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THORIUM NITRATE PILOT-SCALE DEMONSTRATION AND STOCKPILE PROCESSING OPTION RESULTS REPORT

December 1998

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DEPARTMENT OF ENERGY

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ACRONYMS AND ABBREVIATIONS

ADV	ammonium diuranate (process)
AEA	Atomic Energy Act
ASO	Analytical Services Organization
DCP–AES	direct coupled plasma–atomic emission spectrometry
DL	detection limit
DLA	Defense Logistics Agency
DNSC	Defense National Stockpile Center
DOE	U.S. Department of Energy
EIS	environmental impact study
ETTP	East Tennessee Technology Park
FBC	fluidized bed calciner
FMPC	Feed Materials Processing Center
HTGR	high temperature gas reactor
ICP–MS	inductively coupled plasma–mass spectroscopy
LDR	land disposal restrictions
LLW	low-level waste
LMER	Lockheed Martin Energy Research Corp.
LMES	Lockheed Martin Energy Systems
MCL	Materials and Chemistry Laboratory
NEPA	National Environmental Policy Act
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
ppm	parts per million
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RTPC	Radkowsky Thorium Power Corporation
TCLP	toxicity characteristic leaching procedure
ThN	thorium nitrate
ThO_2	thorium oxide
TNH	thorium nitrate hydrate
UTS	Universal Treatment Standard
XRD	X-ray diffraction

EXECUTIVE SUMMARY

The Defense Logistics Agency (DLA) manages the storage of approximately 4,500 metric tons of thorium nitrate* (includes drummed constituents) and sought assistance from the U.S. Department of Energy (DOE) in evaluating technologies, based on DOE's experience in handling and treating radioactive material. There are 3,580 tons of crystalline thorium nitrate (ThN) contained in 21,609 overpack drums of various sizes. Contact with moisture from over 30 years of storage has caked the material into solid monoliths typically contained in three or four plastic and steel drums. The current state of this material poses a potential hazard, which could adversely impact human health and safety and/or the environment.

Two 1-ton thorium nitrate hydrate demonstrations were completed as part of the work scope. This work was completed to form a technical basis for the 3,500-ton stockpile conversion process selection and establish a reference cost and schedule for processing. The thorium end point criteria strongly influences the flowsheet selection, with the basis herein being nitrate conversion processing for long-term thorium storage to meet a future fuel-cycle demand. Direct hot water dissolution of the thorium nitrate from the innermost drum is recommended for the pre-treatment step. The recommended process is thorium oxalate precipitation with calcination at 850°C to thoria (ThO_2). The process selection is based on the pilot-scale demonstration performance results related to product purity and the available process development and design technical data to maintain process availability and control.

This report presents the results from the two wet chemistry pilot-scale process demonstrations and presents the summary conclusions for the production-scale process selection and other key elements. The directive for this work was to convert the thorium nitrate to a more benign form. The radiological nature, secondary waste stream minimization, worker safety, process safety, volume reduction, mass reduction, off-gas control, and financial constraints of a full-scale production operation provide the motivation to assess processing alternatives. The pilot-scale demonstrations conducted verified that the process, health and safety, and product quality variables can be designed and controlled to allow the transformation of the thorium nitrate stockpile into a lower-risk, usable stockpile of thorium oxide. A means of converting the ThN to a stable thorium oxide form with a reduced mass and volume was established. This final form would, with minimum effort, be recoverable for eventual use as a feed in the manufacture of thorium products or be acceptable for placement in a repository.

The most noteworthy considerations in implementing a stockpile conversion program are:

1. The National Environmental Policy Act (NEPA): The NEPA process would evaluate the potential impacts of the processing and non-processing options. A Record of Decision is achievable by

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*Thorium (^{232}Th) can be used as fuel in breeder-style nuclear reactors. Thorium-232 is considered a fertile nuclide because it can be fissioned by high-energy (>1MeV) neutrons to produce fissile uranium (^{233}U). The Defense National Stockpile Center currently has ^{232}Th in storage in the chemical form of thorium nitrate, $Th(NO_3)_4 \cdot 5H_2O$. The potential use of ^{232}Th is uncertain; hence, there is a need to mitigate any potential future environmental or exposure hazards associated with this material. Since ^{232}Th has a long half-life (1.41×10^{10} years), the current program evaluated treatment methodologies to safely produce less leachable reduced forms. The more chemically stable oxide is lower in mass and volume and exhibits low leachability characteristics, making it suitable for licensed long-term storage.

†Based on a review of the fuel cycle literature and the development work completed as part of this project.

November 2000 should the purpose and need be structured around a stockpile conversion option at this time.

2. Schedule and Cost: Stockpile processing could be completed in a nine-year time frame, with five years accounting for production process operations. The estimated program cost is $40 million, which could be incrementally funded. The thorium product end point requirements affect the cost and investment, as can be seen from the information in the table below.

Estimated Stockpile stewardship cost cases ($millions)

Case	Pre-treatment	Treatment	Transport	Disposal	Subtotal	30% cont.	Total
1—Pretreatment to separate ThN from drum and dunnage and denitrate (ref. 31)	13.0	11.7	0.9	1.8	27.4	8.2	35.6
2—Overpack and ship (25% drum basis) (ref. 31)	4.4	0	1.8	3.6	9.8	3.0	12.8
Perma-Fix	~ 10.0	~ 10.0	0.8	1.5*			22.3
Recodyne	~ 15.3	~ 15.3	1	9.2			40.8

*Perma-Fix assumed that secondary nitrate waste could be sold as a commodity, whereas Recodyne assumed the nitrate would be disposed of as a low-level waste.

3. The oxalate process flowsheet is recommended for the stockpile conversion processing—primarily based on the large design data base available and the inherent nature of it being a purification process which preserves product purity. New containers designed for optimum packing efficiency and long-term corrosion resistance may be required.

4. Steam and direct de-nitration: The product is very fine ThO_2, and a pilot-scale test program would be required to validate direct de-nitration processing is viable for final form requirements as currently exist.[‡] Either of the wet chemistry processes tested could be scaled up and operated to form a flowable dry powder.

5. Less technical data exists that can be used to validate scale-up for the hydroxide process. The separation of impurities is more difficult because the hydroxide acts as a sorbent and co-precipitates impurities in the reagent (i.e., without washing, Na content higher than that associated with the nitrate concentration).

6. The oxalate process has a characteristically wide process control range, large data base for design, and results in a high purity ThO_2 product. Recodyne run 10 was the best pilot demonstration calcination operation, where the conversion and product quality was high. The product is characterized in Attachment 4. It is important to attain time at temperature to achieve an

[‡]The ORNL "Sol Gel" process was required as an intermediate step in the processing to make satisfactory fuel pellets.

acceptable degree of conversion. A design concept was proposed for investing in front end drying equipment, separate from the calcination equipment, which would improve process control.

7. The pilot demonstration results confirmed the feasibility of converting DLA ThN to thorium oxide by oxalate precipitation. The ThN was removed easily from its container by a stream of hot water. The thorium in the resulting liquor was precipitated to the oxalate with an efficiency of greater than 99.9%. The thorium oxalate filtered well once the precipitation time was extended to 12 hours. Conversion to thorium oxide was accomplished in a rotary kiln operating at 800 °C. Initial conversion efficiencies of 60 - 80% were increased to 90 - 95% with increases in kiln temperature and/or residence time.

8. The sodium nitrate byproduct might be made clean enough to be recycled for agricultural use as a fertilizer diluent, or dried for use as an ingredient in pyrotechnic materials. The Perma-Fix Environmental Services, Inc., team assumed this to be very feasible, whereas the Recovery Dynamics, LLC, team accounted for the nitrate secondary stream as a low-level solid waste, per use of evaporation equipment.

9. A market survey completed indicates that the thorium product has limited market potential at the present time. Most of the classic industrial or consumer applications of thorium have been replaced with alternate materials, indicating that treated product could remain within the custody of DLA.

The batch processing selected for the pilot-scale demonstration was successful and is recommended for the production operations. There exists the need to apply tight process control to multiple process parameters to control particle size and achieve repeated conversion efficiencies to form the ThO_2 product. The demonstrations results/process data/stockpile engineering assessments, in conjunction with existing fuel cycle processing data as reported in the references, allows for adequately describing and specifying each unit operation to complete detail design and selection of equipment. Predictions of performance of the coupled process systems at full-scale can be made, albeit requiring demonstrations and allowing for implementing modifications in the field as part of the program. Achieving repeatable solids/liquids separation and product/waste specifications is a challenge. Detailed investigation of the literature and data analysis is required to specify each unit operation. Effort remains to validate that certain new, commercially supplied equipment (and existing installed equipment in the case of the fuel fabrication industry) is available to meet all functions.

Selected unit operations and coupled processes required are not validated at the 3 tons per day (ThN basis) required production throughput, as based on any similar past processing plant operation. On that basis, some technical uncertainty exists regarding the capacity to scale-up the integrated system and the accuracy (at this time) of the resultant operations time line predictions. The unit operation performance characteristics should be validated against system design requirements per field scale demonstrations. The integrated system throughput should be established by incorporating a rigorous performance/validation and optimization test phase using the actual production scale equipment.

1. PROJECT DESCRIPTION

The Defense Logistics Agency (DLA) Defense National Stockpile Center (DNSC) has about 7 million lb of thorium nitrate (ThN) crystals (hydrate form) stored at two depot locations in the United States: Curtis Bay, Maryland, and Hammond, Indiana. The DLA is the managing agency and is interested in developing alternatives for the conversion for use and/or disposal of this material, which is radioactive and assumed to be an oxidizer.[1] The material was assumed to require processing to remove the oxidizing characteristic before it could be completely evaluated for disposal at a low-level radioactive disposal site. Although there were several potential methods to accomplish the processing, all involved emerging technologies that had not been shown to work successfully for this type of material. The DLA/DNSC recognized that additional data was needed to determine the most effective and cost-efficient method of conversion for use and/or disposal.[2] The DLA/DNSC also has an obligation under the National Environmental Policy Act (NEPA) to determine whether the method eventually selected represents a significant impact on the human environment. The DLA/DNSC recognized the special expertise of the U.S. Department of Energy (DOE) in matters involving radioactive materials to evaluate conversion for use and/or disposal options and provide recommendations. Lockheed Martin Energy Systems (LMES) was selected as the "name of program contractor to complete the pilot-scale demonstration efforts." The project lead responsibility was transferred in 1998 to the Chemical Technology Division at Oak Ridge National Laboratory (ORNL), which is operated by Lockheed Martin Energy Research Corp.

The method of accomplishment involved a two-phased approach, with the DLA decision to proceed to Phase 2 to be made after Phase 1. The first phase (Phase I) called for the completion of a ~1-ton pilot demonstration and an engineering study for processing the complete stockpile. Two separate demonstrations were completed, with results reported herein. The second phase (Phase 2), to be contracted separately, would involve full-scale processing and disposition of the stockpile. To maximize commercial involvement and research and development (R&D) value added during Phase 1, degrees of freedom existed regarding pilot- and full-scale process design, location, and the final product physical form. The baseline material storage pathway for the product was to assume that the product is returned to the DLA/DNSC. Phase I procurement functioned in initiating a dialogue with the commercial sector. The Phase I procurement was intended to be sufficiently flexible so that upon completion, a full range of the most reasonable flowsheet options could be explored.

Beginning in May 1997, two teams, subcontracted to LMES, planned and performed a pilot-scale demonstration of a chemical de-nitration process for use in converting thorium nitrate into a more stable, reduced-volume form. One team was composed of Perma-Fix Environmental Services, Inc., Performance Development Corporation, and Teledyne Brown Engineering. Another team was composed of Recovery

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[1]The RCRA ignitability characteristic (D001) was assessed (for the new thorium nitrate and a nitrate-rich secondary residual) using the D07 oxidizer test prescribed in 49 CFR 173. Neither of these materials would be considered ignitable based on the results.

[2]The DLA previously has evaluated the potential for using a plasma torch application to treat the thorium nitrate, with technical assistance from DOE. Thorium oxide surrogate tests, conducted at Georgia Institute of Technology, and laboratory-scale de-nitration work, conducted at the Oak Ridge K-25 Site (now known as the East Tennessee Technology Park), demonstrated that a plasma torch should not be used to treat the thorium nitrate in its current storage configuration. It was noted that although a plasma torch might have allowed processing of the material in storage drums without a significant material handling investment, organics in the plastic packaging reacted unfavorably with the nitrates in the thorium nitrate. The results from the tests show the thorium nitrate should be separated from the drums and packing constituents and de-nitrated.

Dynamics LLC and F. W. Hake and Associates. Reports describing how each pilot-scale demonstration was planned, performed, and documented, including evaluations of the results, are included as Attachments 1 and 2.

The over-riding objective of the project was to fully develop a safe and effective de-nitration process and demonstrate that process at pilot scale. Other objectives for the pilot-scale demonstration included the following:

- Develop a safe and effective means of removing thorium nitrate from its original containers.
- Evaluate and refine methods for control of the process.
- Characterize raw materials, products, and byproducts.
- Evaluate radiological control characteristics of the process.
- Evaluate the market potential for products and byproducts.
- From the pilot-scale results document feasibility and resources to scale the process up to a full-scale commercial operation to process the entire 7,000,000-pound stockpile inventory.

The full-scale (stockpile basis) de-nitration process should produce approximately 3.5 million lb of reduced thorium product in powder form. Mixing with additives to consolidate in a well-bound form was an original demonstration requirement. The consolidation requirement was relaxed during the execution of the field work based on the sponsor approving a final product that was flowable with a low tendency to become airborne during pilot-scale processing.[3]

Important process comparison engineering analyses completed include pre-treatment system design, solids handling, and thermal de-nitration in air to form reduced thorium compounds, as compared with aqueous dissolution chemistry methods. The field work required processing at least 1 ton of thorium nitrate by execution of a pilot-scale demonstration. All objectives were met for both pilot-scale demonstrations:

1. convert 1-ton ThN to a stable form;
2. provide data to predict the mass and volume reduction of the present stockpile;
3. produce a thorium product form that is (a) with minimum effort, recoverable for use; and (b) acceptable for placement in a repository; and
4. provide documentation to establish a technical basis that defines the production-scale process economics and investigates product utilization/thorium disposition (including additional R&D requirements and environmental analyses necessary to support the stockpile processing).

The thorium products from the demonstration were returned to the DLA Curtis Bay depot for storage. The packaging constituents were defined as primary waste, and the processing wastes were defined as secondary

[3] A concern in converting the thorium nitrate to a reduced thorium solid form, and processing the resulting powder in this pilot demonstration, is the environmental, health, and safety implications of the processing. An important factor to consider is control of particulates in the processing of very fine powder. Particulate escape in the liquid effluent and/or gas stream during conversion was evaluated.

wastes. Toxicity Characteristic Leaching Procedure (TCLP) data were determined for the thorium product (from processed thorium nitrate) as part of the pilot demonstrations. The subcontractors were responsible for all local, state, and federal permits associated with the pilot demonstration and for the disposal of all primary and secondary waste. The processing yielded a thorium product that met land disposal restrictions (LDRs) and/or Universal Treatment Standard (UTS) limits for all Resource Conservation and Recovery Act (RCRA) constituents.

To adequately bracket the process, subjects that were evaluated and documented in each of the two pilot demonstrations and the stockpile engineering assessments included:

A. Removal and physical conditioning of thorium nitrate from the drums and plastic containers
   1. process methodology
   2. radon removal/control
   3. particulate control
   4. mass balance/volume reduction
   5. secondary waste disposal

B. Conversion of thorium nitrate to reduced thorium product
   1. process methodology and flowsheet/equipment description/test plan
   2. conversion/effluent monitoring/capture of radioactive materials
   3. mass balance/volume reduction
   4. secondary waste disposal/classification

C. Thorium product powders and/or their encapsulation
   1. process methodology and flowsheet/equipment description/performance testing
   2. monitoring the process for ThO_2 dust
   3. mass balance
   4. secondary waste disposal/classification
   5. analytical results for product and waste stream RCRA metals/including product TCLP data

2. PROCESS DEVELOPMENT

Pilot plant demonstrations were conducted to compare two conversion methods for converting ThN to insoluble, chemically stable forms and their storage volume reduction. These demonstrations were designed to yield additional process information to aid in the selection process for identifying the best available method for converting the DLA thorium nitrate stockpile. Recovery Dynamics, LLC (Recodyne) precipitated the thorium with oxalic acid to form thorium oxalate, which was calcined to thorium oxide. In contrast, Perma-Fix Environmental Systems, Inc. (Perma-Fix) precipitated the thorium with sodium hydroxide, which was dried at about 100°C. Perma-Fix calcined small samples of the dried thorium hydroxide to a reduced thorium product at about 538°C for comparison with the Recodyne thorium oxide, which was heated up to 1000°C.

2.1 BACKGROUND

A site at Curtis Bay, Maryland stores most of the inventory, while another site in Hammond, Indiana stores the remainder. The DLA/DNSC is investigating their options for converting the thorium nitrate crystals into a chemical and physical form which reduces environmental and health risks while reducing storage volume. The DLA/DNSC has a secondary goal of consolidating the thorium stockpile at one of the sites. It is assumed in this work that the final thorium product storage site will be at Curtis Bay, Maryland. The choice of final storage location is completely within the discretion of the DLA. Earlier pilot-scale demonstrations investigated how direct thermal conversion technologies might be applied to meet the DLA's goals. With respect to the chemistry, the oxide thoria (ThO_2) is considered the most stable form of thorium reasonably attainable from ThN. To produce thoria, a thorium salt is usually subjected to a thermal process in which the anion is converted to a gas and driven off at a high temperature. This project demonstrated two wet chemistry conversion technologies which may have application.

Chemical analysis of ThN samples taken during a previous pilot test project showed concentrations of arsenic, chromium, lead, and silver, which, if presented throughout the ThN stockpile, would total over 19 tons of combined heavy metals. The current state of this material suggested that a potential metal content hazard existed which could adversely affect human health and safety and/or the environment. Metals analysis was conducted with results reported as part of this project.

2.2 PILOT-SCALE DEMONSTRATIONS — SUMMARY

The project plan for the Perma-Fix pilot-scale demonstration involved two phases; (1) preliminary bench- scale tests, and (2) pilot-scale batch tests. In the preliminary bench tests, the basic chemical and physical attributes of the process and its various feeds, intermediates and final products were evaluated. Competing control schemes of the precipitation reaction were tested, evaluated and refined. Settling and Filtration tests provided feedback for evaluating the liquid/solid separation attributes of precipitated thorium hydroxide solids. Commercial polymeric additives for liquid/solid separation and dry product binding were also evaluated during the preliminary bench-scale tests.

The lessons learned in the preliminary bench scale tests were used to develop the basic process scheme for the early pilot-scale batch tests, and to conceptualize potential process enhancements for testing in the later batch tests. The pilot-scale test facility was designed utilizing data from the bench testing, and was installed inside a quonset hut, inside a building at the Perma-Fix of Florida facility, in Gainesville, Florida.

Detailed operating procedures for all equipment and systems of the pilot-scale test facility were developed, reviewed, and approved prior to first use. In addition, batch test instruction packages were developed for each batch test. These instruction packages provided step-by-step guidance for performance of each batch test, and provided data sheets for recording of measurements performed during the test. Also, a narrative log of test activities was kept for all batch tests.

Although the DLA thorium nitrate inventory contains source material from the United States, France, and India, all of the material used in the preliminary bench tests and the pilot-scale batch tests originated in the United States (lot 71). Nine (9) drums of thorium nitrate from the Curtis Bay depot, and one (1) drum that had been in the custody of Lockheed Martin Energy Systems in Oak Ridge, were shipped to Gainesville for use in the test program. Small samples from the Oak Ridge drum were provided early by Lockheed Martin for use in the preliminary bench scale tests.

The pilot-scale test program was organized into five (5) batch tests, with each batch being composed of the contents of two drums of thorium nitrate. Table 2-1 provides a summary of each batch test performed, and the experimental objective tested during each test.

The pilot-scale tests took thorium to a low-temperature dried product. The incremental benefits of calcining the dried product were evaluated at bench-scale using samples of dry product from the pilot-scale dryer. This experimental scheme evaluated the basic precipitation, settling, filtration, and product rinsing operations incorporated into the process, and provided repetitive testing of the basic process.

