-Plant in 1953 also proved to be problematic. Metallic impurities, as well as the nitric acid content and the presence of Tri-butyl Phosphate (TBP) and its decomposition products required that the UO_3 produced from initial U-Plant product UNH had to be sent to an intermediate metallurgy facility in Cleveland, Ohio further purification before shipment to Oak Ridge. Additionally, the U-Plant UNH foamed, caked and stuck in the pots during the calcining process, so that the UO_3 would have to be vacuumed and even chopped out. This condition was undesirable from the standpoints of efficiency, operator safety, and contamination control. However, changes made in the U-Plant rendered the UNH so pure that the UO_3 Plant product, by the end of 1953, did not have to be sent offsite for further purification, and was suitable to be shipped and used directly at Oak Ridge. That year, the UO_3 Plant processed more than 1.5 times the total fuel inventory of uranium that was received at Hanford.

During 1954, UO_3 Plant capacity increased to 18 tons per day with the addition of two gas-fired calciners. The unit cost per ton also dropped to 79 percent that of 1953. Overall production in 1954 was limited, however, by the quantity of feed available from the REDOX and U plants. REDOX experienced many shutdowns caused by equipment failures that year, and the U-Plant was closed for much of the autumn to allow for system modifications that would allow it to process wastes aged only one year (instead of usual three years). Several problems were encountered and overcome during 1954, including high radiation fields around the calciner pots caused by the processing of newer UNH (higher in zirconium, niobium, and ruthenium) from the two Hanford feed plants. This problem was solved by the addition of special shielding to protect operators during pot unloading. Also, sulfamic acid added to the UNH prior to calcination caused some caking in the calciner pots, and renewed foaming occurred due to the presence of organic decomposition products in the UNH. Silicon anti-foaming agents, as well as

other sulfur-based additives were used to control these situations. A key improvement that year was the use of vacuum cleaning techniques that enabled the plant to recover 90-95 percent of the oxide powder associated with failed filter bags. A large backlog of such bags that had accumulated since startup, were cleaned and discarded. By year's end, plans were underway to expand the UO_3 Plant.

During 1955, monthly UO_3 production averaged 106 percent that of 1954, while the unit costs per metric ton dropped to 92 percent of that for the previous year. The plant had to shut down for portions of the summer due to contamination problems resulting from high gamma feed from the U-Plant. More persistent problems resulted from the gradual corrosion and mechanical wear of equipment and calciner seals and gaskets to the point where a vacuum could not be maintained in the pots. Airborne contamination around the pots increased until operators had to wear masks for respiratory protection. In 1956, equipment modifications, including new pot agitators, shafts, seals, bearings and supports, as well as new pot cover assemblies, off-gas systems and gasketing, were installed to address these problems.

In the meantime, plans went forward to construct the 224-UA Building, a major addition to the UO_3 Plant. The plant was equipped with six large, new, continuous action calciners. These calciners were developed and designed at Hanford, and had large troughs with paddle agitators that essentially turned and mixed the UNH/UO_3 bed throughout the process. The caking and clogging problems that had plagued the pots was obviated by the below-grade valving of the continuous calciners. The new valves used air as an agitant, and maintained a seal between the calciner and the powder pickup bin, while passing a continuous stream of UO_3. The new calciners also produced a pebbly product that consisted of spheres with an average diameter of 200 microns (about 1/100th of an inch), as opposed to the granular oxide product of the pot.

The first three of the continuous calciners began operations in the last quarter of 1956, and, despite mechanical difficulties with their powder handling systems during the earliest months, they soon demonstrated their production potential. That December, UO_3 Plant throughput exceeded that of any previous month by 27 percent. Overall, the 1956 plant production exceeded that of 1955 by 57 percent.

Another salient improvement made during 1956 was the replacement of the old, 900-pound drums used for offsite shipping of the UO_3 powder with new T-Hoppers. These containers left the site on specially fitted rail flat cars and served as feed hoppers for the Oak Ridge plant customer.

Installation of the last three of the continuous calciners was completed at the UO_3 Plant in early 1957. At that time, the 18 pot units were retired from service, and all processing was done through the continuous calciners. Late that year, design scoping was begun for new facilities needed to segregate regular UNH feed from that generated by the processing of E-Metal in the REDOX Plant. The UO_3 powder that resulted from processing the two types of UNH streams had significantly different nuclear reactivity levels, and separation was needed by the customer at Oak Ridge.

