White Paper

Weldon Spring Thorium Processing Investigations

Revision 0

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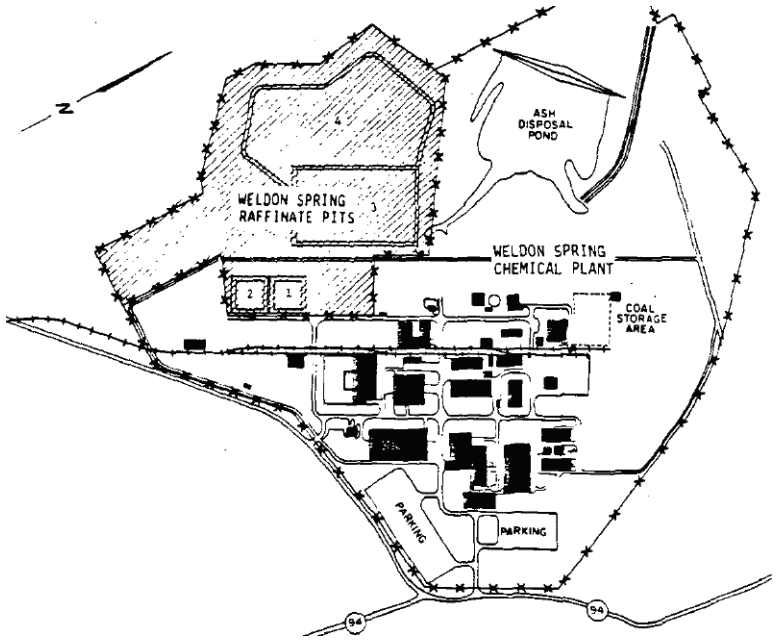
Background

The Uranium Division of the Mallinckrodt Chemical Works operated the Weldon Spring Chemical Plant (WS) for the U.S. Atomic Energy Commission (AEC) from 1957 to 1966. WS converted uranium ore concentrates and scrap to pure uranium trioxide, uranium tetrafluoride, and uranium metal. Wastes from plant operation are referred to as raffinate and include waste from extraction, and solids that result from neutralization. These wastes were pumped as slurry to four large pits (Raffinate Pits) that were constructed immediately adjacent to the plant.



A concern has been raised that workers at WS may have worked with thorium recovered from a nuclear reactor, hereafter referred to as RTh, and that NIOSH has not appropriately addressed any potential exposures resulting from processing the RTh.

The word "recycled" has several different meanings in the nuclear industry, and at times has been used to describe reactor-recovered materials. These different uses of the term "recycled" have been a source of confusion that this paper will confront.

When irradiated thorium is harvested from a nuclear reactor it is mixed with other nuclides that affect the potential worker exposures, which then change the dose assigned to workers. For example, if the WS work were with RTh, dose reconstructions would include actinides and fission product nuclides, but if the work was with natural thorium (Th_{Nat}) those additional nuclides are not included.

There is clear documentation of work with thorium at WS, but because of the impact irradiated-thorium has on the resulting dose, knowledge of the origin and if the thorium was previously irradiated is necessary to determine the dose appropriately.

A petitioner, based on six documents made available through the Freedom of Information Act, raised the concern that WS work was performed with RTh. A summary of those documents is in *Appendix-Petitioner Documents* at the end of this paper.

Discussion

NIOSH undertook two paths of investigation to determine if RTh could have been processed at WS. First, NIOSH researched WS inventory records again, searching for any indication of a source of thorium that could have included RTh. Then NIOSH researched records pertaining to the project to recover thorium from reactors looking for evidence of transfers of RTh to Fernald, since all thorium transfers to WS came via Fernald.

Which type of thorium did WS process?

Historical Nuclear Materials Balance Report for the Former AEC Owned WS Chemical Plant WS, MO (DOE, Jul1986) is a DOE report that identifies the quantities of nuclear material received and processed at WS. The report states that its accuracy was verified by comparison to audited performance-data reported to or generated by the AEC. The search for data in this report included: (1) two thorough searches of retired AEC/DOE files retained in Oak Ridge, TN, (2) an inspection of the files retained at WS, (3) contacts with the U. S. Government Records Center, St. Louis, MI, and (4) reviews of active DOE files.