Table 2-1. Summary of pilot-scale batch tests

Batch test number	Batch size (lb thorium nitrate)	Experimental objective
1	389.81	Evaluate Basic Precipitation Process
2	410.34	Evaluate Basic Precipitation Process
3	385.27	Add Serial Rinsing to the Process
4	385.52	Add Serial Rinsing to the Process
5	387.73	Add Liquid Byproduct Recycle to the Process
Total	1,958.67	

Data collection around the process, and sampling of process streams were performed, during each batch test, to ensure that sufficient data were collected to allow calculation of material balances. Also, bench-scale tests to evaluate precipitation, settling, filtration, and serial rinsing were performed in parallel with each pilot-scale batch test using samples collected from the batch.

The thorium de-nitration process tested during this project is a variant of the sol-gel process which was used in the 1970's at the DOE Feed Materials Processing Center (FMPC) at Fernald, Ohio. Thorium nitrate hydrate crystals are dissolved in demineralized water, and the thorium nitrate is neutralized with sodium hydroxide to produce a thorium hydroxide precipitate and a sodium nitrate supernate. Liquid-solid separation and rinsing steps are used to improve the separation between the thorium hydroxide and the sodium nitrate. The thorium hydroxide is concentrated in this process, and then dried and repackaged. The steps of the process are as follows:

1. Removal of thorium nitrate crystals from packaging
2. Weighing and dissolving thorium nitrate in hot demineralized water
3. Heating and mixing while precipitating thorium using sodium hydroxide
4. Gravity separation of sodium nitrate mother liquor from the thorium hydroxide sludge
5. Optional serial rinsing of the thorium hydroxide sludge blanket
6. De-watering and rinsing of thorium hydroxide product
7. Drying of thorium hydroxide filter cake
8. Filtration and ion exchange polishing of secondary process liquid streams
9. Recovery of process heels
10. Packaging of dried product

Recodyne developed an approach to convert the ThN to thorium oxide via aqueous precipitation of an intermediate thorium compound. Besides reducing or eliminating the need to control nitrogen oxide emissions, the conversion of ThN to an aqueous feed facilitates easy removal from its packaging, since the caked material dissolved readily in a stream of hot water. Although precipitation of thorium salts and their conversion to ThO_2 has been successfully operated on a pilot or commercial scale in the past, the poor chemical and physical state of the DLA ThN precluded their direct application without obtaining additional information from pilot testing. This demonstration was thus required in which a pilot plant converted 1 ton of DLA ThN to ThO_2 over a two week period. The results of the pilot plant can be used to confirm the feasibility of ThN conversion and provide the bases for full-scale design and estimation of life-cycle costs.

Bench-scale tests with synthetic solutions of thorium nitrate and silver indicated that thorium could be selectively precipitated as the peroxide leaving the heavy metals in solution. A relatively complex process was thus initially proposed for the demonstration which not only had the capability to convert the ThN to the oxide, but also to isolate and convert the heavy metals to a form that had commercial value as a silver concentrate. It was suspected, however, that the analytical results obtained in previous studies, and which the peroxide precipitation process was based on, were high—biased such that the actual concentration of heavy metals in the ThN was much lower than reported. In subsequent discussions with LMER/LMES, it was agreed that a much simpler conversion process utilizing the intermediate precipitation of thorium oxalate could be demonstrated if the heavy metals were not present or would otherwise not cause the final thorium oxide product to be considered characteristically hazardous. Recodyne considered this approach in its development of the original demonstration proposal; however, it had been discounted, since review of the chemistry indicated that the bulk of the silver and lead would precipitate along with the thorium. Since Recodyne confirmed at bench scale the chemistry of the proposed process with the actual ThN to be used in the demonstration test, an opportunity existed to further analyze the ThN composition and determine if switching to the oxalate precipitation was feasible.

The oxalate precipitation and thorium oxide calcination steps were tested in the laboratory on a composite sample of the DLA ThN. The sample was diluted down to 110 g/L thorium and oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) added. The resulting precipitate was filtered, washed and calcined in a muffle furnace at a temperature of 800°C to form thorium oxide. Analysis of the filtrates by direct coupled plasma–atomic emission spectrometry (DCP-AES) indicated that essentially all of the thorium was precipitated by the oxalate addition 1-ppm in filtrate). None of the four heavy metals were detected. Based on these positive results, generation of a final wastewater meeting Nuclear Regulatory Commission (NRC) criteria for free release was also considered a possibility.

The possibility was further examined by determining if the radium left behind after thorium precipitation could be reduced to an acceptable level by the standard technique of co-precipitation on barium sulfate. A single stage precipitation with barium chloride and filtration of the resulting barium sulfate provided a 99.9% removal of radium. A two-stage barium sulfate precipitation was thus included in the pilot plant flow sheet as an option

with the expectation that radium activity could be reduced to less than 50 pCi/L. Regulatory approval, however, for the free release of wastewater from a radioactive process has a degree of uncertainty that preclude it as the sole approach to nitrate liquor disposal. The final step in the pilot demonstration was therefore based on a zero discharge to be achieved by evaporation of the nitrate wastewater to dryness.

To finalize the pilot plant flow sheet, potential hazards associated with the ThO_2 product were also examined. The ThO_2 product generated from the composite sample was leached with acetic acid as specified by the TCLP. The four heavy metals were not detected by DCP-AES analysis indicating that the final ThO_2 product would not be considered as characteristically hazardous. The other concern with the thorium product was its physical nature and the associated requirements for storage in a repository. The future handling and long term storage of the ThO_2 product as an unconsolidated material, particularly a fine powder, could pose a risk of becoming an airborne hazard. Preliminary bench-scale tests indicated that the product could be pressed into tablets with the addition of a binder such as lime. A tablet press was added to the pilot plant operation to demonstrate the feasibility of this approach.

Based on these positive bench-scale results, it was decided that the conversion process to be demonstrated would be based on the intermediate conversion of ThN to thorium oxalate.

Attachments 1 and 2 are the Perma-Fix and Recodyne results reports, which describe the pilot plants, their operations, and the results obtained. Included in the reports are engineering studies which provide the design bases and preliminary process flow diagrams and mass/energy balances for the full-scale systems. The life cycle cost for constructing, operating, and decommissioning full-scale systems for converting the entire DLA inventory were estimated based on these designs. Potential health and environmental issues regarding full-scale operations were also examined.

2.2.1 Equipment and Process Operations

Attachments 1 and 2 give detailed descriptions of the process equipment and operations. The results reported in these attachments are utilized by ORNL in the process selection and analytical data review sections of this report. Selected pilot demonstration project photographs are included as Attachment 3.

2.2.2 Analytical Data

The available data collected during the two demonstrations is summarized and presented in Attachment 4. Data were generated by the vendors at their sites or using an outside laboratory of their choice. Split samples were obtained for comparative analyses performed by the Lockheed Martin Energy Systems Analytical Services Organization (ASO) at ETTP with results reported herein. Permafix took many samples at various points of their process, and enough data are available to evaluate the quality of the final product generated. On the other hand, Recodyne did not gather as many samples during their process demonstration, and therefore, less data was available to assess completely the quality of the final product from their process.

2.2.2.1 Analytical techniques used

ASO used ICP–MS (inductively coupled plasma–mass spectroscopy) for the metal analyses. This technique provides detection limits which are among the lowest achievable; it is also less prone to interferences, especially spectral interferences due to highly interfering elements like thorium, which are troublesome when using techniques like DCP or ICP-AES. Permafix used a radiochemical method for the thorium analyses and ICP-MS

for the metals. Recodyne used DCP for thorium analyses as well as for the analyses of the liquid wastes generated.

It is important to note that using the wrong analytical technique results in the generation of data which do not meet the data quality objective of detection limit being below regulatory limits, and render these data useless. The laboratory used by Recodyne utilized a technique with a detection limit too high for comparison with UTS limits for metals.

2.2.2.2 Evaluation of the final product with the RCRA regulations

The TCLP results obtained on the final product generated by the two processes are found in Table 2.2. The concentrations of the RCRA elements are found below the UTS limits except for beryllium and selenium. Both of these elements have reported detection limits higher than the UTS limits and even though the found concentrations in the TCLP extracts were below the reported detection limit, this does not prove that the concentration is actually below the UTS limit. Complementary analyses could be performed as necessary to fulfill this need.

Table 2.2. Analyses obtained from the TCLP test for comparison with the UTS RCRA limits

	Permafix process			Recodyne process		RCRA-UTS limits (mg/L)
	Dried product BT2-	Dried product BT4-007e	Dried product BT5-007e	Dried Product E-125-L1	Dried Product J-125-L1	
TCLP extract						
Antimony (mg/L)	0.2	<0.2	<0.2			2.1
Arsenic (mg/L)	1	<1	<1	<0.5	<0.5	5
Barium (mg/L)	0.71	<0.1	0.84	<0.1	<0.1	7.6
Beryllium (mg/L)	0.02	<0.02	<0.02			0.014
Cadmium (mg/L)	0.03	<0.03	<0.05	<0.03	<0.03	0.19
Chromium (mg/L)	0.05	<0.05	<0.05	<0.1	<0.1	0.86
Lead (mg/L)	0.05	<0.05	<0.05	<0.3	<0.3	0.37
Mercury (mg/L)	0.02	<0.02	<0.02	<0.002	<0.002	0.2
Nickel (mg/L)	0.039	<0.3	<0.3			5
Selenium (mg/L)	0.4	<0.4	<0.4	<0.5	<0.5	0.16
Silver (mg/L)	0.02	<0.02	<0.02	<0.05	<0.05	0.3
Thallium (mg/L)	0.02	<0.02	<0.02			0.078
Vanadium (mg/L)	0.02	<0.02	<0.02			0.23
Zinc (mg/L)	0.39	<0.2	0.21			5.3

2.2.2.3 Purity of the final products

One alternative for the final product generated is its use as fuel in Russia. The requirements for the purity of the thorium oxide needed for this application are provided in Table 2.3.[32]

The data obtained on the final product for both processes are compiled in Table 2.4.

The major impurities found in the final products from both processes are mainly nitrate and chloride. The Perma-Fix process contains nitrate in concentration ranging from 2.7 to 15.5% in the calcined product, and levels of chloride around 500 ppm in the dried product. The Recodyne process is more pure and contains nitrate in the range of 0.04 to 0.5%, and chloride around 100 to 200 ppm. Nevertheless, both nitrate and chloride are volatile at high temperature, and should not remain in the thorium product once it has been appropriately thermally reduced.

Table 2.3. Russian purity requirement for ThO_2[32]

Impurity	Maximum permissible
Iron oxide	0.05% (500 ppm)
Silicon dioxide	0.02% (200 ppm)
Chloride	0.01% (100 ppm)
Heavy metals	0.01% (100ppm)
Rare earth elements	0.10% (1000 ppm)

Analysis data of major impurities (e.g., calcium, silicon, iron...) in the final products was limited. A direct evaluation of the content of iron oxide was made based on a separate analysis for comparison with the Russian fuel cycle application. Analytical results performed on the thorium nitrate (Lot #71–Drum #2, results from ref. 13) at the beginning of the project indicated that the amount of silicon dioxide (SiO_2) was 0.10%, and iron oxide (Fe_2O_5) was 0.003%. The amount of SiO_2 is slightly above data obtained for the Radkowsky Thorium Power Corporation (RTPC) application, but at this low level only an analysis made on the real product could lift the ambiguity. The purity is very close to that required, but complementary analyses are required as part of a program focused on meeting this end point use.

The concentration of heavy metals in both products is far below the Russian standard. The rare earth elements (cerium, praseodynium...) were not found in the products at the time the radiological analyses were performed.

2.2.2.4 Evaluation of the purity of the final products by X-ray diffraction

Chemical analyses are providing data on the elemental composition of the samples; however, they do not provide any information about the nature of the minerals which are making that sample. X-ray diffraction (XRD) is a powerful tool which allows the recognition of any crystallized material. It is important to examine by XRD the final products obtained by both processes to appreciate the purity of the thoria formed. Samples of the final products generated by both processes were examined by the Materials and Chemistry Laboratory

Table 2.4. Analyses of the final product obtained with both processes, and general comparison with the purity data for Russian application

	Permafix process								Recodyne process		
	Dried product BT1-008d	Calcined product BT1-009	Dried product BT2-007e	Calcined product BT2-008e	Solid dried product BT4-007e	Calcined product BT4-008e	Dried product BT5-007e	Calcined product BT5-008e	Solid product E-125-L1	Solid product J-125-L1	Russian purity
% moisture			23.5	<1	14.1	<1					
Mercury (mg/kg)	0.00039	0.016	<0.0002		<0.0002	<0.0002	0.00063				
Thorium (mg/kg)			490 000	780 000	27 000	810 000	570 000	770 000			
Thorium (mg/kg)			542 000	733 000	648 000	794 000	538 000	725 000	710 000	560 000	
Sodium (mg/kg)			32 000	43 000	13 900	16 000	29 200	36 200			
Sodium (mg/kg)	79 500		31 200		12 400		27 300				
Nitrate (mg/kg)			58 000	66 000	22 000	24 000	70 000	88 000	4700	350	
Nitrate (mg/kg)	149 700	154 600	45 000	82 000	16 500	26 500	13 300	97 000			
Chloride (mg/kg)			525	520		510		570	110	170	
Antimony (mg/kg)	0.0015	<0.05	<0.00005		<0.0005	<0.0005	0.0228				
Arsenic (mg/kg)	0.0041	<0.099	<0.001		<0.001	<0.001	0.0032				
Barium (mg/Kg)	1.16	<0.497	0.52		0.635	0.146	2.77				
Beryllium (mg/kg)	0.0022	0.041	<0.0002		<0.0002	<0.0002	0.0143				
Cadmium (mg/kg)	0.0002	<0.02	0.0002		0.0002	<0.0001	0.0009				<100 ppm
Chromium (mg/kg)	0.0796	4.58	0.0053		0.0061	0.0041	0.0847				
Lead (mg/kg)	0.0231	<0.199	0.0105		0.0053	0.0006	0.0237				
Nickel (mg/kg)	0.0327	0.563	0.002		0.0037	0.0011	0.0264				
Selenium (mg/kg)	0.0127	<0.199	<0.002		<0.002	<0.002	0.0261				
Silver (mg/kg)	0.0002	0.013	0.0001		<0.0001	<0.0001	0.0004				
Thallium (mg/kg)	<0.0001	<0.01	<0.0001		<0.0001	<0.0001	<0.0001				
Total (mg/kg) or ppm	1.3163	6.271	0.54145		0.6542	0.1558	2.9726				
SiO_2 contained in the feed thorium nitrate used for the demonstration: 0.10 wt %											<0.02%
Fe_2O_5 contained in the feed thorium nitrate used for the demonstration: 0.003 wt %											<0.05%
The rare earth elements (Ce, Pr...) were not detected in the radiological data of the final products from both processes											<0.10%

(MCL) at East Tennessee Technology Park (ETTP). Two samples of the products from two separate runs from each pilot plant demonstration were presented for characterization with respect to phase identify, crystallite sizes and particle sizes. The results of these analyses are discussed below and are presented in Attachment 4.

X-ray diffraction data of Perma-Fix samples designated BT4-007e and 7A1-5 revealed poorly crystalline ThO_2 and ThO_2 plus $NaNO_3$, respectively. Similar data for Recodyne samples E-125-L1 and J-125-L1 revealed two phases ThO_2 and $Th(C_2O_4)_2 \cdot 2H_2O$ in the former sample whereas the latter sample consisted of well crystallized ThO_2.

Crystallite sizes for the four samples were computed from the diffraction peaks on the basis of their breadth at half their maximum intensity. Recodyne products contained larger crystallites than those recorded for the Perma-Fix samples, which is indicative of a greater degree of crystallinity for the ThO_2 from Recodyne.

Image analyses of the two pilot plant samples show a difference in particle size. The sample from Perma-Fix has a smaller median diameter 1.31 micrometer versus 2.15 micrometers for Recodyne powders.

3. A REVIEW OF THORIUM NITRATE DE-NITRATION PROCESSING

There is a need to identify a safe, cost-effective, conservative process to transform hydrated thorium nitrate to ThO_2. The product from such a process should meet certain criteria: ThO_2 shall be specified as the final compound; the ThO_2 will be dry and flowable either as a powder or in granules; and special attention should be paid to maintaining ThO_2 in as pure a state as is reasonable, without incorporating contaminants. There are a number of conversion methods that could be employed. They include

- Thermal de-nitration—direct. (Earlier phases of this project included lab-scale data for de-nitration in-drum with dunnage contact and as separated ThN material, which is reported on in ref. 1, and pilot-scale plasma vitrification of ThO_2 surrogates, which is reported on in ref. 2.)
- Precipitation of thorium hydroxide from aqueous solution with sodium hydroxide, followed by ignition of the hydroxide
- Precipitation of thorium oxalate with oxalic acid, followed by ignition of the oxalate in air
- Precipitation of thorium hydroxide from aqueous solution with NH_3, followed by ignition of the hydroxide

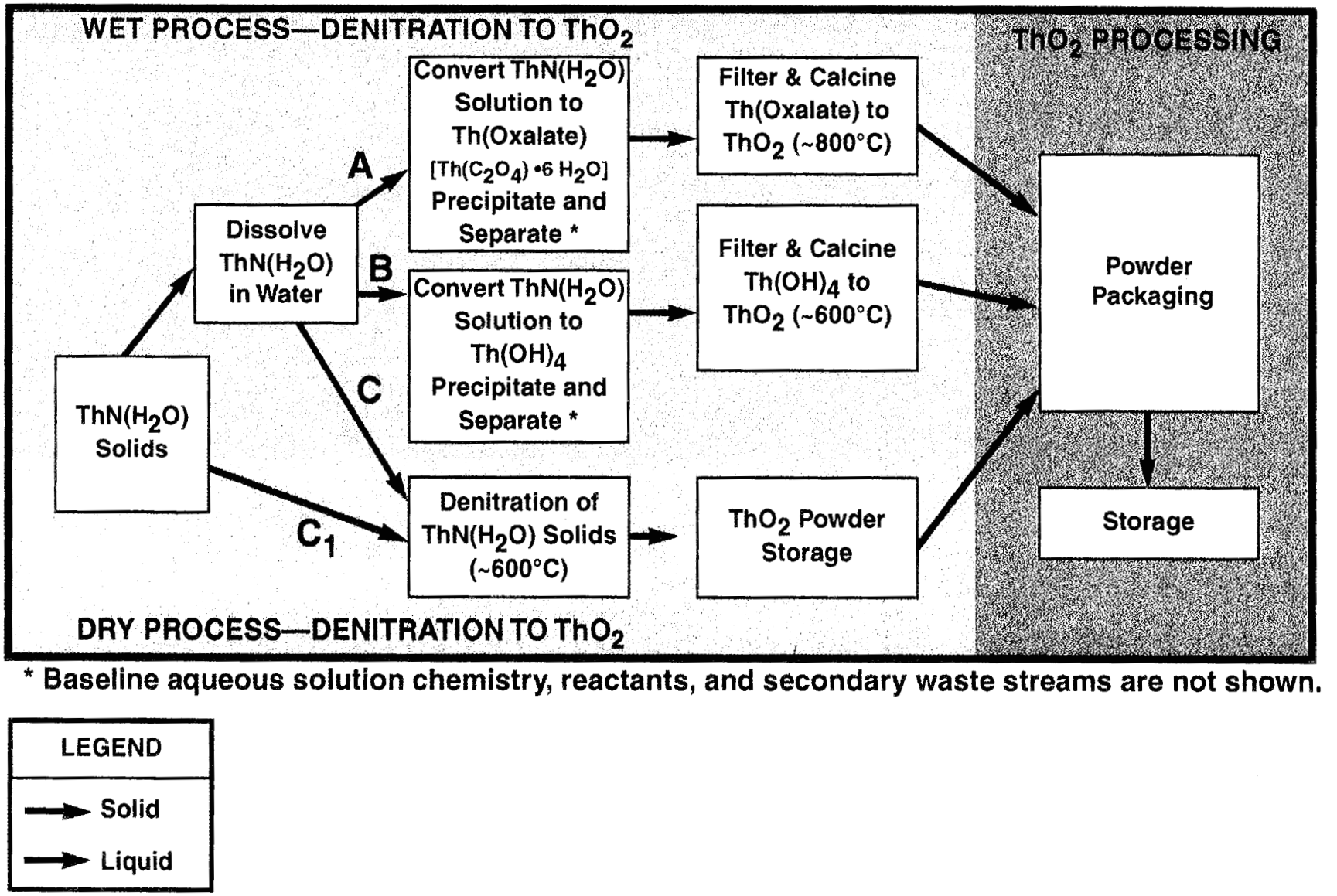
Thermal de-nitration involves the thermal decomposition of thorium nitrate solids to form thorium oxide and nitrogen oxides gases. The other methods are aqueous precipitation methods that require washing, drying, and possibly calcination steps. Some of the reagents that give insoluble precipitates with thorium nitrate solutions are hydroxide, peroxide, fluoride, oxalate, iodate, and phosphate. The last four of those give precipitates even in strongly acidic solutions. The three methods that have been used historically to convert ThN to ThO_2 are presented in Fig. 3.1.