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During 1958, two new tanks with associated piping and instrumentation were installed and fitted to receive the enriched UNH from the stainless steel, overhead pipeline that brought the UNH from the REDOX Plant. Routine transfers of enriched UO_3 from Hanford to Oak Ridge began in early 1959. Meanwhile, in 1958, the UO_3 Plant established another high production record that was 5.5 percent higher than that of 1957, and almost double that of 1954. Metallurgical examination of the two-year old continuous calciners showed their condition to be excellent.

In 1958, the U-Plant finished its mission and was shut down. However, PUREX's UNH feed to the UO_3 Plant far surpassed that which had been coming from U-Plant. Together, the UO_3 and PUREX Plants went on to set and surpass production records almost continually, while the REDOX Plant continued to supply a small stream of enriched UNH until its shutdown in 1967. During 1959, the concentration equipment and the acid recovery system at the UO_3 Plant were automated, and in 1960, for the first time, the calciners were automated so that they could be operated and shut down remotely. Programming of the calciners included preliminary air blowing and steam heating of the feed points, admission and regulation of the feed, and control of the UO_3 bed temperature. Steep production climbs at the plant continued through 1961, but dropped off slightly in 1962 due to mechanical and process difficulties at the feed plants (PUREX and REDOX). By 1963, production again was so high that serious consideration was given to constructing a pipeline, or converting an existing one, to carry UNH from PUREX to the UO_3 Plant. However, the project did not go forward, and transfers by tanker truck continued. That same year, production of UO_3 shipped offsite rose to about 12,000 tons per year, and the capability was added to process UNH derived from "125 Metal." During 1965-1966, an experimental process of conversion of thorium nitrate into thorium oxide powder was carried out in the UO_3 Plant, using the old electric pots. The goal of this work was to produce thorium oxide powder suitable for fabrication into reactor target elements for ^{233}U production. However, for reasons unrelated to the UO_3 Plant, the use of thorium oxide powder was abandoned, in favor of experiments with thorium wafer targets.

Beginning in 1967, UO_3 Plant operations were tied exclusively to those of the PUREX Plant. That year, UNH concentrator modifications in the UO_3 Plant improved heat distribution and allowed the calciner feed to maintain a uniformly higher specific gravity, thus producing more powder in the same operating time. Both the UO_3 and PUREX plants closed in 1972. However, PUREX resumed operations in late 1983 -- closely followed by UO_3 Plant in early 1984. Since that time, there have been 17 startups at the UO_3 Plant, averaging about eight days each, as the plant could calcine UNH at a much faster rate than the PUREX Plant could produce it. Final deactivation orders came for both plants in 1992. In April 1993, the UO_3 Plant resumed operations to convert the final 200,000 gallons of remaining UNH to UO_3 powder. That run was the plant's last.

In general, waste management was handled very simply and efficiently at the UO_3 Plant. Radiation levels in the UNH were relatively low, as compared with levels in the chemical processing feed plants, as there was no high-level waste generated or processed by the UO_3 process. Process condensate was sent to various U-Plant cribs

over the years, specifically the 216-U-12 crib in the 1980s and the 216-U-17 crib for later operations. Various ditches and swamps received equipment cooling water and the steam condensate, previously the U-Pond and more recently the 214-U Ditch. Airborne UO_3 powder was trapped in primary bag filters, with secondary bag filters and then HEPA (High Efficiency Particulate Air) filters added during the 1972 - 1984 shutdown. That period also witnessed the addition of fire protection improvements, a backup power supply for instrumentation, an open faced hood and associated exhaust and filtration equipment for the UO_3 loadout, and a nitrous oxide (NO_X) monitor for the 296-U-4 stack. Beginning in the late 1950s, the main off-gas from the UO_3 process (NO_X), was routed through "wet scrubbers," which sprayed the gas with nitric acid to capture the NO_X vapors and dissolve any entrained solid oxide particulates. The acid mixture was then routed through an acid absorber (bubble-cap tower) and stored in chemical tanks awaiting transfer to PUREX. In the late 1980s, a Fiber Mist Eliminator was added to scrub acid vapors from the UNH concentrator to minimize entrained solution and particulates.

G.2 Process Operations

The major unit operations performed at the UO_3 Plant were concentration of UNH, calcination of UNH to UO_3, packaging of the UO_3 product, and nitric acid recovery. Uranium containing wastes were generated during routine operation. The primary waste streams were the liquid effluents discharged to the ground and gaseous effluents released to the atmosphere.