In the Summary, the report states, "from June 1957 through December 1966, **four** (4) types of nuclear material were processed in the AEC-owned WS Chemical Plant". These materials were:

(1) Natural uranium (U_{Nat}) (98% of WS throughput),

(2) Depleted uranium (0.14% of WS throughput),

(3) Slightly enriched uranium (U_{En}) (0.68% of WS throughput), and

(4) Th_{Nat} (0.76% of WS throughput).

The processing of these four materials is further described as "continuously throughout the life of the plant" for U_{Nat}, and the three remaining material types were "received and processed on an intermittent basis".

Section 5.1.4 shows the annualized Th_{Nat} balances for the entire ten-year WS operating life. There is an entry for a trivial amount (44 kg) at the start of WS operations in 1958, but that amount remained static until 1962. There is a similar case for U_{En}. These materials appear to be concentrates "stored at the site prior to the start of the processing" as identified in Section 2.0. However, significant receipt and processing of Th_{Nat} is shown to start in FY1964.

The material balances shown in the *Historical Nuclear Materials Balance Report* (referenced above) are corroborated by a separate balance report generated by the plant owners (Mallinckrodt), and presented in *Weldon Spring Plant Nuclear Material Balances Final Report Summary by Year and Annual Material Balances*, Appendix A (Mallinckrodt, Jan1986). In it, Mallinckrodt similarly reports receiving 44 kg of Th_{Nat} in 1958, in a section of the report labeled "other materials" whose quantities remained static. Those same 44 kg remain on their balance until 1962 when 39 kg were shipped off site. The Mallinckrodt report remains in agreement with the DOE report and shows WS receiving the first significant quantity (13,111 kg) of Th_{Nat} after July 1, 1963. This report also shows Th_{Nat} processing started after July 1, 1963 by showing additions to Raffinate Pit 3 at that time.

Reports that show waste (Raffinate) generation can also be used to determine when processing occurred. Material processing at WS generated significant quantities of waste; ~ 2 lbs. of waste generated for each 1 lb. of material processed. Sections 2.1.4 and 5.1.4 of *Historical Nuclear Materials Balance Report for the Former AEC-Owned Weldon Spring Chemical Plant, Weldon Spring, Missouri* (DOE, Jul1986) indicate that Th_{Nat} was received in a nitrate or oxide form, batch processed in the refinery and wastes were sent to the Raffinate Pit. Section 2.3.1 of *Interim Work Plan for the Weldon Spring Site Remedial Action Project (WSSRAP)* (DOE, Jun1986) states that Th_{232} Raffinates were sent to the Pit between July 1, 1963 and December 16, 1966 (Note: Th_{Nat} is, by mass, virtually all Th_{232}). To summarize this: (1) processing generates waste, (2) all waste was sent to Pits 3 and 4, and (3) Pits 3 and 4 received this waste from July 1, 1963 to December 16, 1966.

There was some processing at WS of some extremely pure thorium nitrate tetrafluoride for the production of thorium oxide documented (Bonfer, 1988; Thorium, 1965-1967). This material was shipped from Fernald to WS starting in November 1963 until December 1966, and was concentrated Th_{Nat} not RTh.

Where was the RTh prior to the 1966 WS closure?

The figure, *Flow of Materials through the Nuclear Weapons Complex* (DOE, 1997) shows the typical flow of nuclear materials in the mid 1960's, and for WS to receive RTh from a reactor site (i.e. SRS or Hanford) it would first have to be processed at Fernald. Fernald could not have shipped RTh to WS, because they did not receive any until after AEC operations ceased at WS in 1966.