The balanced equations for each process are shown in Table 3.1.

The following sections discuss those three conversion methods, including the pilot-scale demonstration results for the hydroxide and oxalate flowsheets.

3.1 THERMAL DE-NITRATION

Steam de-nitration of ThN was the method of choice for converting ThN to ThO_2 for use in the sol-gel process. Several different systems incorporating steam de-nitration were used in the later part of the 1950s and throughout the 1960s. The two steam de-nitration methods utilized at the Mallinckrodt Chemical Works in Weldon, Missouri were the pot method and the fluidized bed calciner (FBC), whereas the steam de-nitration method used at ORNL employed a rotary calciner. It should be noted that the selection of steam de-nitration for conversion of ThN to ThO_2 was predicated on the need to have a fine ThO_2 powder that was readily dispersable in a liquid to form a sol. Figures 3.2 and 3.3 illustrate the steam de-nitration processes used at Weldon Springs and ORNL.



* Baseline aqueous solution chemistry, reactants, and secondary waste streams are not shown.

Fig. 3.1. Simplified block diagram for wet and dry volume reduction processing methods.

Table 3.1. ThN to ThO_2 conversion processing

Thermal De-nitration

$$Th(NO_3)_4 \cdot 4\,H_2O \xrightarrow{\text{heat}} ThO_2 + 4\,HNO_3 + 2\,H_2O$$

Thorium hydroxide route – caustic

$$Th(NO_3)_4 \cdot 4\,H_2O + 4\,NaOH \rightarrow Th(OH)_4 + 4\,NaNO_3 + 4\,H_2O$$

Thorium hydroxide route – ammonia (not demonstrated but discussed)

$$Th(NO_3)_4 + 4\,NH_3 + 4\,H_2O \rightarrow Th(OH)_4 + 4\,NH_4NO_3$$

$$Th(OH)_4 \xrightarrow{\text{heat}} ThO_2 + 2\,H_2O$$

Thorium oxalate route

$$Th(NO_3)_4 + 2\,H_2C_2O_4 \cdot 2\,H_2O \rightarrow Th(C_2O_4)_2 \cdot 2\,H_2O + 4\,HNO_3 + 2\,H_2O$$

$$Th(C_2O_4)_2 \cdot 2\,H_2O + O_2 \xrightarrow{\text{heat}} ThO_2 + 4\,CO_2 + 2\,H_2O$$

Approximately 900 tons of thorium nitrate (hydrate) were converted to thorium oxide (ThO_2) via thermal de-nitration processes during the 1960s at the Weldon Springs, Missouri facility.[3] Steam de-nitration was performed in pots previously used for uranium de-nitration. The product from processing ThN as the feedstock was a fine, fluffy dispersable powder which was almost dust-like. Greater than 30% of the powder (ThO_2) was lost to the fume collection system. Recapture of the carryover powder was labor intensive as well as a safety problem which increased the cost and difficulty of processing. The computed crystallite sizes determined for the ThO_2 powders produced in the pot denitrators, range from 90Å to 120Å, but no quantitative data is available for the particle sizes of the powders. However, for these particles (powder) to form a sol, one would expect them to be in the submicron size range.[4]

In addition, exposure of these powders to the atmosphere results in contamination with carbon dioxide which results in the formation of thorium carbonate leading to detrimental effects on the quality of the sol that is produced. Even enclosing the pot denitrators failed to improve the system significantly. Problems inherent to the pot de-nitration process include: (1) poor temperature control; (2) escape of fine, dust-like particles into the environment, (3) contamination on air exposure; and (4) variability in crystallite size due to temperature gradients.

To circumvent the problems associated with the steam pot denitrator at Weldon Springs, the company directed their attention to fluid bed technology.[5] Enclosure of the FBC system was an important modification of that system which served to optimize safety in handling the ThO_2 fine powders. Contamination was further minimized by using dense ThO_2 as the seed bed material. The feed material was introduced into the FBC as a ThN solution through a series of nozzles. The computed crystallite sizes for the ThO_2 powders ranged from 45Å to 60Å which is approximately half the size of crystallites from the pot denitrator. As in the paper on pot de-nitration no quantitative measurements of particles were reported. Whether the smaller crystallite sized correspond to smaller particle sizes is not known.

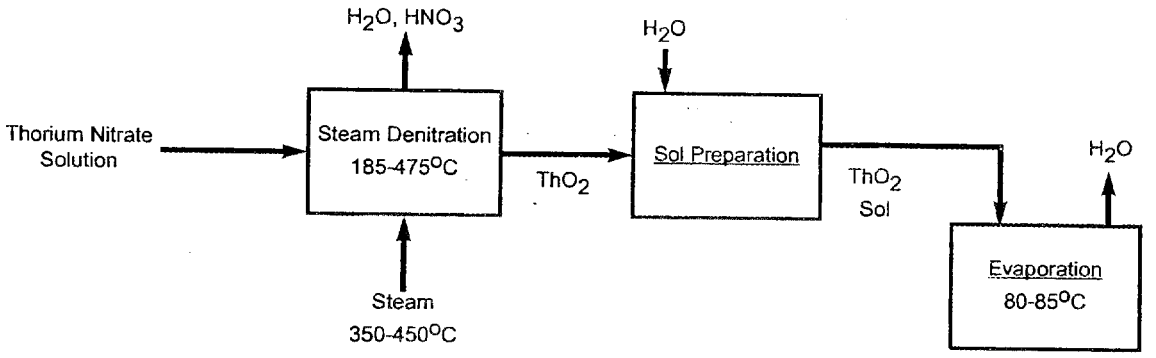


Fig. 3.2. Process flowsheet for steam denitration performed at ORNL.

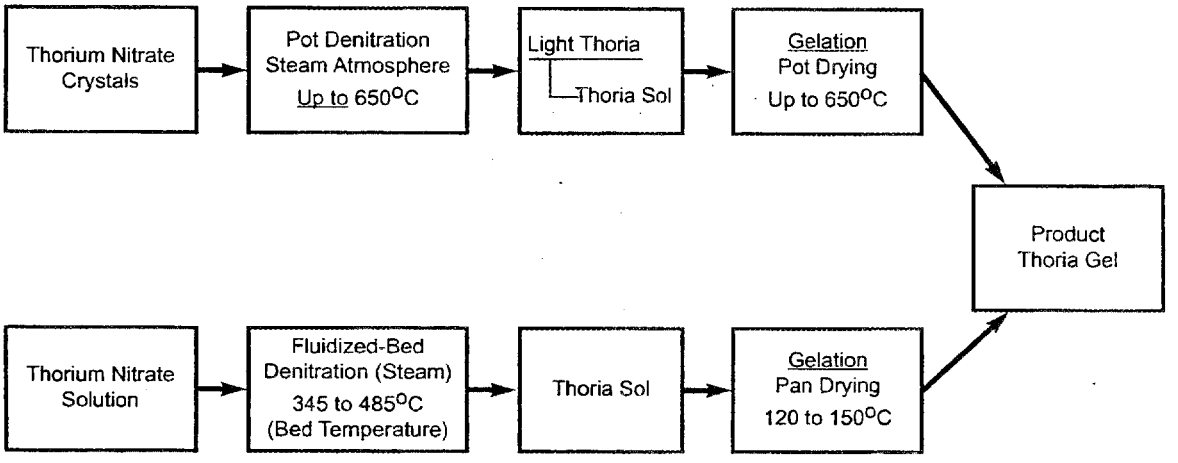


Fig. 3.3. Process flowsheet for steam denitration performed at Weldon Springs.

However, the FBC powders were reportedly more easily and completely dispersed. The results from implementing a FBC system were avoidance of the dangers associated with the pot system, production of more uniform ThO_2 powders which were readily dispersable in water and restricted the exposure of the powder to CO_2. However, the drawbacks to the FBC system are [6-7] (1) maintenance of the seed bed stability; (2) complexity of the system; (3) fine particles subjected to entrainment in the off-gas leading to a burden on the system that could result in significant costs; (4) and bed caking.

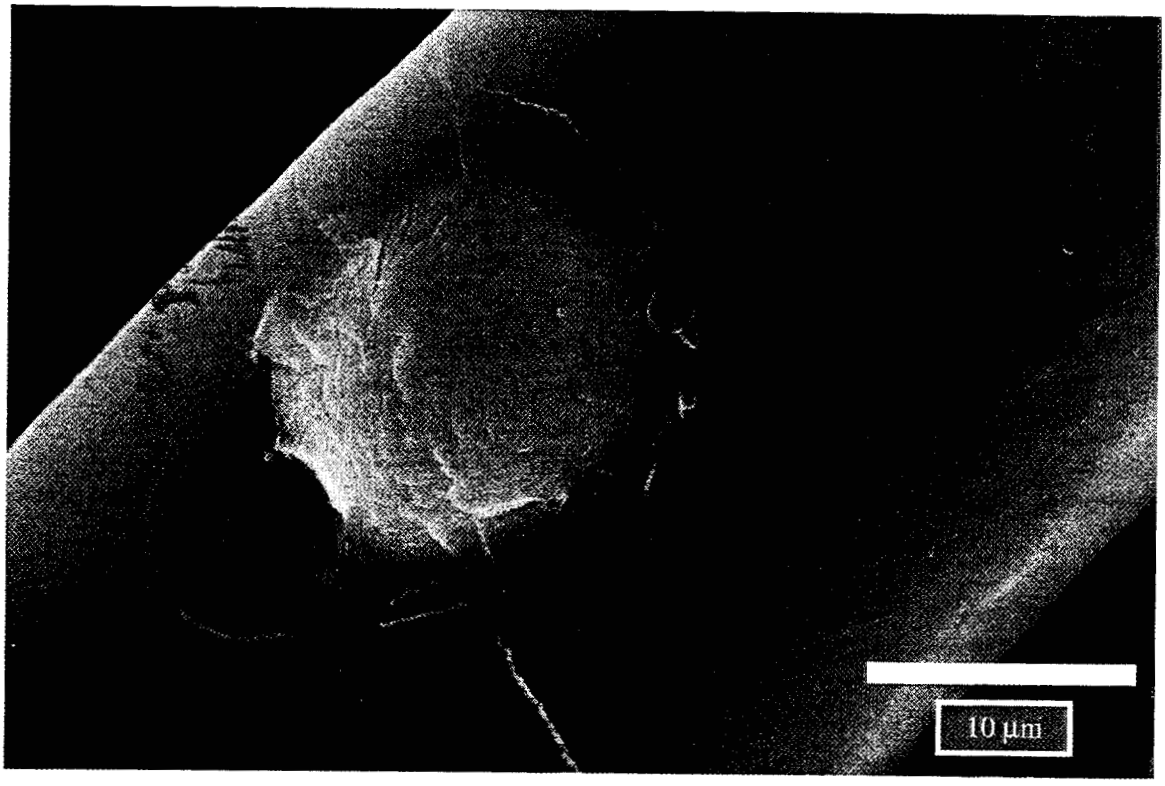
During the 1960s at ORNL, steam de-nitration methods for the conversion of ThN were also being pursued.[8] A procedure was developed involving the use of a rotary calciner which was surrounded by an electric furnace with superheated steam used as the heat source within the calciner. The presence of an electric furnace on the outside of the calciner was to minimize any de-nitration taking place on the calciner walls. The off-gas mixture of NO_x and H_2O combines to yield a dilute HNO_3. The product was a readily dispersable powder.

Critical in this procedure was the flow rate of steam which was found to govern the ThO_2 particle entrainment in the off-gas. Any attempt to scale up this process requires close monitoring of the steam flow rates and the calciner temperature versus the outer electric furnace. Inherent in this system as well as all other thermal de-nitration methods is the accumulation and build up of NO_x gas during continuous processing and the potential for accumulating ThO_2 particles.

Several studies of ThO_2 prepared by direct thermal de-nitration were performed over the years (refs. 9–12). The products from these studies were reportedly coarse powders of low quality for fabricating dense fuel pellets. In one of these studies particles of ThO_2 were observed to average 60 μm with computed crystallite sizes of 110D. However, more recently (1996), a direct thermal de-nitration test for a small quantity of ThN (100 lb) was performed.[13] The test involved use of ThN from a DLA drum and heating the ThN in a rotary calciner operated at 600°C for complete conversion. The ThO_2 produced in this test consisted of fine, fluffy powders, which reportedly dispersed easily with air flow or other movements similar to the powders produced in the earlier steam de-nitration tests. Handling of these powders proved to be difficult to the extent that any air movement disturbed the powders and they became airborne, making the handling of these powders difficult and an inhalation hazard. A bench-scale test using direct de-nitration on gram size samples was performed at K-25 plant of the Oak Ridge facilities.[1] The products from these studies were particles that ranged from 50 μm to submicron size with crystallite sizes of 100Å which agrees with similar data reported in reference 10. Also observed in these studies was the carry-over of a ThO_2 particle (15 μm) in the off gas and found embedded in a HEPA filter. Additional finer particles are believed to be embedded in the filter cross-hatch as depicted in Fig. 3.4.

Summary

Thermal de-nitration processes using steam have been shown to produce fine, fluffy, dust-like ThO_2 powders. This highly dispersable product served to meet specific nuclear fuel needs in the 1960s, e.g., the sol-gel process. However, these ThN de-nitration processes reveal some important problems with regard to particle size and entrainment in the off-gas system and its effect on safety and costs. All thermal denitrating methods have in common the carryover of ThO_2 particles and the need to control the exhaust of the NO_x gases in a safe, expedient way. The need for control of NO_x emissions adds cost for maintaining and permitting the off-gas system. Any attempt to convert the stockpile by thermal de-nitration would require a development and demonstration program for fluid-bed reactor or rotary calciner systems integrated with the off-gas system. This would be contrary to the present needs which are to produce a flowable (i.e., not readily airborne) ThO_2 powder which could be readily packaged for return to the DLA or to a disposal site where retrievable storage could be achieved.



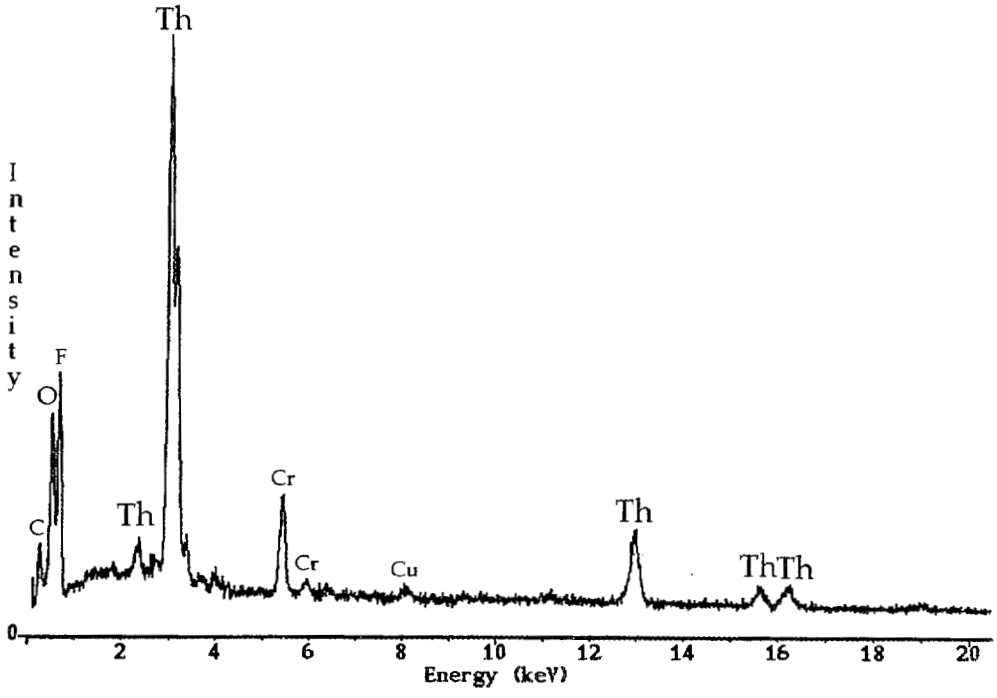


Fig. 3.4. SEM photomicrograph of Th-rich particle embedded into a teflon fiber of the filter (top). ESD data of Th-rich particle shown above (bottom).

3.2 THORIUM HYDROXIDE

There are several methods of converting thorium nitrate to thorium hydroxide. Alkali (sodium, potassium; etc.) hydroxides, ammonium hydroxide, and calcium hydroxide are the commonly used precipitating agents. Other methods that have been used are sol-gel methods, which include external, internal, and alkoxide conversions.[14–17] Thorium hydroxide microspheres can be made by the external and internal methods which can be calcined to make thorium oxide microspheres. The size of the microspheres can be controlled in the 0.1 to 2 mm range. These processes have been developed to the extent that the final densities of the microspheres can be controlled by the process chemistry and calcination procedures. The internal and external sol-gel methods were developed for use in the production of nuclear reactor fuels and have a number of other process advantages; however, these methods probably are too expensive to be employed by the DLA considering the limited conversion needs. The alkoxide method of forming thorium hydroxide involves the controlled hydrolysis of solutions of heated thorium ethoxide/alcohol solutions. This sol-gel method would not be practical and would be too expensive for the DLA to use because the thorium is in the nitrate form. Furthermore, only fine thorium hydroxide or oxide powders can be made by this method.[16]

Perma-Fix Environmental Services, Inc. (Perma-Fix) selected sodium hydroxide as the precipitation agent for its thorium de-nitration pilot project. It chose to have thorium hydroxide rather than thorium oxide as the final storage product. The reasoning for these choices were certainly acceptable at the start of the project. The goal was to reduce the storage volume of the thorium and convert it to an insoluble, stable form, with a low tendency to be made airborne.

Perma-Fix believes that the hydroxide would be a stable form if exposed to groundwater. That is true if the pH of the ground water is always above the pH of precipitation of the thorium nitrate. Most information in the literature suggest that the pH of precipitation is in the range of 2 to 4. The pH of most groundwaters[18, 19] would be in the range of 6 to 8. The pH of seawater is about 8. Landfill waters on the other hand are more acidic. The pH of the TCLP leachant which simulates landfill water[20] is 4.9. Some conditions arise as the result of acid rain in which the pH can be much lower (3 to 4). Thorium hydroxide exposed to solutions in this pH range would be vulnerable to some dissolution. Thorium oxide, on the other hand, is very stable. Pure thorium oxides prepared at temperatures above 700° C are considered high-fired oxides and are difficult to dissolve. The standard procedure used to dissolve these oxides is to heat them at 70 to 90°C in 12 *M* HNO_3 which contains 0.02 *M* HF. Thorium oxides which are calcined at temperature below 700°C are easier to dissolve but the same acid strength are also used.