The UNH solution was transferred to the UO_3 Plant and stored in Tank C-1 in C-Cell. During operation the UNH solution was accumulated in storage tanks and then transferred to the concentrators in D-Cell. The UNH was concentrated to approximately 100 weight per cent UNH in thermosiphon evaporators. The optimum operating temperature was 125°C to 127°C. The concentrated UNH was stored in a steam heated tank. Off-gas from the concentrator knockout pot was routed through a catch tank to a fiber mist eliminator. The mist eliminator captured UNH droplets entrained from the concentrators and the recycle unit concentrator. The recovered UNH was eventually recycled to PUREX. Part of the condensate, was used as reflux water in the acid absorber tower, and the balance of the condensate was neutralized and pumped to the U-17 crib [Raab 1978; Harmon 1979; Strickland 1993] .

Concentrated UNH was pumped to the 224-U building where the calcination process was conducted and UNH converted to UO_3 powder. Initially calcination was performed using pot calciners. The UO_3 product from the pot calciners was unloaded using a pneumatic unloading system, which conveys uranium oxide from the pots and conveys it to bulk storage. The system consisted of an exhauster, a bag filter, a cyclone collector, a rotary valve, a hammer mill, and various pipe and fittings. The pot calciners were replaced by 1956 with continuous calciners. The UO_3 particle bed in the calciner was maintained at 270°C. The shell temperature was maintained at about 500°C for optimal efficiency.

The UO_3 powder was collected from the calciners in ground-level pickup bins and then transferred by the pneumatic transfer system, using air, to the fourth floor of the UA tower to the cyclone separator. From there it flowed by gravity through a hammer mill (not normally used) on the third floor of the tower, then to a storage hopper on the second floor, and was unloaded from the hopper into T-Hopper shipping containers in the powder loadout room. The exhaust air from this operation was routed through primary and secondary bag filters in series, a prefilter, and HEPA filter before discharge to the environment, via a roof exhauster. Powder from the cyclone and primary bag filter was collected in the powder hopper. Powder from the secondary bag filter was also collected.

As the UNH was thermally decomposed, oxides, of nitrogen and water were driven off and drawn through the vent piping to the Acid Recovery Tower where they were converted to nitric acid. The system consisted of calciner off-gas scrubbers that remove fine particles of entrained UO_3, a vapor cooler, an absorber tower and a system of reflux water addition. The acid was collected and pumped to the 211-U Tank Farm for storage and return to the processing plants. Net acid recovery was about 92 percent of that represented by the incoming UNH solution. The nitric acid had a low residual level (0.043 molar) of UNH.

G.3 Waste Generation [Harmon 1979]

The processing of 1,000 MTU at the UO_3 Plant typically resulted in the generation of ~15 million gallons of cooling water, plus steam condensate from the acid recovery and uranium nitrate concentration steps, and chemical sewer waste. Total radionuclide content of this water which totaled 120 million gallons in 1972 was less than 2 Ci of combined fission products and alpha-emitting nuclides. This stream was sent to 216-U-10 Pond.

Process condensate, largely from the UNH concentrators in the 224-U Building, averaged about 300,000 gallons annually, containing about 0.01 Ci of total mixed fission products. It was sent to the 216-U-12 Crib.

Approximately 1.2×10^9 ft^3 of gases were discharged to the atmosphere from the UO_3 Plant annually, containing an average (total) of 6×10^{-3} Ci of fission products and 9×10^{-5} of alpha emitting radionuclides. The radionuclides were essentially all ^{106}Ru and uranium, respectively.

Solid uranium waste was generated from failed and replaced equipment and normal line-generated process waste. About 120 to 140 ft^3 (total) was generated during a six week campaign mode of operation. This represented approximately 0.01 Ci of total beta emitters; 0.01 Ci of combined ^{90}Sr, ^{137}Cs and ^{106}Ru nuclides; and less than 0.2 kg of total uranium. The solid wastes were buried in the 200 Area waste burial grounds.

G.4 Radiation Exposure

The early years of UO_3 Plant operations were plagued with dusting and radiation problems around the calcination pots and during bag filter changes. Gustavson mentioned [Gustavson 1950] that "the dust problem in the pot room was one of the greatest obstacles in designing the UO_3 Building." Gerber cited [Gerber 1993] that Annual Reports reported occasions when "airborne contamination around the pots increased until operators had to wear assault masks." Two separate ventilation systems were installed to address the dust problems [Gustavson 1950]. Manual unloading of the calciner pots and high levels of maintenance were also reported. Radiation fields around the pot calciners resulted in the addition of special shielding in 1954 to protect the operators during pot unloading. The installation of continuous calciners greatly reduced exposure and dusting problems associated with the calcination process. Exposure during bag filter changes was also a concern in the early years of operation due to dusting problems. As a result, protective clothing and respiratory protection were used at these locations.