SRS records indicate the first Thorex campaign (1964-1965) did not recover the thorium during the separation of U-233. It was not until the second campaign (1965-1966) that they recovered the thorium in nitrate form and shipped it to Fernald. The document, *By-Product Thorium Nitrate Solution Handling and Storage* (Hobert, 1965) discusses a meeting held "on November 15, 1965, to inform interested persons on the plans for handling and storage of the thorium nitrate solution that will be produced in 221H building during the Uranium -233, Thorex program". A schedule in this memo indicates the first loading of thorium nitrate would begin later in the November 1965 and continue through the beginning of 1966. Then the material would be aged in the tank cars for a year before shipping. This is the earliest shipment of significant quantities of RTh to Fernald from the reactor sites which based on the schedule, could not have occurred prior to November 1966.

As documented in *Interim Work Plan for the Weldon Spring Site Remedial Action Project (WSSRAP*), Fernald conducted a feasibility study, starting in January 1966 and finished in March 1966, to determine the safe handling of RTh (DOE, June 1986). This study examines possible *future* handling of RTh and refers to six rail carloads of RTh generated as part of the Savannah River Site's (SRS) Thorex campaign.

Fernald conducted another feasibility study in March 1967 to determine, among other things, waste disposition options for their thorium hydroxide production. This process utilized RTh from the SRS Thorex campaign and is documented in *Radium and Ruthenium in Effluent from the Production of Thorium Hydroxide* (Ross, 1967).

Conclusion

The results obtained during this two-pronged NIOSH investigation show the WS processed Th_{Nat} from 1963 to 1966 inclusive, and WS did not process RTh.

Inventory records were extensively searched and closely examined, and no evidence was discovered that show WS possessed any thorium types other than $Th_{Nat.}$

Materials recovered from reactors operated as part of the nuclear weapons complex were positively controlled and well documented during this period. These documents clearly show the majority of the RTh at Fernald was not received until after 1967 and into the 1970s, and therefore were not available to WS prior to the end of AEC operations there in 1966.

References

Bonfer, 1988, *Thorium-A Search of Available Records at the FMPC*, PO(DCB)88-012; D. C. Bonfer; November 15, 1988; SRDB Ref ID: 9012

DOE, Jun1986, *Interim Work Plan for the Weldon Spring Site Remedial Action Project (WSSRAP)*, select pages, DOE/OR-869; Department of Energy (DOE); June 1986; SRDB Ref ID: 3645, pdf pp. 311-317

DOE, Jul1986, *Historical Nuclear Materials Balance Report for the Former AEC-Owned Weldon Spring Chemical Plant, Weldon Spring, Missouri*, DOE/OR-872; Department of Energy (DOE); July 1986; SRDB Ref ID: 3645, pdf pp. 130-160

DOE, 1997, *Flow of Materials through the Nuclear Weapons Complex*, diagram from page 122 of *Linking Legacies* document; Department of Energy (DOE); January 1997; SRDB Ref ID: 3645, pdf p. 2

Heatherton, 1967, *Analysis of Health Problems in Processing Recycle Thorium*, correspondence to J. A. Quigley; R. C. Heatherton; April 10, 1967; SRDB Ref ID: 29545

Hobert, 1965, *By-Product Thorium Nitrate Solution Handling and Storage*; R. H. Hobert; November 19, 1965; SRDB Ref ID: 58541

Kleeschulte, unspecified, *Compilation and Preliminary Interpretation of Hydrologic Data for the Weldon Spring Radioactive Waste-Disposal Sites, St. Charles County, Missouri—a Progress Report*; Michael J. Kleeschulte and Leo F. Emmett; unspecified date; SRDB Ref ID: 3645, pdf pp. 254-263

Mallinckrodt, Jan1986, *Weldon Spring Plant Nuclear Material Balances Final Report Summary by Year and Annual Material Balances*, Appendix A; Mallinckrodt; January 13, 1986; SRDB Ref ID: 3645, pdf pp. 265-272

Ross, 1967, *Radium and Ruthenium in Effluent from the Production of Thorium Hydroxide*, correspondence to R. H. Starkey; K. N. Ross; March 13, 1967; SRDB Ref ID: 42850