All the cations (sodium, ammonium, etc.) of the precipitating agent used to convert thorium to the hydroxide end up as soluble nitrate salts. A large fraction of this salt is removed in the filtrate during filtration; however, even after being filter pressed, there are considerable amounts of interstitial liquid remaining in the solids which contain the same concentration of salt as that of the filtrate. The pilot-scale demonstration by Perma-Fix showed the importance of rinsing the precipitated thorium hydroxide with deionized water to remove the salt. In Batch Test 4 the solids were rinsed five times with deionized water to determine the number of rinses needed for salt removal. Analyses found that the dried thorium hydroxide product [169.1 lb (76.7 kg)] contained 2.7 lb (1.22 kg) nitrate and 1.0 lb (0.45 kg)of sodium or 3.7 lb (1.68 kg) of sodium nitrate, which is about 2.19 %. Mole calculations show that about 2.7 lb of nitrate are needed to form stoichiometric sodium nitrate with 1.0 lb sodium. The percentage of sodium nitrate in the calcined sample with all the water removed was 2.68%. The percentage of sodium nitrate in the product samples for the other batch tests were much higher. If it turns out that purity of the thorium product is not a concern, Perma-Fix products for all the batch tests passed the DOT oxidizer tests. If thorium product purity is needed, ammonium hydroxide would be the precipitating agent used. Ammonium nitrate can be decomposed at temperatures below 500°C. Nitrogen oxide gases are generated. In Batch Test 2, in which the thorium hydroxide solids were rinsed with deionized water, the percentage of

sodium nitrate in the dried product (194.5 lb) was 5.9%. It was assumed that all the nitrate (8.4 lb) was present as sodium nitrate. There was a total of 6.3 lb sodium in the product. Of this, 3.1 lb was bound as sodium nitrate. The remaining sodium(3.2 lb) was probably sorbed by the thorium hydroxide (or hydrous thorium oxide). Thorium hydroxide—like many other hydrous metal oxides of other metals such as Zr, Ti, Hf, Fe, Al, Ce, etc—is an excellent ion exchange material.[21] The general formula may be written $ThO(OH)_nXnH_2O$. These materials are prepared by alkali precipitation of hydrous thorium oxide with sodium or ammonium hydroxide. Distribution batch tests using air-dried, hydrous thorium oxide[9] showed that the K_d for Na^+, Sr^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Cr^{3+}, were 38, 61, 112, 40, 6, 5, and 40 mL/g. In these batch tests the solution (ml) to sorbent (g) ratio used was 100. The pH of the solutions was 4.5 to 6. The K_d for Na is not very large and may account for the excess sodium being removed by the five rinses in Batch Test 5. The inability of the hydroxide process to maintain the product purity for recovering for re-use in the fuel cycle is the largest single difference when compared against product criteria.

The thorium hydroxide filter cakes were dried in the Plowshare Dryer at temperature in the range of 96 to 116°C using steam heating. The agitator speed was 50 rpm in all the batch tests but Batch Test 1 (20 rpm). If the agitator speed is too fast, it can contribute to a larger fraction of fine particles. The criterion used to decide if the products were dry was visual observation. The Perma-Fix report said they were dried to 'apparent dryness'. Samples of the products were taken and heated at higher temperature to determine water content. The water content ranged from 18 to 25%. Thermogravimetic analysis and differential thermograms of samples of air-dried thorium hydroxide which was prepared by NaOH precipitation of thorium nitrate have been reported in the literature by C. Heitner-Wirguin.[22] These results showed that the air-dried thorium hydroxide began to lose water at 85°C and the greatest loss was attained at 200°C (about 28% of the weight was lost.). An additional 7% of the initial weight was lost in heating between 200 and 500°C. No further weight loss was observed while heating between 500 and 1000°C.

These data show that free water and water of hydration (chemically bound water) was lost between 85 and 200°C. Between 200 and 500°C only hard to remove chemically bound water and hydrogen from the conversion of thorium hydroxide to thorium oxide were removed.

In its batch tests Perma-Fix learned an important and basic lesson in control of precipitation to obtain a more filterable precipitate. When the NaOH is added rapidly to the thorium nitrate solution whose pH is at or past the pH at which the thorium hydroxide begins to form, the thorium hydroxide formed will be more gelatinous, slower to settle and harder to filter. When the NaOH is added slowly at and past the pH of precipitation, the hydroxide precipitate settles more rapidly and is easier to filter. Slow precipitation results in larger crystals and fast precipitation results in smaller crystal. Thorium hydroxide with larger crystals also have larger pore size and interstitial liquid containing impurities are easier to remove by washing with water. There is generally an ideal temperature at with the best results can be obtained. Perma-Fix found that by heating a thorium nitrate solution in 88 to 95°C range (the ideal temperature range), it could add 25% NaOH at a fairly fast rate as long as the pH of the solution remained below the pH of precipitation, but it needed to switch to a 10% NaOH solution which was added slowly while the thorium hydroxide was precipitating. Sources in the literature show that thorium hydroxide precipitates in the range of 2 to 4 which is consistent with what Perma-Fix found. Additional NaOH was added to obtain a pH of 11 to make sure the precipitation was completed. Information in the literature suggests that the precipitation is completed at a pH of 5.8. One of the problems Perma-Fix discovered was that the test drums of thorium nitrate had different amounts of free nitric acid. The range of initial pH was from 0.13 to 0.92. The initial pH of the thorium nitrate in Batch Test 3 was 0.92 meaning it had much less nitric acid. By using the addition rate of the 25% NaOH that was used in Tests 1 and 2 which had lower pHs (0.13 and 0.41), Perma-Fix overshot the pH of the precipitation range in Test 3 and obtained a gelatinous precipitate that was difficult to settle and filter. In its discussion of how it would solve these

problems in its proposed Full Scale De-nitration Process, Perma-Fix came up with some reasonable fixes for some of the problems it encountered in the pilot-scale tests which are discussed in the summary of this section.

Considering the presence of varying amount of nitric acid in the thorium nitrate, reliable continuous measurements during precipitation of the thorium hydroxide are important. However, sometimes pH measurements are not very reliable at very low pHs because of electrode shock. Before starting the addition of caustic to the thorium nitrate in the reaction vessel, a titration of a sample of the well mixed thorium nitrate solution with a standard NaOH solution would provide very valuable information needed to calculate the amount of caustic that would be needed to reach a predetermined pH (say 1.5). The operator would then meter this amount of 25% caustic to the reactor vessel and allow the solution to mix for a period of time to allow solution equilibrium to occur. At this point a check would be made of the online pH to see how it compared with the calculated pH value. A sample would then be taken to inspect for signs of permanent precipitate. Localized precipitation occurs with the addition of strong caustic as the pH of precipitation is closely approached. If the pH is below the pH of precipitation, the localized precipitate will dissolve. If the pH check is OK and there is no permanent precipitate, the operator could then start slowly adding the 10% NaOH to precipitate the thorium hydroxide.

The Perma-Fix pilot-scale demonstrations showed the importance of agitation speed during the precipitation and drying steps. If the agitation speed is too fast or vigorous, it can contribute to a larger fraction of fines in the precipitation step which are more difficult to filter. It also results in a larger fraction of fines in the drying step caused by the breakup of granular or agglomerated particles. Perma-Fix had a serious problem in each of the batch tests with the fraction of thorium hydroxide fines that were not retained by the 1 micron bag filters during filtration of supernatant and rinses. Even in Batch Test 4 about 30% of the thorium ended up in the process heels from various sources. In the full-scale process, Perma-Fix proposes to use ultra filtration such as cross-flow filtration to remove the fine thorium particles from the heels. If a filter press had a less than a 1 micron rating, that would be very helpful in the coarse filtration step.

Summary

A significant amount of precipitated thorium hydroxide was carried over into the supernatant and filtrate that had to be recovered to complete the total product. Even in Batch Test 4 in which the thorium was precipitated under ideal conditions, about 29% of the thorium was recovered from the various process heels. This problem had to do with the fairly large pore size (1 micron) of their filters.

A significant amount of Th was carried over into the supernate and filtrate that had to be recaptured to complete the total product. Rinsing of the filter cake improved it; however, it also served to increase the Th content of the filtrate. The use of the ploughshare unit as the furnace at temperatures of ~280°F failed to achieve the necessary temperature to remove $NaNo_3$ and crystallize to make ThO_2. The product that results from the ploughshare operation are a poorly crystalline ThO_2 that is associated with the sodium nitrate (two-phase material). This fact was clearly shown by a comparison of two samples, one from the ploughshare (~280°F) unit, the other from bench scale heating to 1000°F which yielded 54.2% and 73.3% thorium, respectively.

The conversion of thorium nitrate to thorium hydroxide or to thorium oxide by calcination of the thorium hydroxide could be a viable method if the lessons learned in the pilot-scale demonstration and available literature were utilized, and the criterion for maintaining purity was not a program driver. The main lessons from the demonstration had to do with process precipitation controls and filtration, which were addressed with explanations and possible corrective actions in the above paragraphs of this section. Perma-Fix's proposal (in the Engineering Assessment) for the full-scale process installation seems reasonable. Rather than use of a

Plowshare reactor/design concept, which did not work as well as planned, use of two-conical screw agitated precipitation reactors was proposed. These reactors use a tapered helical screw agitator on an orbital arm to provide low-sheer mixing which would help minimize small particle formation during precipitation. They also proposed to install three pH sensors in each reactor which will provide feedback data to an automatic pH controller with programmable logic to follow a prescribed titration curve for the precipitation step. The system will have a refined caustic injection control. Perma-Fix also proposes to use ultra filtration such as cross-flow filtration to remove the fine thorium particles from the heels. Heating the thorium hydroxide to 200°C in the drying step with a humidity control loop incorporated in the design to determine when the moisture has been removed, should result in consistently dried product. A temperature of 200°C is needed to remove both the free water and the chemically bound water. If thorium oxide is the chosen storage product, heating the thorium to 600°C for an adequate period of time would be needed. Thorium oxide that is heating at temperatures above 700°C results in a product that is much harder to dissolve if that were needed in the future.

The hydroxide conversion method has severe problems if a very pure product is sought by the DLA. Because thorium hydroxide is a good co-precipitation media and is also a fairly good inorganic ion-exchange material, it would be almost impossible to remove impurities. Aqueous NaOH solution could not be used as the precipitating agent because of sodium contamination. If NH_4OH were used, it would add an additional problem of dealing with the nitrogen oxide gases formed during calcination.

3.3 THORIUM OXALATE

Most thorium oxide (thoria) powder is produced commercially by calcining the precipitate of hydrated thorium oxalate. Since purified thorium is usually produced in the nitrate salt form, thorium oxalate is most commonly precipitated by the addition of oxalic acid to a solution of thorium nitrate.[1] As a by product, four moles of nitric acid are created for every mole of thorium nitrate reacted, resulting in 0.95 metric tons of HNO_3 for each metric ton of ThO_2 produced. Precipitation with oxalic acid followed by calcination to the oxide has the advantage of separating thorium from several impurities such as uranium, iron, and titanium that remain in nitric acid solution.

A thorium oxalate precipitation process developed at Iowa State for the U. S. Atomic Energy Commission was used on a production scale by the National Lead Company at Fernald, Ohio. At 60°C, oxalic acid powder was added to an aqueous thorium nitrate solution (200 g Th/liter and 0.5 molar HNO_3) at 105% of the stoichiometric amount to convert all thorium to the oxalate. After the solution was stirred for 5 min to complete precipitation, the crystalline oxalate precipitate was readily filtered on a vacuum filter and washed with about half the feed solution volume of distilled water at 35°C. The precipitate was dried in a twin-screw drier with a jacket temperature of 120°C to a water content of 10 wt %. The dried oxalate was then converted to oxide in an externally fired rotary kiln, with counterflow of air. The exit gas temperature was controlled at 820°C to produce a reactive, free-flowing oxide containing less than 0.5% carbon and about 0.5% moisture.[23]

The Homogeneous Reactor Program at ORNL included studies of breeding in a thorium blanket. It was anticipated that the blanket would be a slurry of thoria in heavy water containing 1000 g Th per liter of slurry. Thoria was prepared in the Chemical Technology Division Pilot Plant Section, Building 3019, by converting thorium nitrate to thorium oxalate and then calcining the oxalate to the oxide.[24] Reagent-grade oxalic acid was added to a thorium nitrate solution at 40°C, precipitating thorium oxalate. After agitation for one hour, the slurry was vacuum filtered and the oxalate was washed. The thorium oxalate was calcined in three stages: 370, 520, and 800°C. The installed equipment had a capacity of 340 kg thoria per week, and a total of 5,000 kg of oxide was produced for engineering studies. The loss on ignition of thoria samples at 1000°C ranged from 0.06 to 1.17 wt %.

Laboratory studies were conducted in support of the Homogeneous Reactor Program to characterize the thoria produced by the thermal decomposition of thorium oxalate. The effects of oxalate precipitation temperature, calcination temperature, and calcination time on the nitrogen adsorption surface area, x-ray crystallite size, and sedimentation particle size of thoria products was determined (see Table 3.2).[25]

Precipitating the oxalate at 10 and 40°C and decomposing at 400°C yielded nearly cubic oxide particles 1 to 2 microns in size. Increasing the precipitation temperature to 70 or 100°C and decomposing at 400°C gave plate-like oxide particles approximately 6 microns in average size. Refiring at 500, 650, 750, or 900°C did not change the shape or size of the original oxide but increased the average crystallite size and decreased the surface areas. The thorium oxalate samples were prepared by precipitation from 1 molar thorium nitrate solution by dropwise addition of excess oxalic solution with vigorous stirring. The precipitates were washed, dried, calcined for 4 hr at 375°C and then fired for 16 hr at 400°C. The resulting oxides were used as stock materials for final 24 hr firing periods at higher temperatures. As shown in Table 3.2, the loss on ignition of the fired thoria samples ranged from 0.1 to 1.47 wt %.

Precipitation processes are generally complex and often nonreproducible with regard to particle shapes, sizes, settling times, and hydrates produced. The inhomogeneous mixing of reactants can result in a wide spectrum of particle morphologies.[26] In most studies a slight excess of oxalic acid was added to a thorium nitrate solution. The precipitation temperature is a significant variable which affects surface area, bulk density, particle size, and size distributions of the oxalate and calcined thoria powder. Lower precipitation temperatures result in greater surface areas, smaller particle sizes, and lower bulk densities for the calcined thoria. The degree of agitation, digestion time, and acidity also affect the size of the thorium oxalate crystals. Magnetic stirring during precipitation and longer digestion times favor formation of particles with improved filtering characteristics. The greater the acidity (free nitric acid) during precipitation, the denser the thorium oxalate precipitate. The free nitric acid in the thorium nitrate solution affects the crystallite size by controlling the concentration of oxalate ions available to react with the thorium ions to form the oxalate crystallites. Reducing the concentration of available oxalate ions by increasing the free acid level favors the growth of the crystallites and thereby reduces the surface area of the powder. Other precipitation parameters affecting the physical properties of oxalate precipitate and resulting thoria powder include pH, concentrations of the reactants, and rate and sequence of combining the reactants. The calcination temperature of the thorium oxalate is a critical parameter in determining the properties of the thoria powder. Low calcination temperatures produce a more active thoria powder, consisting of porous particles and having a large surface area. However, if the calcination temperature is too low, incomplete decomposition will occur leaving impurities such as carbon in the thoria powder.

Recovery Dynamics Corporation (Recodyne) has developed a method to convert crystalline thorium nitrate presently stored in overpack drums to a stable oxide form with a reduced mass and volume.[27] This final form would either be recoverable for eventual use as a feed in the manufacture of thorium products or be acceptable for placement in a repository. Recodyne's approach was to convert the thorium nitrate to thoria by aqueous precipitation of an intermediate compound, thorium oxalate. Besides reducing the need to control nitrogen oxide emissions, the conversion of thorium nitrate crystals to an aqueous feed facilitated the removal of nitrate from the original packaging by dissolution in hot water. The thorium nitrate solution generated from the washout operation was pumped into an agitated tank where powdered oxalic acid was added.

Table 3.2. Effect of oxalate precipitation temperature and calcination temperature on selected properties of ThO_2

Oxalate precipitation temperature (°C)	Surface area	Average X-ray crystallite diameter, *D* (Å)	Average particle size sedimentation analysis (μ)	Loss on ignition[a] (wt %)
		Final firing temperature—400°C[b]		
10	35.3	61	1.2	1.27
40	41.7	69	1.3	
70	45.6	57	5.6	
100	51.0	56	4.2	1.47
		Final firing temperature—500°C[c]		
10	40.1	78	1.1	1.09
40	40.9	74	1.6	
70	36.9	89	5.2	
100	48.0	92	3.9	0.85
		Final firing temperature—650°C[c]		
10	25.4	143	1.4	0.41
40	27.4	127	1.4	
70	21.3	166	5.2	
100	16.7	185	4.2	0.54
		Final firing temperature—750°C[c]		
10	12.8	250	1.1	0.1
40	16.7	231	1.5	
70	14.2	325	8.5	
100	6.9	350	4.2	0.37
		Final firing temperature—900°C[c]		
10	6.3	550	1.3	0.1
40	8.5	616	2.4	
70	7.0	696	7.2	
100	3.3	775	5.1	0.20

[a]Dried at 200°C and heated to 1000°C.
[b]Stock preparation.
[c]Fired at temperature for 24 h.

Initially the oxalate precipitation was carried out at 32°C for one hr, however in subsequent lots, the precipitation time was increased to 12 hr. The longer hold time improved the filterability of the oxalate solids. From the filter press, the oxalate cake containing 40 wt % moisture was fed to a rotary kiln capable of operation up to 1000°C. The kiln was operated at 800°C for 8 of the 10 batches and also at 600 and 900°C. Operation of the kiln at 800 to 900°C was without problems creating a free flowing thoria powder with some lumps. Visual observations while handling the oxide indicated that the powder was not prone to dusting. One of the more disappointing results was that eight of the thoria product batches contained large fractions of unconverted thorium oxalate and relatively low bulk densities (1.0 to 1.5 g/mL). The last oxalate calcination run demonstrated a 95 wt % conversion to the oxide with a bulk density of 1.9 g/mL. The total bulk volume (380 L) of the thoria product batches represented a volume reduction of 50% from the original thorium nitrate solids (760 L).

As a consideration for oxalate process utilization for the DLA stockpile conversion application, there are similarities between the thorium oxalate precipitation process and the ammonium diuranate (ADU) process. Most licensed, commercial nuclear fuel fabricators utilize the ADU process to produce ceramic grade UO_2 powder. For the ADU process, a uranyl salt solution is mixed with ammonium hydroxide to precipitate ADU. The precipitate is collected by centrifugation or filtration and washed to remove the ammonium nitrate. The ADU filter cake is calcined in air to produce U_3O_8, and subsequently reduced with hydrogen to prepare UO_2 powder.[28] The commercial-scale equipment used by the nuclear fuel fabricators could possibly be utilized for the thorium oxalate conversion process with only minor alterations.

Summary

Recodyne used the demonstrated equipment capacities and performance as the bases for a full-scale plant design (40 to 45 kg thoria per hr).[27] Key processing features will be washing of the oxalate filter cake and subsequent drying of the solids to reduce the moisture content from 40 to 5 wt % prior to the rotary kiln. Disposal of the aqueous filtrate from the automatic pressure filter will generate a low-level-waste (LLW) disposal problem. Recodyne plans to neutralize the filtrate with sodium hydroxide and evaporate the resulting waste water to dryness in a batch evaporator. The resulting sodium nitrate solids will be packaged for disposal at a LLW facility. Recodyne assumed that the full-scale process would be located at an existing commercial facility licensed by the Nuclear Regulatory Commission. The option to design and build an entire new process facility is described in the Recodyne Engineering Assessment.

In the future, there may be a market for thoria as a breeding material in nuclear reactors. For nuclear-grade UO_2 pellets, the surface area and particle size distribution of the urania powder are critical parameters. A urania powder with a surface area of 6 ± 4 m^2/g and a narrow particle size distribution (average size of 4 ± 3 microns) are preferred.[29] In addition, impurity limits have been imposed on nuclear fuels to prevent specific problems. Although any potential fuel fabricator may choose to dissolve the thoria powder to control impurity levels, the oxalate precipitation process is capable of producing a nuclear ceramic grade thoria powder.[26] This driver, as related to maintaining the purity of the product for potential fuel cycle use, is a unique benefit the oxalate process offers. As can be observed from the references, extensive design data is available for use during detail design equipment specification and process design optimization.

Thorium oxalate precipitation conditions have been investigated on a laboratory scale to produce thoria powder that can be sintered to high-density pellets without milling of the oxide powder.[30] Oxalate precipitation conditions examined were temperature, digestion time, and agitation method. The sinterability results indicated that thoria powders can be pressed and sintered to pellets approaching 95 to 96% of theoretical density without powder milling.

The companies in the business of fuel fabrication would review the processing history used to produce the nitrate form. Oxalate processing will remove additional impurities that remain in the stockpiled thorium nitrate. The effect of impurities in the oxalic acid feed stock would be assessed prior to use. Upon comparing the demonstration derived analytical data with the thorium product purity data (see Sect. 2.2.2) for a fuel cycle application, the potential exists to directly use the ThO_2 powder resulting from oxalate stockpile processing. Further study of the specific analytical data and physical morphology requirements, such as particle size, wold be employed during design. Samples wold ultimately be taken by the fuel fabricator and the analysis results would be compared against a specific thorium specification.