After many modifications and improvements to process operations, the total complement of workers when the UO_3 Plant was in full operation was approximately 30, including operations, maintenance and supervision during the latter years of UO_3 Plant operations. In 1971 to 1972, the average annual whole body occupational radiation dose of the UO_3 workers was approximately 1 rem; the maximum was 2.3 rem and the minimum was 0.09 rem. However, because this plant operated only part time, the process operations workers were assigned elsewhere for more than half of the operating year [Harmon 1979].

G.5 Contaminate Partitioning

The major unit operations performed at the UO_3 Plant were concentration of UNH, calcination of UNH to UO_3, packaging of the UO_3 product, and nitric acid recovery. None of these unit operations would preferentially concentrate or decontaminate the plutonium or neptunium from the uranium. The chemical and physical properties of the actinides are similar under the concentration and calcination operating conditions used at the UO_3 Plant such that there was no separation of one transuranic radionuclide from another. The ratio of transuranic constituents to uranium in the UO_3 product, residual uranium in waste streams, and uranium in any recovery streams, would have been the same as that in the UNH feed to the UO_3 Plant.

There is some evidence, however, of fission product partitioning during calcination. There is a statement in the UO_3 Fission Product Specifications [Knights 1966] that "^{95}ZrNb and ^{99}Tc are carried almost quantitatively through the concentration and denitration processes, whereas ruthenium concentration is reduced by a factor of 2 to 5. An early report indicated an average decontamination factor (DF) of 6 across the UO_3 Plant from U Plant UNH. This was attributed to volatilization of ruthenium during the calcination operation. The acid specific fission product analyses indicated that 95

percent was ruthenium. [Abrams 1955]. In contrast, the DF from REDOX UNH was less than one, indicating that the ruthenium concentration was significantly lower.

Some technetium heptoxide (Tc_2O_7 – pertechnatate), which has a boiling point of 310°C, could be expected to be volatilized during the uranium calcination step, which operated at < 300°C. The off-gas from the calciners was driven off and drawn through vent piping to the Acid Recovery Tower. This system consisted of calciner off-gas scrubbers that remove fine particles of entrained UO_3, a vapor cooler, an absorber tower and a system of reflux water addition. Any ^{99}Tc that would have been volatilized would have been recovered along with the NO_2, entrained uranium and fission products and been recycled as nitric acid to the reprocessing plants. There is no evidence that any ^{99}Tc reached the final exhaust filters. The presence of other beta-gamma fission products would have masked any radiation from the soft beta of the ^{99}Tc.

G.6 <u>UO_3 Related Incidents</u>

One incident involving UO_3 powder occurred April 12, 1960 when the flexible hose used to load powder into a large shipping container broke and spilled about 1.5 tons of powder in the loadout room, of which 2 to 5 Kg escaped to the loadout pad. This powder spread over the asphalt loading ramp and to the road around the UO_3 Plant. Most of the powder was swept up and put in drums for recovery, but the rest of the powder was washed off the asphalt and onto the ground surface. Contaminated soil was removed and buried. The contamination was limited to the immediate areas of the spill. There was no general spread in the 200 West Area, no detectable contamination offsite, and no personnel contamination problems of concern were encountered [HW-64898 1960].

There were several incidents involving UNH and liquid effluents. On December 30, 1954 2,000 gallons of UNH were spilled on the main roadway just east of the 200-East Area hill. No external exposure in excess of permissible limits is known to have resulted from this incident. All individuals involved in this incident were surveyed and found to be free of contamination, and an analysis of the bioassay result indicated no detectable deposition of soluble uranium [HW-34494-DEL 1955].

The most serious radiation event identified during this study involving personnel exposure at the UO_3 Plant occurred in December 1960, when the fresh air mask hose being used by an employee was blocked by condensate in the line and the mask was improperly adjusted. The employee inhaled/ingested 7-12 mg of uranium [DOE/AD-0015 1991]. Up to that time, this was the highest recorded deposition at the plant. Within 24 hours, 80% of the uptake had been eliminated, reducing the body burden to 10% of the permissible level. Subsequent whole body counter examinations a week after exposure showed no detectable uranium.

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