Thorium, 1965-1967, *Transfer of Thoria/Thorium Nitrate to Weldon Spring*, various memos; authors include J. H. Cavendish, J. H. Noyes, C. L. Karl, and George Rennich; various dates from September 21, 1965 through April 19, 1967; SRDB Ref ID: pdf pp. 15-19, 32-36, 41-42, and 48-55

Appendix-Petitioner Documents

This Appendix includes select statements and information from documents provided by the petitioner through an email to SC&A, dated March 20, 2012. The petitioner supplied the following documents:

- *Occupational Exposures of Workers to Chemicals during Uranium Processing 1942-1966*

Figure III-3, on page 8 (pdf p. 14) of *Occupational Exposures of Workers to Chemicals during Uranium Processing 1942-1966*, is a table showing potential exposures; the last line shows that Thorium (ThO_2) processing was conducted during 1964-1966 and is consistent with figure III-2. The line labeled "Raffinate Chemicals++" that shows potential exposures to chemical agents in the raffinate is true because the chemicals were also used in the uranium separation process. The ++ footnote to this table lists the raffinate chemicals and states, "Th-230 was recovered" for the period 1947-1966. This is not consistent with Figure III-1 and III-2, which does not show raffinate processing at WS. This 1984 document was a chemical exposure study, and as such did not appear to concentrate on the radioactive details of the materials.

The last paragraph on page 9 and 1st paragraph on page 10, states that solid residues (raffinate) were processed for recovery of ionium (thorium-230). "During some periods (after 1947)..." This statement is true for Plant 7E for 1955~1958, as verified in Figures III-1 and III-2, but does not appear to apply to WS from the information in this document.

- *Process Development Quarterly Report - Part I Laboratory Work*, April 1, 1958

Process Development Quarterly Report - Part I Laboratory Work discusses the demonstration of a process for the recovery of nitrate values from raffinate on a laboratory scale, and states that thorium concentrations must be considered if this method is used, especially if high-thorium Canadian refinery feed is used.

- *Weldon Spring Site Background Report*

Pages 26 and 27 state that WS processed uranium ore concentrates and recycled scrap and that "some processing of *thorium residues* was also performed."

- *Engineering Evaluation of Alternatives for the Disposition of the Weldon Spring Raffinate Pits Site*

The Executive Summary on page 1, (pdf 4), discusses the types of waste at the pits site, to include "neutralized raffinates from uranium refining operations, washed slag residues from uranium metal production operations, and raffinate solids from the processing of *thorium recycle materials.*"

In May of 1983, Bechtel National Inc. (BNI) analyzed sludge from the four Raffinate Pits and calculated the following:

	Thorium (total tons)	Th-230 (pCi/g)	Th-232 (pCi/g)
Pit 1	4	24000 ± 1000	100 ± 20
Pit 2	6	24000 ± 1000	120 ± 20
Pit 3	40	14000 ± 1000	120 ± 20
Pit 4	15	1600 ± 100	120 ± 20

Source: Table 3.1, page 15 (pdf 10) and Table 3.2, page 17 (pdf 12) of *Engineering Evaluation of Alternatives for the Disposition of the Weldon Spring Raffinate Pits Site*

- *Raffinate Pit Sampling Plan*, May 27, 1988

The *Raffinate Pit Sampling Plan* states that the pits contain "... raffinate solids from the processing of *thorium recycle materials.*"

- *EPA Environmental Impact Statement*, September 1989

The *EPA Environmental Impact Statement* states that Pits 1 and 2 contain residues and waste from uranium mining operations and washed slag residue from uranium metal production, while Pits 3 and 4 contained "...similar waste plus thorium-contaminated raffinate solids from processing *thorium recycled products."*

Evaluating these documents as a whole indicates that the term "thorium recycled materials" or "products/residues" refers to the Th-232 production process that took place during 1963-1966, not to the recycling of pit raffinate material for the recovery of thorium (Th-230). The one article describes the processing of raffinate material on a lab scale, and points out that thorium needs to be concentrated if this process was used.