With the objective of producing a purified thoria powder product for potential nuclear fuel fabricators, the decomposed oxalate powder storage containers would need to be compatible with maintaining product purity for the long term in their final storage environment. Storage in new, more durable containers, such as Teflon-coated stainless steel drums, may be required. The Recodyne Engineering Assessment basis involved re-use of the 30-gal carbon steel drums.

3.4 PROCESS SELECTION RECOMMENDATION

The process selection decision is based on the thorium product end point criteria in conjunction with study and analysis of the available process design data, from both the laboratory and pilot demonstration development completed within the scope of this project and the fuel cycle data reviewed to date. The sponsor requested the work be conducted and results reported in a manner such that the process selection be premised on the fact the pilot-scale equipment testing phase is complete. The reference processes studied within the entire scope of the work completed by Oak Ridge to date included: direct thermal de-nitration; de-nitration by formation and subsequent drying/calcination of thorium hydroxide; and de-nitration by formation and subsequent calcination of thorium oxalate. The new data for the hydroxide calcination was very limited at laboratory scale, but existing fuel cycle references were consulted, along with the authors of each of the previous sections having direct thorium process development and processing experience.

Figure 3.5 depicts the contrast between the two wet chemistry demonstrations completed.

Two significant economies should be mentioned which were considered in the wet chemistry demonstrations performed. They involved the pre-treatment step, where the solid (monolith formed) thorium nitrate was extracted from the drums and dunnage separated, and the RCRA metals and radiological analytical analyses performed for the thorium product (analytical basis), potential by-products and secondary wastes. These results are reported in section 2.2.2.

It is noteworthy that the hydroxide team utilized and reported upon manually separating the solid thorium nitrate from the drums and the oxalate team utilized direct hot water dissolution. Results are reported in Attachments 1 and 2 respectively, with the ORNL recommendation being that direct hot water dissolution from the innermost container is preferable, based on improved health and safety with operation by personnel outside the enclosure and tighter mass balance control.

The final form criteria for the thorium product was not specified in quantitative terms during the course of structuring and executing the pilot-scale demonstrations. A strategy was adopted to use general final form criteria, in part to allow for ease in partnering with the commercial sector on an effort to uncover new and efficient processing methods, but largely because the end point critieria for re-use in the fuel cycle versus

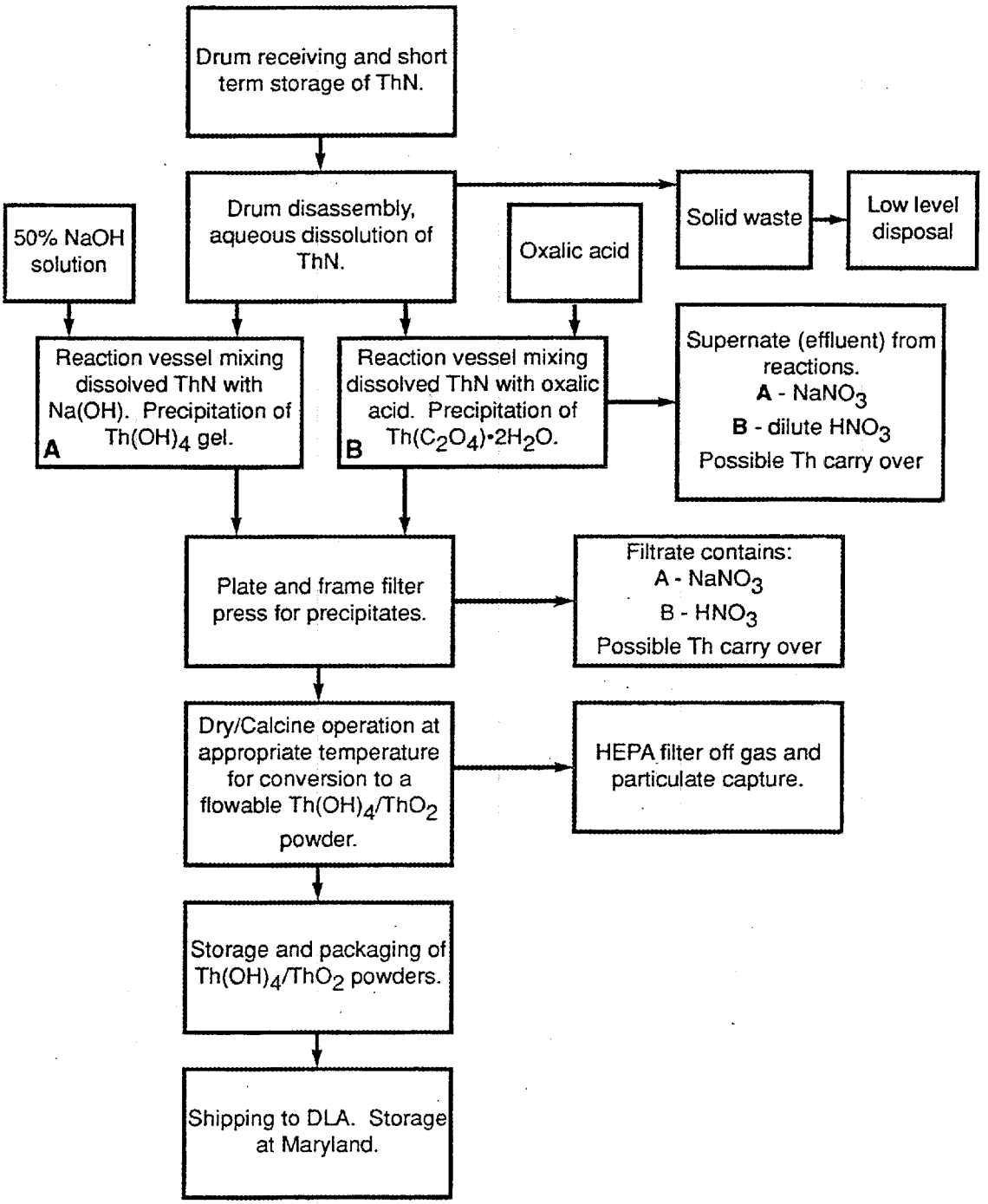


Fig. 3.5. Simplified wet process diagram for pilot plant tests.

disposal through retrievable long term storage at a low-level waste repository was not quantified at that time. Those issues remain tied to pending programmatic decisions that will be made by the DLA, in part as a result of the pilot-scale demonstration results reports and recommendations.

The processing decisions reported here-in are based on the final form requirements that result from pilot-data/experience in hand and the program basis as defined today. General thorium product final form requirements as defined to date are listed below for comparison with the process comparison summary information included in Table 3.3.

- The ThO_2 shall be specified as the product compound without reference to the inclusion of special ThO_2 processing steps, such as binding or pressing.

- Dry, flowable chunks or powder is a satisfactory thoria product with proper container and acceptable long term dispersal risk. (Average particle size is estimated at ~5 microns [33] to minimize airborne potential, with both processes controllable to meet that requirement.) Particle size data was not obtained, but would be during the full-scale field demonstration.

- Minimizing unnecessary addition of impurities shall be a goal to maintain product thoria purity based on the thoria product use in the nuclear fuel cycle (use deionized process water, without lubricant/binder/ nuisance cation addition—the driver is to keep thorium product relatively pure for possible future application).

Summary

The following points are noteworthy, based on a review of the fuel cycle literature, the development work completed as part of this project, and on special consideration given to implementing a stockpile conversion program.

1. Steam and direct de-nitration: product very fine ThO_2 (required sol gel process to make good pellet) pilot-scale test program would be required to validate direct de-nitration processing is viable for final form requirements as currently exist. Either of the wet chemistry processes tested could be scaled up and operated to form a flowable dry powder with average particle size controllable to ~5 microns.

2. The hydroxide process is viable, but fewer data exist that can be used to validate scale-up at this time. The separation of impurities is more difficult—hydroxide acts as sorbent/co-precipitates impurities in reagent (i.e., without washing, Na content higher than nitrate)

3. The oxalate process has a characteristically wide process control range, large data base for design, and results in a high purity ThO_2 product. Recodyne run 10 was the best pilot demonstration calcination operation, where the conversion and product quality was high. The product is characterized in Attachment 4. It is important to attain time at temperature to achieve an acceptable degree of conversion. A design concept was proposed for investing in front end drying equipment, separate from the calcination equipment, which would improve process control.

The oxalate process flowsheet is recommended for the stockpile conversion processing—primarily based on the large design data base available and the inherent nature of it being a purification process which preserves product purity. New containers designed for optimum packing efficiency and long term corrosion resistance may be required. The batch processing selected for the pilot-scale demonstration was successful and shall be

Table. 3.3. General thorium nitrate conversion (de-nitration) process

Process	Pro	Con	Comment
Thermal-Direct De-nitration with thermal decomposition to ThO_2	Eliminates solids/liquids product separations which reduces unit operations/wastes	Particulate carry-over/developed to meet specific fuel cycle product characteristics/requires fluid bed pilot development	Could be considered more difficult to permit due to NOx and particulate
Oxalate with drying through calcination (with air) conversion to ThO_2	Wide range to achieve process control of product precipitate/large fuel cycle data base/conversion efficiency and availability high/controllable to form flowable non-airborne dry powders	Use of oxalic acid feedstock; calcination requires ~850 °C and correct time at temperature; maintaining purity requires long term container basis, which eliminates re-use of existing containers	Pilot demo completed confirmed existing data and added new data basis for pre-treatment/handling and improving flowsheet to meet product end points, which include preserving product purity
Hydoxide with drying to thorium hydroxide/oxide product. Higher temperatures would decompose thorium intermediates to ThO_2	Lower temperature process with product easier to dissolve for future purification and controllable to form flowable, non-airborne powders; allows re-use of existing containers	Tighter control required for operating range to achieve process control for wet product precip; Hydroxide acts as impurity sorbent and co-precipitates reagent impurities; adds sodium to product (with NaOH); moisture in product >10 wt.% for demo temperatures/equipment constraints; minimum temperature should be 200 °C vs 100 °C to remove chemically bound water	Pilot demo completed confirmed existing data and added new data for improving flowsheet to compare with product final form requirements; should purity requirements not be important to preserve, the hydroxide processing flowsheet may be preferable over all others.

adopted for the production operations. There exists the need to apply tight process control to multiple process parameters to control particle size and achieve repeated conversion efficiencies to form the ThO_2 product. The demonstrations results/process data/stockpile engineering assessments, in conjunction with existing fuel cycle processing data as reported in the references, allows for adequately describing and specifying each unit operation to complete detail design and selection of equipment. Predictions of performance of the coupled process systems at full-scale can be made, albeit requiring demonstrations and allowing for required modifications in the field as part of the program. Achieving repeatable solids/liquids separation and product/waste specifications is a challenge. Detailed investigation of the literature and data analysis is required to specify each unit operation. Effort remains to validate selected new, commercially supplied equipment (and existing installed equipment in the case of the fuel fabrication industry) is available to meet all functions. Selected unit operations and coupled processes required are not validated at the 3 tons/day (ThN basis) reported throughput as based on any exactly similar past processing plant operation. On that basis, some technical uncertainty exists regarding the capacity to scale-up the integrated system and the accuracy (at this time) of

resultant operations time line predictions. The unit operation performance characteristics should be validated against system design requirements per field scale demonstrations. The integrated system throughput should be established by incorporating a rigorous performance/validation and optimization test phase using the actual production scale equipment.

4. STOCKPILE PROCESSING ENGINEERING STUDY—SUMMARY

Perma-Fix and Recodyne each completed an Engineering Study (ES) that included detailed process descriptions, flow diagrams, mass balances, approximate physical layout, scale-up issues, equipment list, operations time line, and life cycle cost information. Environmental considerations include cost impact on managing air emissions and primary and secondary waste disposal. These assessments are found on pages 60-80 of Attachment 1 and 33-62 of Attachment 2.

The time line results documented are consistent with a five-year processing campaign, with the annual operations costs exceeding the initial plant design, construction, and start-up costs. A general summary of selected cost cases is provided as Table 4.1.

Table 4.1. Stockpile stewardship cost cases ($millions)

Case	Pre-treatment	Treatment	Transport	Disposal[c]	Subtotal	30% cont.	Total
1—Pretreatment to separate ThN from drum and dunnage and denitrate	13.0	11.7	0.9	1.8	27.4	8.2	35.6
2—Overpack and ship (25% drum basis)[b]	4.4	0	1.8	3.6	9.8	3.0	12.8
Perma-Fix—dirty	~ 10.0	~ 10.0	0.8	1.5[a]			22.3[a]
Recodyne—pure	~ 15.3	~ 15.3	1	9.2			40.8

Notes:

[a]Waste disposal cost of the nitrate residuals was ignored in the Perma-Fix estimate (based on potential market) but constituted ~25% of the Recodyne overall cost estimate. The transport and disposal cost elements are based on the full stockpile.

[b]Cases 1 and 2 are referenced to an earlier stockpile project estimate by LMES (ref. 31). In case 2, 25% of the drums are overpacked, which is consistent with the need to overpack 3,500 drums at Curtis Bay, and provide some components for Indiana drum clamping/sealing.

[c] "Retrievable storage" at an LLW repository such as NTS is theoretically possible, but has never been done in this country. The cost for supplying stewardship could be significant. It would probably require a separate engineered cell disposal facility. The containers are not considered at NTS, so after some time, the existing DLA outer metal containers would be corroded/gone, leaving their plastic liners. One DLA drum configuration is simply "bagged inside 55-ga metal drums." An engineered facility would need to accommodate retrieval/mining in such a scenario and dictate consideration be given to containers. It is noteworthy that drum handling/pre-treatment efforts are cost drivers and should be avoided if possible. In lieu of not having an active or even viable thorium fuel cycle based nuclear power program in this country, "stewardship costs" are difficult to justify. The NTS currently has two engineered facilities. If NTS or another disposal site is not used for the reuse/retrievable storage option, the long-term location option would be the commercial sector. This would lead back to DLA ownership and a leasing agreement, which is opposed to the DLA mission of eliminating the ThN stockpile in the next ten years or so. If the Strategic Material path is limited to retrievable storage at disposal sites, processing adds value by reducing volume, but special containers to store the purified and stable oxide form are required.

The RCRA ignitability classification/data reported by Perma-Fix (see pages 53 and 57 of Attachment 1) suggests that there is a reasonable path to consider in maintaining the stockpile in the nitrate form. This logic preserves the ThN for use as a strategic material, albeit still requiring significant cost to meet the program objective of depot elimination.

Based on any future DLA decision to categorize the stockpile to be assessed for waste category (data indicates low-level), the DLA should consider verifying the initial ignitability test results for the DOT characteristic oxidizer test. A statistically based assessment of the drums and key attributes of drum contents at both depots could be performed. This assessment would provide the DLA with a defined confidence level for assessing the stockpile in the NEPA process as a single entity. Based on the number of lots at each depot and the source of the thorium (France, India, and the USA), a representative number of drums would be selected, opened, and sampled for analysis to verify the limited oxidizer classification data. A secondary goal would be to verify consistency of the thorium nitrate physical form. Other analyses could be run on these samples in the event the form of the material in the drums raises concerns or analysis is called for to address special program issues.

Consideration could be given to the final thorium form, with and without processing, if **disposal** is an achievable and reasonable alternative.[1] The forms could be nitrate (no processing), hydroxide, oxalate, carbonate, and oxide. The most stable and lowest volume is the oxide. The estimated processing cost is in the millions of dollars, however. The decision to process or not should be determined on a life cycle cost basis considering the disposal Waste Acceptance Criteria and NEPA interfaces. The processing would not be done unless driven by acceptance at the disposal facility. Technical assessment of the "processing to waste" technology could be completed in parallel in the NEPA completion time frame so that element is completed in a timely manner. The scope of such a program could thus be structured to examine potentially lower cost options that exclude conversion.

It is noteworthy that pre-treatment and treatment are the cost drivers. The largest savings can be accrued from the conversion scenario by minimizing operating cost. These savings can be achieved by investment in the initial process design rigor.

For any stockpile stewardship and disposition program, a detailed cost and schedule baseline must be defined and maintained. A detailed engineering-based assessment is required to structure and control the project objectives, cost, and schedule. Utilization of data obtained from these initial baseline stockpile processing engineering assessments would be utilized. It is necessary to validate these projections and continually improve accuracy as tied to the programmatic requirements that will evolve with this work. The objective is to supply the decision makers improved accuracy and completeness per path of the transportation, disposal, process equipment, containers, facility, design, installation, testing, permitting, and other costs. Best contracting options/government agreements available to accomplish this project should be defined as part of initial scoping.

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[1]DOE is self-regulating per the Atomic Energy Act (AEA) for low-level waste (LLW) and in the end is the logical agency to handle this stockpile if proven to be borne for use as energy or defense material. This finding could open up the NTS Federal Repository. For commercial source material, the Nuclear Regulatory Commission (NRC) regulates under the LLW Policy Act, and Barnwell, Hanford, Envirocare, and Waste Control Specialists (WCS) are candidate disposal sites.

5. STOCKPILE NEPA APPROACH

A federal undertaking, such as the conversion of the thorium nitrate inventory by DNSC/DLA, must conform to the provisions of the National Environmental Policy Act (NEPA) (Public Law 91-190, as amended by Public Laws 94-52 and 94-83). The procedural aspects of NEPA are implemented by regulations (40 CFR Parts 1500-1508) developed by the President's Council on Environmental Quality (CEQ). As detailed in those regulations, a NEPA review is conducted to ensure that environmental factors are given adequate consideration early in the decision-making process. The NEPA process provides federal agencies with a firm basis for weighing the significance of the environmental impacts of a proposed action against those of alternatives prior to a decision on implementing any action.

The elements of the NEPA process are discussed below. The activities are not necessarily sequential (Table 5.1). For example, scoping may occur internally before the notice of intent is prepared. External scoping occurs after the notice of intent has appeared in the *Federal Register*, but preparation for the scoping meetings may occur prior to the appearance of the notice of intent.

A clearly defined statement of the action and the purpose and need for the action is fundamental to the NEPA process. The purpose and need limit the range of alternatives which must be considered. For any follow-on environmental impact statement (EIS), the statement of the action and the purpose for the action might be similar to the following:

> The DNSC/DLA proposes to convert the current thorium nitrate inventory into thorium oxide. The purpose of the proposed action is to allow DNSC/DLA to upgrade its thorium stockpile to reduce its volume, achieve chemical stability, and assure compatibility with potential future use in the thorium fuel cycle.

There needs to be a carefully crafted statement of need for the proposed action which answers the question, Why does DNSC/DLA choose to accomplish this purpose?

The alternatives to be analyzed for potential impacts in the proposed EIS must include, at a minimum, the proposed action and no action. The no action alternative is required by Council on Environmental Quality regulations implementing NEPA. The potential impacts associated with the no action alternative comprise the benchmark against which impacts from other alternatives can be compared. Additional alternatives which could satisfy the purpose and need should also be analyzed in the proposed EIS.

The first step in the NEPA process is for DNSC/DLA to publish a notice of intent to prepare this proposed EIS in the *Federal Register*. The notice of intent (1) describes the proposed action and possible alternatives, (2) describes the process by which the agency will determine the scope of issues to be addressed in the proposed EIS and will identify the significant issues related to the proposed action, including the time and place of public meetings if such are to occur, and (3) states the name of a person within the agency who can answer questions about the proposed action and the EIS.

DNSC/DLA, at its discretion, requests other federal agencies to participate in the preparation of the proposed EIS. Any federal agencies which have jurisdiction by law or special expertise with respect to any environmental issue or issues which should be addressed in the proposed EIS may be requested to participate in the NEPA process as cooperating agencies.

Table 5.1. Draft schedule for accomplishing NEPA process

Task name	Duration (work days)	Proposed start date	Proposed end date
Define action, purpose, and need	15	January 5, 1999	January 25, 1999
Conduct three scoping meetings	33	January 26, 1999	March 11, 1999
Prepare notice of intent	20	January 5, 1999	February 1, 1999
Notice of intent published in *Federal Register*	10	February 2, 1999	February 15, 1999
Preliminary draft EIS	176	February 16, 1999	October 19, 1999
Cooperating agency review	22	October 20, 1999	November 18, 1999
Cooperating agency review meeting	15	November 5, 1999	November 25, 1999
Prepare draft EIS (DEIS)	30	November 26, 1999	January 6, 2000
Prepare notice of availability for DEIS	20	December 10, 1999	January 6, 2000
Notice of DEIS availability in *Federal Register*	20	January 7, 2000	February 3, 2000
Public review of DEIS	34	February 4, 2000	March 22, 2000
Response to DEIS comments	20	March 23, 2000	April 19, 2000
Prepare final EIS (FEIS)	40	April 20, 2000	June 14, 2000
Prepare notice of availability for FEIS	20	May 18, 2000	June 14, 2000
Notice of FEIS availability in *Federal Register*	30	June 15, 2000	July 26, 2000
Federal agencies review FEIS	23	July 27, 2000	August 28, 2000
Comments on Final EIS	15	August 29, 2000	September 18, 2000
Prepare & sign record of decision	34	September 19, 2000	November 3, 2000
Record of Decision published in *Federal Register*	10	November 6, 2000	November 17, 2000
NEPA completed	0	November 17, 2000	November 17, 2000
Contract awarded	1	November 20, 2000	November 20, 2000

A preliminary step in the scoping process has been taken. The 1990 census records were examined to determine if there are substantial minority populations near the Hammond, Indiana and Curtis Bay, Maryland storage sites. It was determined that there is not a substantial minority population near the Curtis Bay site, but over 25% of the population within 1 km of the Hammond site is Hispanic (see Attachment 2 for additional information). The large Hispanic population makes it desirable to provide residents near the Hammond site with Spanish language translations of announcements concerning the proposed action. The translated announcements would be evidence that DNSC/DLA has exerted considerable effort to encourage public participation in the scoping process.

During the scoping process, the range of actions, alternatives, and impacts to be considered in the proposed EIS are determined. In addition, issues which are not significant or which have been covered by prior

environmental review are identified and eliminated from detailed study. Invitations to participate in the scoping process are extended to federal, state, and local agencies, affected Indian tribes, and the public.

In the preliminary draft version of the proposed EIS, the proposed action and the full range of possible alternatives, including the no action alternative, are presented, described, and analyzed for impacts, as appropriate. It is not necessary to examine all alternatives in equal detail. Those alternatives which are unreasonable or which do not fully satisfy the stated purpose and need for the proposed action may be dismissed from detailed examination.

Based upon the example of proposed action and purpose given above, an example of the suite of alternatives for the proposed EIS may include

- no action
- conversion of the ThN to ThO followed by storage or disposition (note: transportation between current storage locations and possible conversion locations may also be required)
  - on-site conversion
  - off-site conversion
    - DOE facilities: East Tennessee Technology Park or Fernald Environmental Management Project
    - commercial, licensed facilities
  - eventual storage
    - DNSC site
    - DOE site
    - commercial, licensed facility
  - disposition
    - sale
    - disposal

The completed preliminary draft of the proposed EIS is provided to the cooperating agencies for their review. Comments are received and resolved at a review meeting unless additional analyses are determined to be required as a result of the comments.

The changes resulting from the cooperating agency review meeting are folded into the next version of the document. The result is the draft version of the proposed EIS which must be released for public review and comment for a minimum 45-day review period after the notice of availability appears in the *Federal Register*. The draft version of the proposed EIS is filed with the Environmental Protection Agency, which announces it in the *Federal Register*.

All comments received on the draft version of the proposed EIS must be addressed and considered in the preparation of the final version of the proposed EIS. The resolution of some comments may require extensive interaction between ORNL and DNSC. The comments and responses are displayed in the final version of the proposed EIS and changes to the draft version of the proposed EIS are made as needed.

Concurrently, DNSC/DLA distributes copies of the final version of the proposed EIS and files it with the Environmental Protection Agency, which announces the final version of the proposed EIS in the *Federal Register*. The formal announcement of the agency's course of action, the record of decision, is to be published in the *Federal Register* after a 30-day review period. The formal NEPA process is concluded with the publication of the record of decision.

6. STOCKPILE REGULATORY ISSUES/ PERMITTING STRATEGY

This section will focus on the primary regulatory approaches/ scenarios associated with the ThN itself. A broader and more detailed document will be issued in FY 1999 delineating the waste management needs and issues of the proposed processes. Appendix 5 is a preliminary analytical and regulatory assessment focused on the RCRA metals in the ThN. The scenarios discussed below are drawn from this assessment. Scenario 1, ThN declared a source material, is the project's planned approach. The other two scenarios are delineated for completeness.

6.1 SCENARIO 1: ThN EXCLUDED AS A RCRA SOLID WASTE

In this scenario the ThN is declared a source material under the Atomic Energy Act (AEA) [U.S. Code, Title 42, Sect. 2011 – Sect. 2259]. As a source material it would be excluded from consideration as a solid waste via 40 CFR 261.4(a)(4). Section 2014 (z) of the AEA defines the term "source material" :

> The term "source material" means (1) uranium, thorium, or any other material which is determined by the Commission pursuant to the provisions of section 2091 of this title to be source material; or (2) ores containing one or more of the foregoing materials, in such concentration as the Commission may by regulation determine from time to time.

Since the ThN is not considered a solid waste, then it can not be a hazardous waste. This then obviates the concerns as to whether the material exhibits the RCRA characteristic of ignitability (D001) and whether or not the conversion to ThO_2 is a treatment process. Additionally, the current storage location would not require Part B permitting under RCRA. Finally, since the ThN is not a solid or hazardous waste and the conversion process is not treatment, the ThO_2 would not be considered a solid waste.

ThN meets the definition of source material in that it is "uranium or thorium, or any combination thereof, in any physical or chemical form."

10 CFR 962.3 limits the AEA exemption for certain DOE-owned or -produced radioactive materials. Once it is proven that the materials were made at the behest of DOE (or its predecessors), then the ThN should fall within the exemption.

The DLA will need to retain the documentation that establishes why the ThN is not subject to the land disposal restrictions found in RCRA (40 CFR 268). According to 40 CFR 268.7(a)(7):

> Generators must retain on-site a copy of all notices, certifications, demonstrations, waste analysis data, and other documentation produced pursuant to this section for at least five years from the date that the waste that is the subject of such documentation was last sent to on-site or off-site treatment, storage, or disposal. The five-year record retention period is automatically extended during the course of any unresolved enforcement action regarding the regulated activity or as requested by the Administrator. The requirements of this paragraph apply to solid wastes even when the hazardous characteristic is removed prior to disposal, **or when the waste is excluded from the definition of hazardous or solid waste under 40 CFR 261.2 through 261.6** (emphasis added), or exempted from RRA Subtitle C regulation, subsequent to the point of generation.

As stated throughout this document, the plans for the thorium are that its present form be upgraded/ improved for future use and to enhance storage in anticipation of that use. This course of action will remove the oxidizer label from the thorium and thus eliminate any concerns regarding storage or treatment under the RCRA regulations.

This course of action should be pursued as the project's first choice since it has no impacts on the cost estimates or schedules. Additional arguments can be added to reassure the regulators that the most prudent and environmentally sound approaches are being taken. However, the foundation of our approach must be that the thorium is a source material.

6.2 SCENARIO 2: ThN MANAGED AS RECYCLABLE MATERIAL

This scenario requires that the project demonstrate that the ThN is being recycled by the upgrade/ conversion process and, as such, is not a solid waste when recycled per 40 CFR 261.2(e). The outcome, programmatically, is similar to that of Scenario 1 in that if it is not a solid waste it cannot be a hazardous waste.

This approach seems somewhat tenuous but may have merit as (1) a set of complementary points to make with the regulators (in addition to those in Scenario 1) or (2) if, for some unforeseen reason, the thorium is not considered a source material.

First, the case must be made that the ThN is being recycled per the definition found in 40 CFR 261.2(e)(1):

(i) Used or reused as ingredients in an industrial process to make a product, provided the materials are not being reclaimed; or
(ii) Used or reused as effective substitutes for commercial products; or
(iii) Returned to the original process from which they are generated.

The conversion to the oxide does not fit (ii). The case for (i) would have to be developed around the potential breeder fuel cycle: that the conversion process chosen is an "industrial process" and the ThN is the normal feed to the oxide conversion process for the breeder target material. While the ThN is truly the feed material for the conversion process, this country does not have a breeder fuel cycle industry. Therefore, convincing the regulators that any of the proposed conversion processes (oxalate, sodium hydroxide, and direct thermal) are "industrial" may prove difficult. While the ThN is a step along the purification process, arguing the point that we are returning the material to the original process [to meet the requirements of (iii)] would not stand up under scrutiny.

The regulators must also be convinced that the ThN (and by extension the ThO_2) is **not** being stored before or in lieu of being abandoned. If the regulators are unconvinced that the market for the thorium is real (or at least real to DLA), then the ThN would be considered a solid waste by definition (unless Scenario 1 prevails) and thus has to be assessed against the hazardous waste regulations. Since it is acknowledged that the ThN is considered an oxidizer by the Department of Transportation, then it becomes D001 and thus must be stored in a permitted storage facility (unless it can be treated within 90 days in a facility that qualifies for treatment exemption) and then treated in a permitted facility to the Universal Treatment Standards (see Scenario 3).

As in Scenario 1, the DLA must maintain all documentation used to exclude the ThN from consideration as a solid waste.

Should the project be forced to follow this scenario as its primary approach, more time and effort will have to be spent convincing the regulators that our efforts meet the definitions sited above. While much of these efforts would be performed in parallel with the NEPA process to prevent schedule impacts, there would be additional costs. The consequences to costs and schedules will be dire should the case presented to the regulators fail to persuade them. Those impacts are discussed in Scenario 3 below.

6.3 SCENARIO 3: MANAGEMENT OF ThN AS RCRA HAZARDOUS WASTE

The decision is made, in this scenario, that this material is a solid waste (not a source material and not being recycled) and therefore has to be assessed against RCRA criteria to determine whether or not it is a hazardous waste. Since it is acknowledged that the ThN is considered an oxidizer by the Department of Transportation, then it becomes D001 [per 40 CFR 261.21(a)(4)]. At the point of determination that the material is a solid waste and a hazardous waste, the DLA could store the ThN for 90 days without a permit. If it were feasible and their facility met the requirements of a containment building per 40 CFR 264 Subpart DD, then the ThN could be treated/ converted without a permit. Obviously, for several obvious reasons, this alternative is not viable. Thus the ThN must be transported to a permitted storage facility (within 90 days of the hazardous waste determination) and then treated in a permitted facility to the Universal Treatment Standards prior to disposal. This is the course of last resort.

The impacts of this approach could range from inconvenient to devastating. As mentioned above, once the ThN is considered a solid waste— hazardous waste—the DLA will have 90 days to do one of the following:

- treat the material on-site in a containment building
- find a permitted storage facility and ship the ThN to that facility
- find a permitted treatment facility that can take the material immediately

Since it is not within the realm of possibility to get the entire stockpile treated within 90 days (from a NEPA standpoint, if nothing else), it will be critical to have at least identified a possible storage site for the material (in advance of the hazardous waste determination). The storage options include these:

- The States of Indiana and Maryland should be consulted to see if some sort of dispensation is available since the DLA plans to process the material starting in the year 2002.
- Contact disposal/ storage facilities such as Waste Control Specialists in Texas and Envirocare of Utah to see if their permits (RCRA and radiological) allow for storage of the ThN.
- Assess the current state of the storage facilities at Hammond and Curtis Bay in case the DLA wishes to get them permitted.

If allowances can be made for "temporary" storage on-site without a permit (declared waste or not) until the NEPA contract award process is completed, then the only costs will be the political capital spent with no significant impact to schedule (assuming no modifications are required to the existing locations). If the ThN has to be shipped for storage and a site is found that can accept the material under their current permits, then some significant costs will be incurred. Cost items will include repackaging for shipment, characterization for receipt at the storage site, transportation (to and from storage site), and storage prior to treatment. If there is no site capable of receiving the ThN in a timely manner, the impacts to the project could be devastating. A Part B storage permit would have to be written and approved in the 90-day period (unless the regulators provide an extension [40 CFR 262.34(b)]). Both locations would have to meet the physical and financial requirements found in 40 CFR 264 and 265. Depending on the current condition of the buildings in which the ThN is being stored, significant renovations made be required.

Should the ThN be declared a hazardous waste, then the conversion/ upgrade process would be considered treatment by the definition found in 40 CFR 260.10. Since the process is considered treatment, it will have to be performed at a site permitted under RCRA. The permitting process can be an arduous one. To prevent too great a perturbation of the schedules, the NEPA and permitting activities can be done in parallel. To accomplish this, conditional contracts can be awarded with the caveat that before treatment can occur, they must have their processes and permits in place and the NEPA Record of Decision has to be in hand. To provide them a target schedule, it can be stated in the Request for Proposals that the NEPA process should be completed within two years (for example) and at that time (assuming a Record of Decision was forthcoming) the final contract can be awarded and the shipment of wastes could be initiated. The costs associated with the conversion process will obviously be higher should the vendor have to obtain this permit.

In addition to the costs mentioned above, numerous other costs will be incurred as a result of the conversion/upgrade process being considered treatment. Although not exhaustive, the following items must be dealt with/ budgeted for:

- record keeping
- reporting
- Inspections
- characterization/ verification that resulting ThO_2 meets LDR standards
- decontamination and decommissioning to RCRA standards
  treatment bond

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Attachment 3

Selected Pilot Demonstration Photographs

Thorium Nitrate Stockpile
Curtis Bay

Perma-Fix Environmental Services, Inc.

Recovery Dynamics Corporation

GENERAL DESIGN AND COMPUTATION SHEET

JOB

ESO NO.

DATE

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GENERAL DESIGN AND COMPUTATION SHEET

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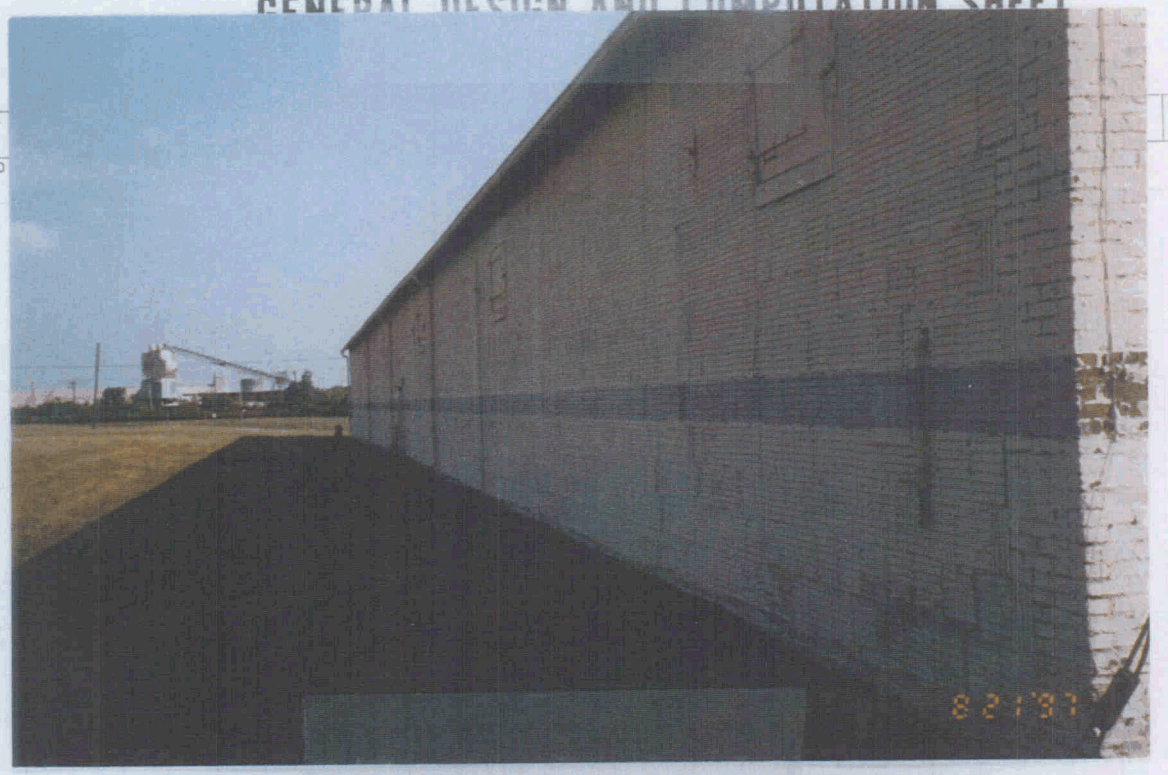

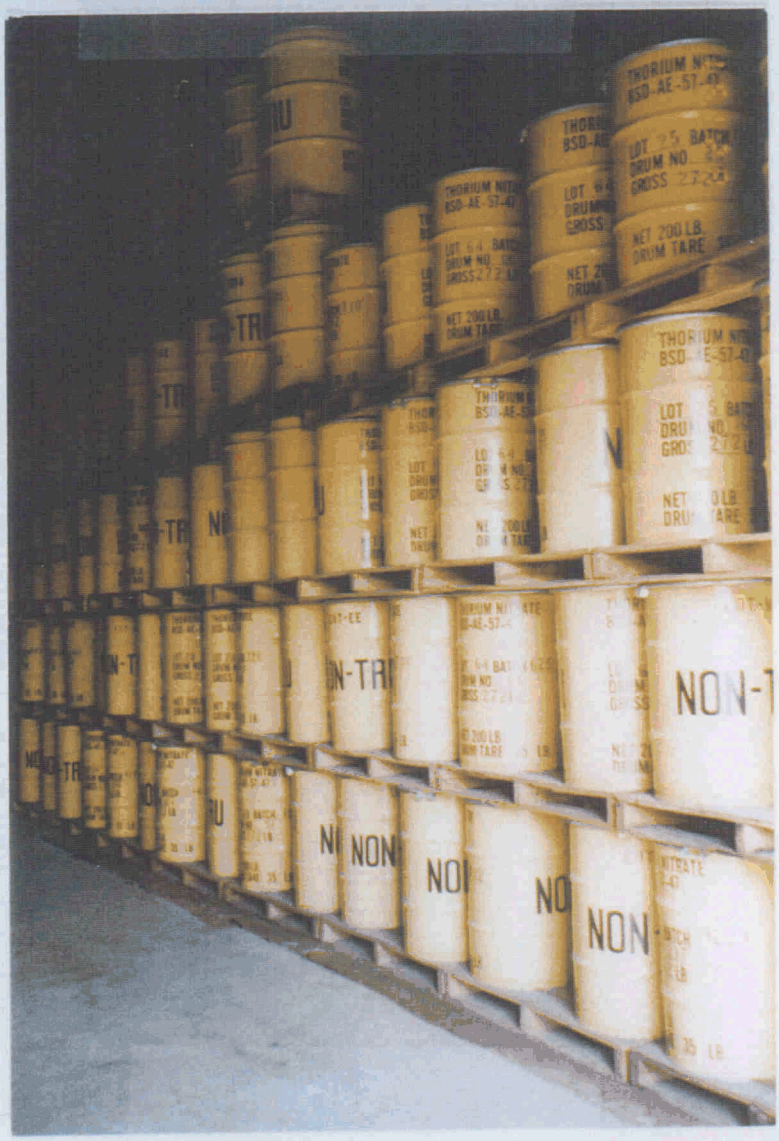

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Pilot Demonstration Photographs
Perma-Fix Environmental Services, Inc.

GENERAL DESIGN AND COMPUTATION SHEET

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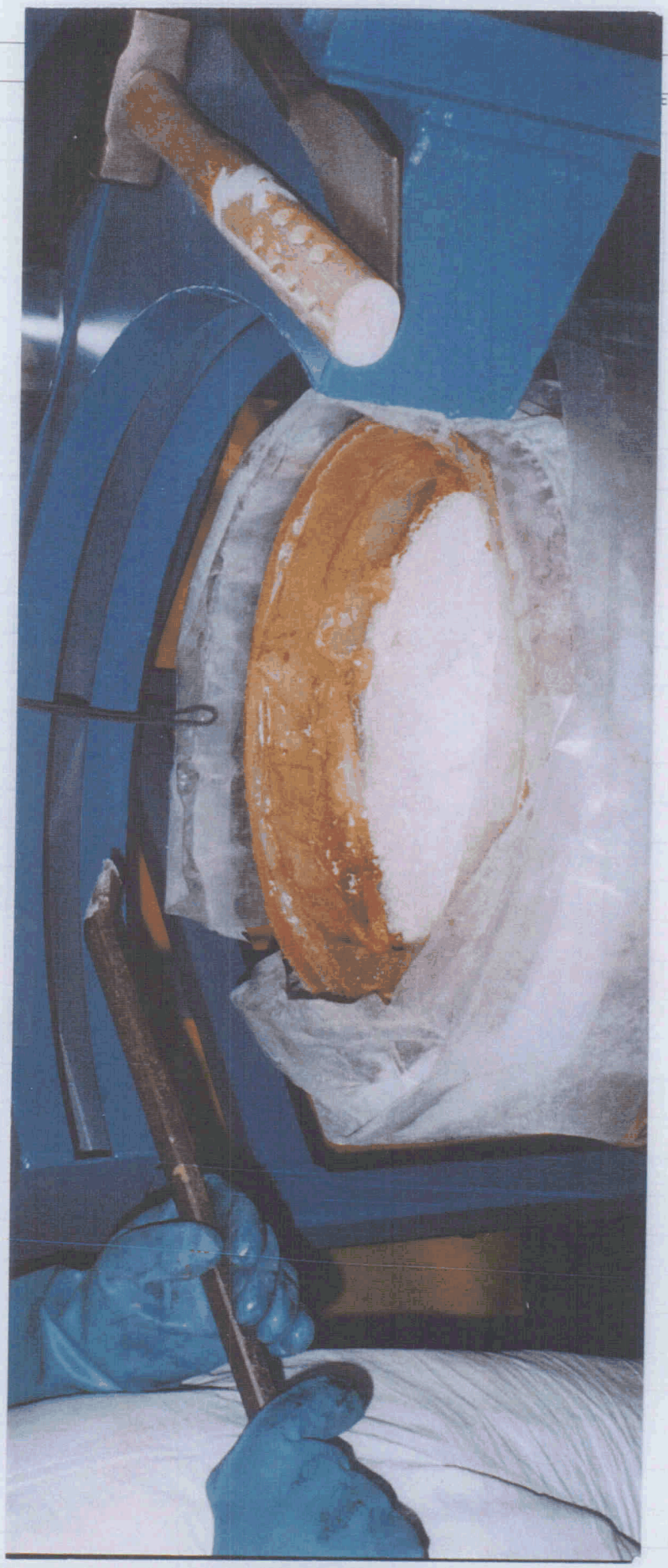

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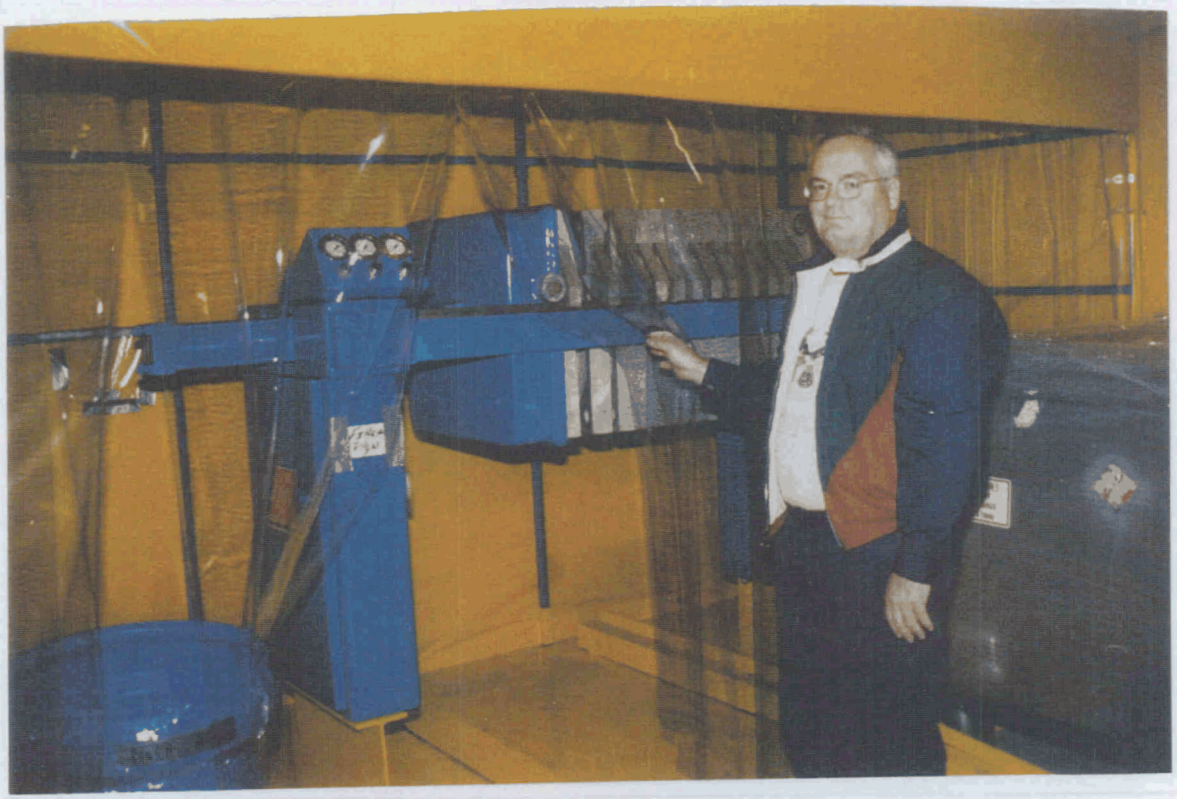
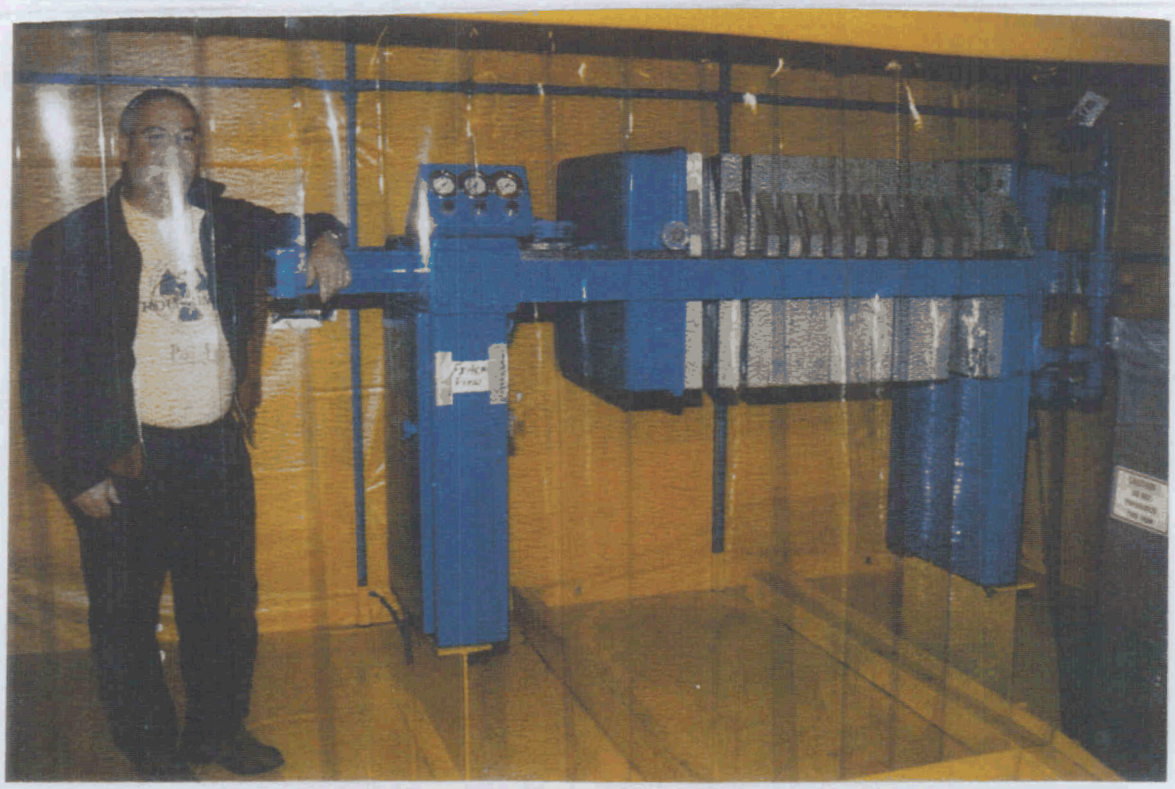
Transferring filter cake to Plough Share Mixer for drying (Batch Test 4)

Filter cake in Plough Share Mixer prior to drying (Batch Test 4)



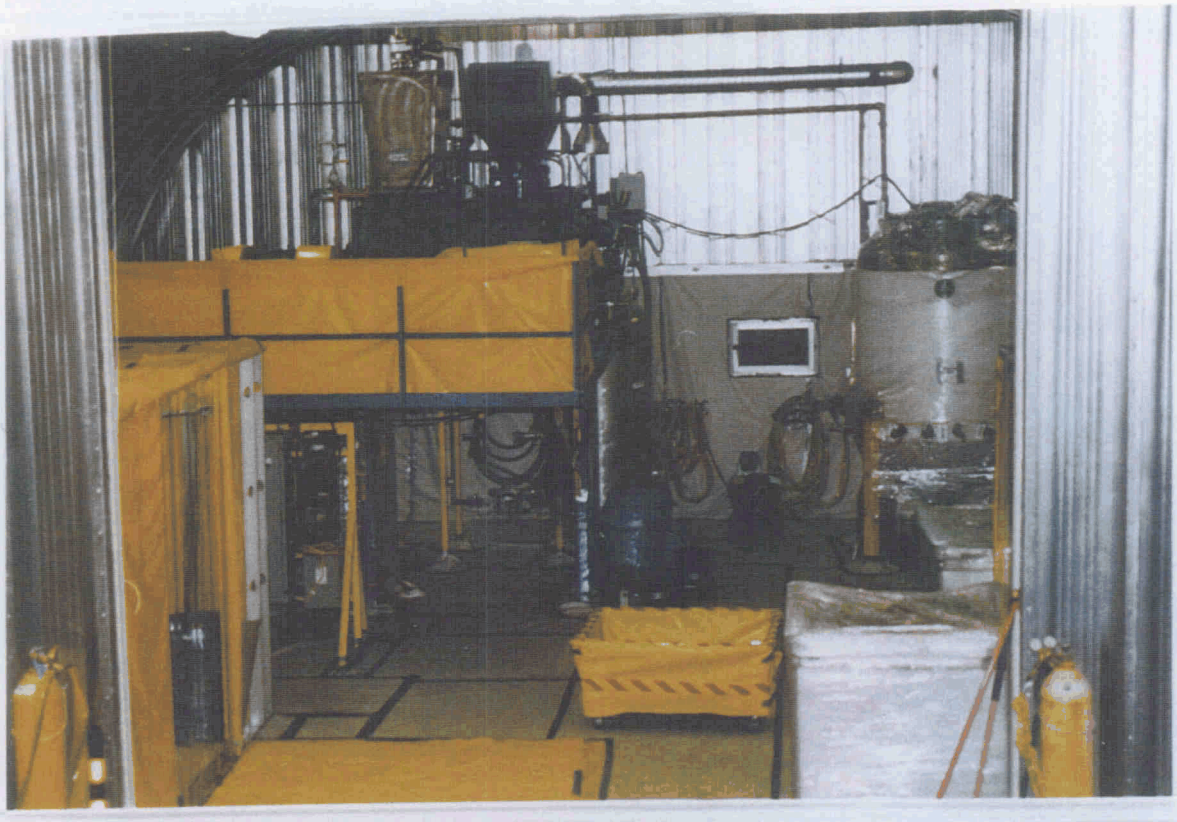
Ben Crocker and Filter Press

Ben Crocker and Filter Press



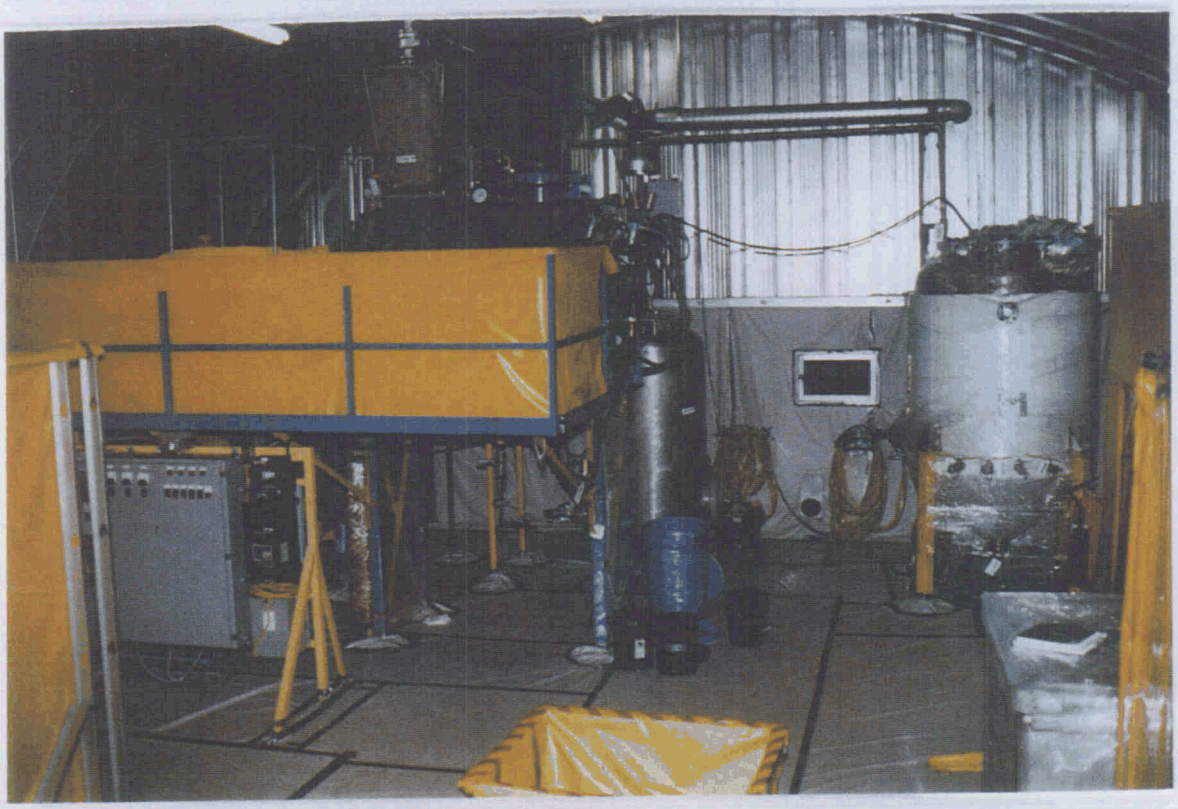
Boiler and Shed

Quonset Hut containing Process Equipment

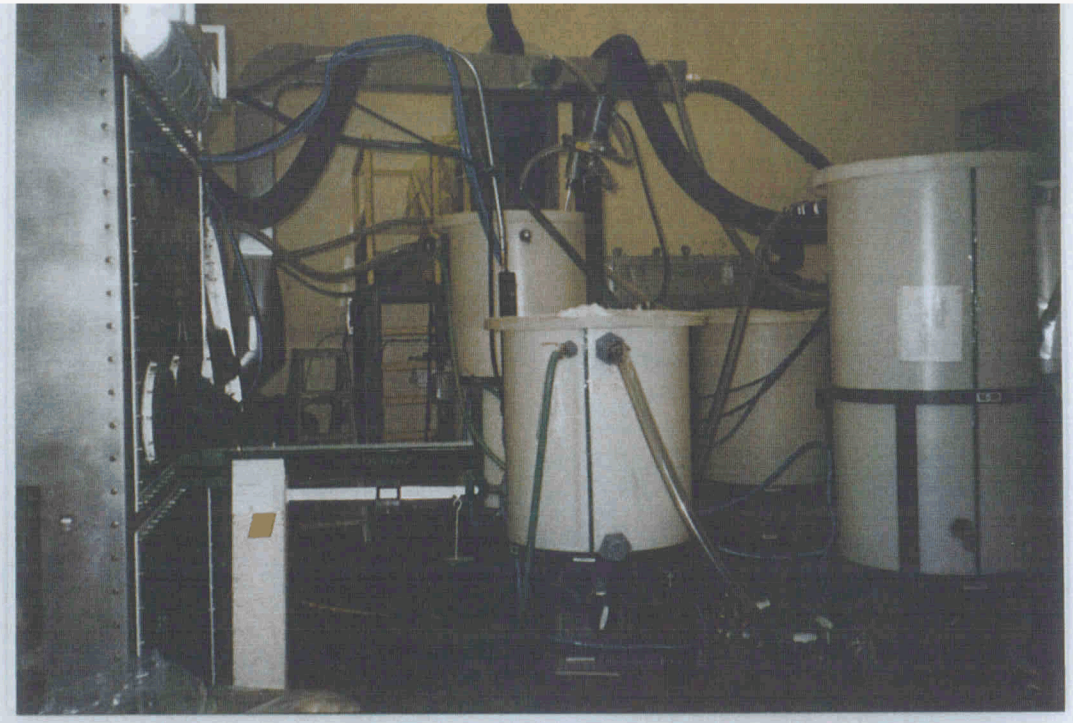


View of Process Area

View of Process Area



Pilot Demonstration Photographs
Recovery Dynamics Corporation



Process Equipment

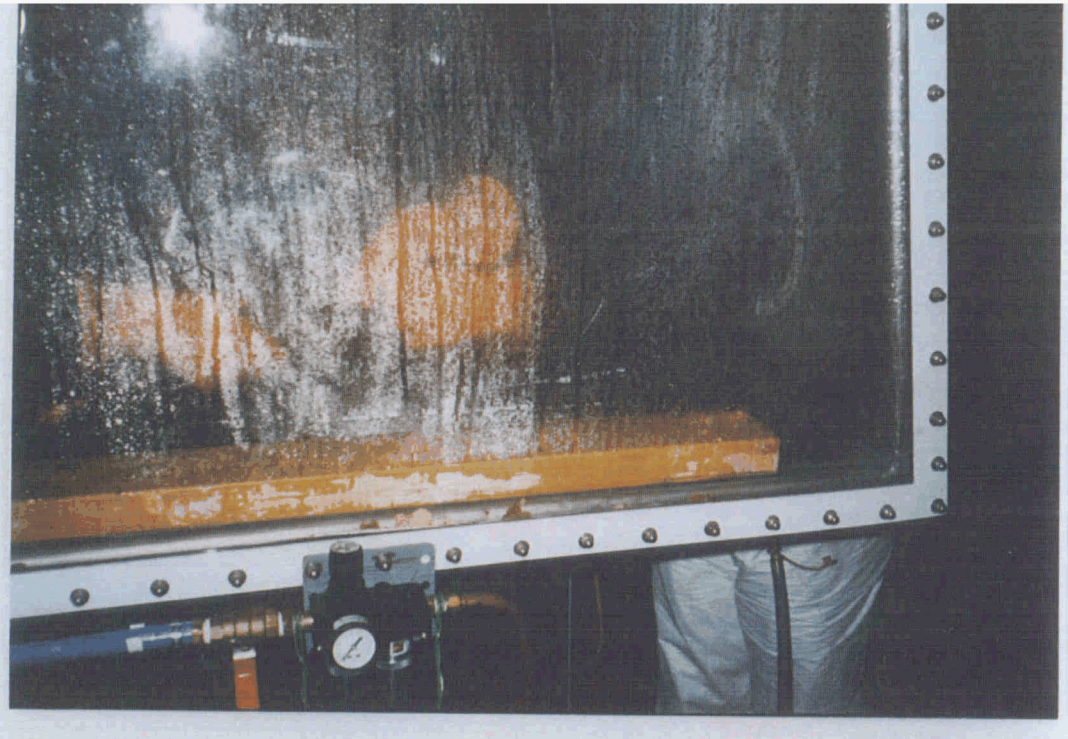
Thorium Oxalate Mixing Tank

Loading Thorium Nitrate Drum into Drum Dump

Clamping Thorium Nitrate Drum into Drum Dump

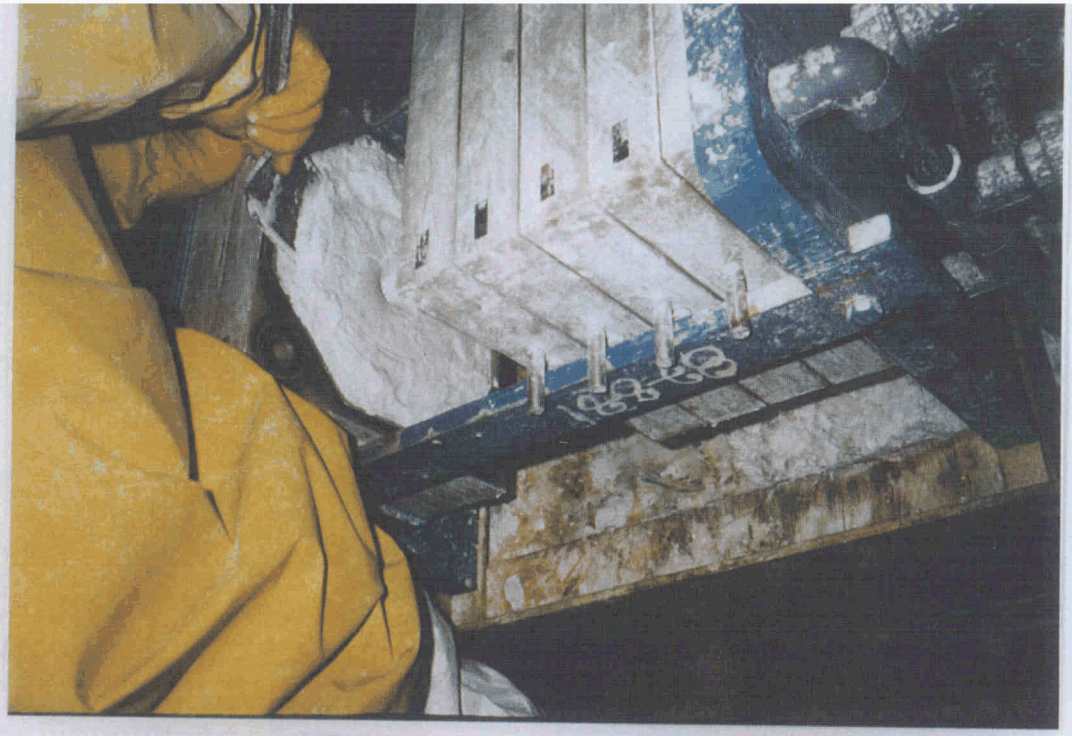
Dissolving Thorium Nitrate with Hot Water

Lumps of Thorium Nitrate

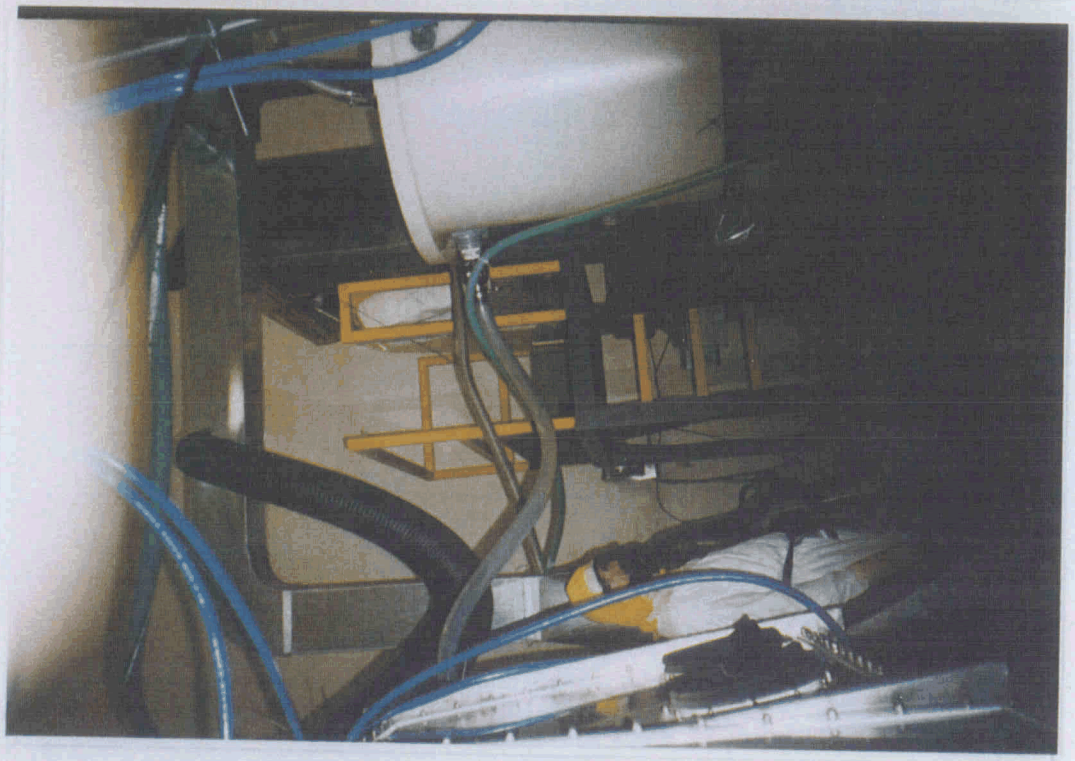


Dissolving Thorium Nitrate

Breaking Apart the Lumps of Thorium Nitrate



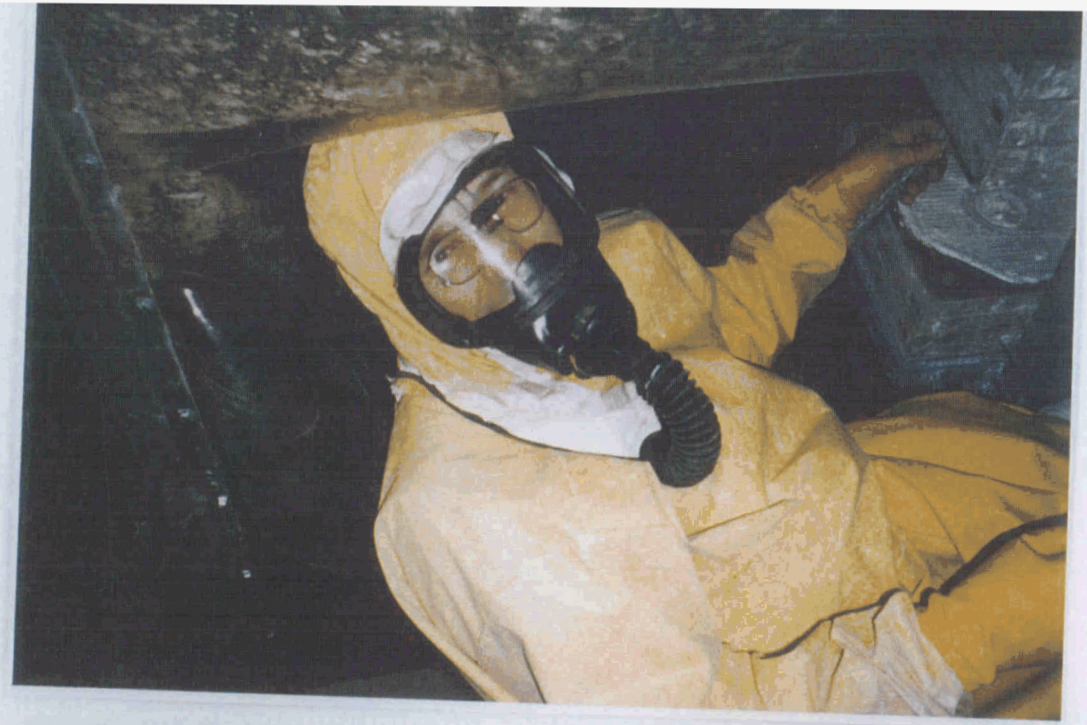
Jerry Scraping the Cake off the Plates



Jerry on Top of the Stand Dumping the Cake

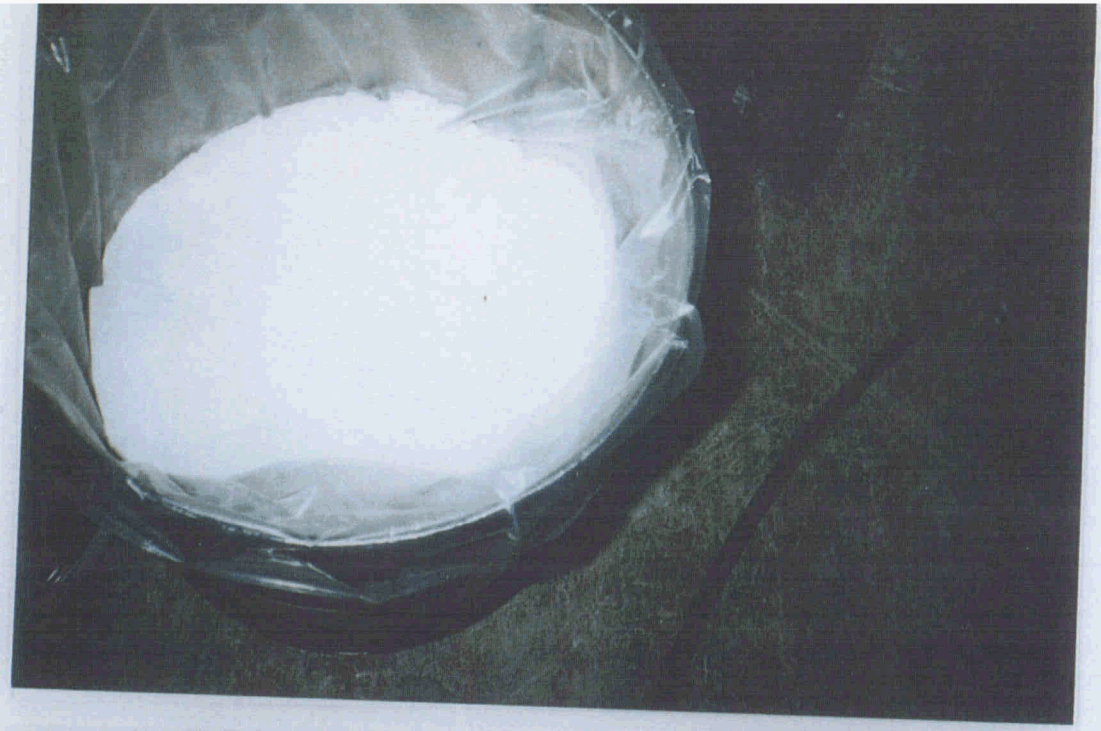
Thorium Oxalate Filter Cake

Thorium Oxalate Filter Cake



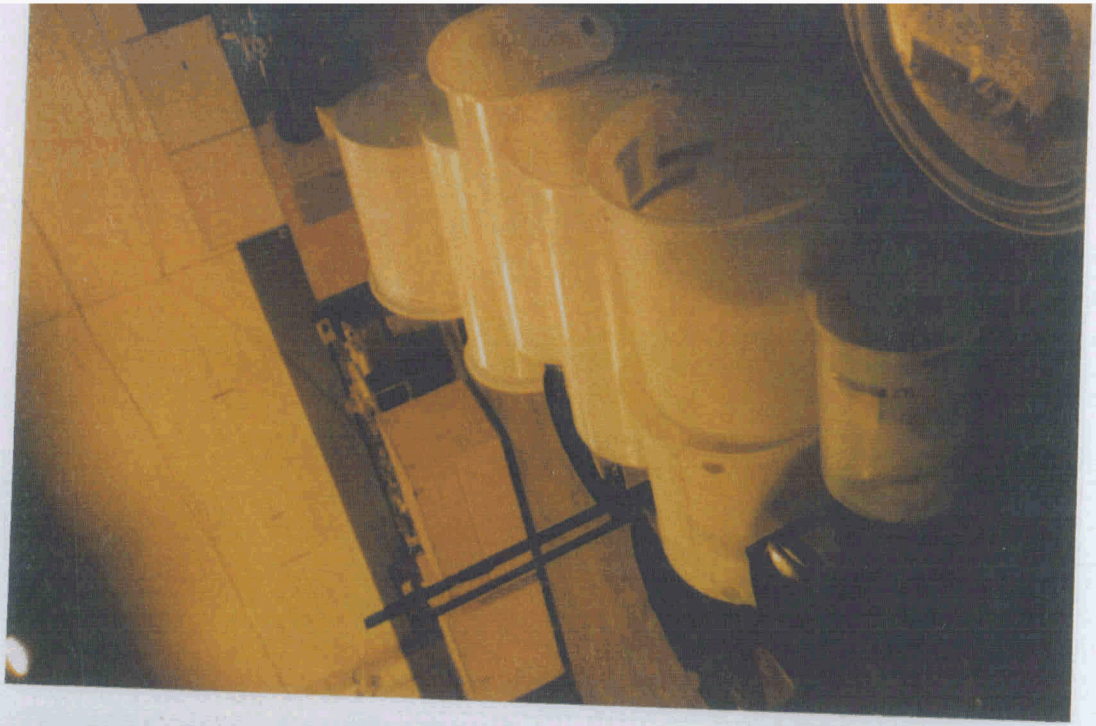
Jerry Cleaning the Plates

Thorium Oxalate in the Hopper to the Rotary Kiln



800 °C Thorium Oxide Powder

900 °C Thorium Oxide Powder



Tanks and Stands in Frisking Area

Six Thorium Oxide Product Drums to be Returned to DLA

Attachment 4

Analytical Data Summary Tables

and XRD/SEM Analysis

PERMAFIX Process

Analytical Results from

Batch 1

	solid dry ThN BT1-001	ThN mother solution BT1-002C	ThN+NaOH slurry BT1-004b	condensate water BT1-005b	wet cake BT1-006b	supernate filter press BT1-007a	dried product BT1-008d	calcined product BT1-009
% moisture		100						
% moisture	**0.1**							
mercury (mg/L) or (mg/kg)	**0.047**	< 0.02					**0.00039**	**0.016**
Thorium (mg/L) or (mg/kg)		230 000						
Thorium (mg/L) or (mg/kg)	**380 000**	**173 000**						
Sodium (mg/L) or (mg/kg)			47 600	4.37	37 200	55 000	79 500	
Sodium (mg/L) or (mg/kg)								
Nitrate (mg/L) or (mg/kg)		310 000						
Nitrate (mg/L) or (mg/kg)	**423 000**	**259 000**	208 600	97.9	42 500	157 700	149 700	154 600
Chloride (mg/kg)								
Antimony (mg/L) or (mg/kg)	< **0.036**	< 0.2					**0.0015**	< **0.05**
Arsenic (mg/L) or (mg/kg)	< **0.073**	< 1					**0.0041**	< **0.099**
Barium (mg/L) or (mg/Kg)	< **0.364**	< 1					**1.16**	< **0.497**
Beryllium (mg/L) or (mg/kg)	**0.078**	< 0.2					**0.0022**	**0.041**
Cadmium (mg/L) or (mg/kg)	< **0.015**	< 0.3					**0.0002**	< **0.02**
Chromium (mg/L) or (mg/kg)	< **0.364**	< 0.5					**0.0796**	**4.58**
Lead (mg/L) or (mg/kg)	< **0.146**	< 0.5					**0.0231**	< **0.199**
Nickel (mg/L) or (mg/kg)	< **0.364**	< 5					**0.0327**	**0.563**
Selenium (mg/L) or (mg/kg)	**0.385**	< 1					**0.0127**	< **0.199**
Silver (mg/L) or (mg/kg)	**0.027**	< 0.2					**0.0002**	**0.013**
Thallium (mg/L) or (mg/kg)	< **0.007**	< 0.2					**<0.0001**	< **0.01**
Vanadium (mg/L) or (mg/kg)		< 0.2						
Zinc (mg/L) or (mg/kg)		< 2						
Total activity (pCi/L) or (pCi/g)		246 +/- 0.5e6						
Alpha activity (pCi/g)	**1.7+/-0.1e5**							
Beta activity (pCi/g)	**1.3+/-0.1e5**							
Isotopes (pCi/L) or (pCi/g)								
Ac-228 **(AC-220)**	**3.2+/-0.3e4**	21.4+/- 0.15e6						
Cd-109		20.6+/- 0.8e6						
Ce-139								
Ce-141								
Ce-144		nd						
Cs-137								
Pb-212	**2.9+/-0.3e4**	22.2+/- 0.1e6						
Pr-234m								
Ra-224		nd						
Ra-228		nd						
Th-234		3.59+/- 0.37e6						
Th-232	**5.3+/-0.5e4**	10.5+/- 1.6e7						
Th-228	**5.4+/-0.5e4**	nd						
Tl-201								
Tl-208 **(Tl-209)**	**1.0+/-0.1e4**	6.97+/-0.07e6						
U-235								
I-129								
Total Radium alpha								
Th-230	**3.1+/-0.6e3**							
	95% crystalline main phase Th(NO3)4.5H2O						80% crystalline from which ~50% ThO2 ~50% NaNO3	

Permafix results are shown in bold

PERMAFIX Process

Analytical Results for

Batch 2

	TnN mother solution BT2-001C	filter press feed slurry BT2-003	supernate TnN+NaOH BT2-004	wet cake BT2-005d	filtrate drum BT2-006a	filtrate drum BT2-006c	dried product BT2-007e	calcined product BT2-008e	condensat wat BT2-009c
% moisture	100			46.5	100	100			100
% moisture		**72.2**	**84.3**	**0.1**	**85.1**		**23.5**	**<1**	**99.8**
mercury (mg/L) or (mg/kg)	< 0.02			< 0.2	< 0.02	< 0.02	**< 0.0002**		< 0.02
Thorium (mg/L) or (mg/kg)	260 000			780 000	< 0.1	0.24	490 000	780 000	530
Thorium (mg/L) or (mg/kg)	**178 000**	**121 000**	**17.9**	**332 000**	**7.51**		**542 000**	**733 000**	**30.1**
Sodium (mg/L) or (mg/kg)				21 200	30 700	3570	32 000	43 000	20
Sodium (mg/L) or (mg/kg)		**26 500**	**51 800**	**20 200**	**29 300**		**31 200**		**10.4**
Nitrate (mg/L) or (mg/kg)	350 000			36 000	94 000	11 000	58 000	66 000	1 300
Nitrate (mg/L) or (mg/kg)	**318 000**	**38 000**	**120 000**	**27 000**	**122 000**		**45 000**	**82 000**	**1608**
Chloride (mg/kg)			**1100**		**536**		**525**	520	
Antimony (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< 0.02	**< 0.00005**		< 0.02
Arsenic (mg/L) or (mg/kg)	< 1			< 10	< 0.1	< 0.1	**< 0.001**		< 0.1
Barium (mg/L) or (mg/Kg)	< 1			< 10	< 0.1	< 0.1	**0.52**		< 0.1
Beryllium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< 0.02	**< 0.0002**		< 0.02
Cadmium (mg/L) or (mg/kg)	< 0.3			< 3	< 0.03	< 0.03	**0.0002**		< 0.03
Chromium (mg/L) or (mg/kg)	< 0.5			< 5	0.21	< 0.05	**0.0053**		< 0.05
Lead (mg/L) or (mg/kg)	< 0.5			< 5	< 0.05	< 0.05	**0.0105**		< 0.05
Nickel (mg/L) or (mg/kg)	< 5			< 50	< 0.5	< 0.5	**0.002**		< 0.5
Selenium (mg/L) or (mg/kg)	< 1			< 10	< 0.1	< 0.1	**< 0.002**		< 0.1
Silver (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< 0.02	**0.0001**		< 0.02
Thallium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< 0.02	**< 0.0001**		< 0.02
Vanadium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< 0.02			< 0.02
Zinc (mg/L) or (mg/kg)	< 2			< 20	< 0.2	< 0.2			< 0.2
Total activity (pCi/L) or (pCi/g)	28.4+/-0.05e7			3.73+/-0.04e5	7.55+/-0.31e4	7.94+/-0.09e5	5.76+/-0.04e5		9.77+/- 0.1e5
Alpha activity (pCi/g)				3.20+/- 0.13e5			1.36+/-0.07e5		
Alpha activity (pCi/g)		**2.9+/-0.1e5**		**3.1+/-0.1e5**			**2.6+/- 0.1e5**		
Beta activity (pCi/g)				1.33+/- 0.06e5			6.63+/- 0.37e4		
Beta activity (pCi/g)		**1.2+/-0.1e5**		**1.5+/-0.1e5**			**1.1+/- 0.1e5**		
Isotopes (pCi/L) or (pCi/g)									
Ac-228	24.4+/-0.16e6			3.24+/- 0.07e4	6.49+/-0.62e3	9.07+/- 0.16e4	5.73+/-0.07e4		9.21+/-0.17e4
(Ac-220)		**6.3+/-0.5e4**		**3.5+/-0.4e4**			**4.0+/- 0.5e4**		
Cd-109	23.5+/- 0.76e6			2.05+/-0.28e4		3.72+/-0.53e4	3.77+/- 4.0e3		6.42+/-0.67e4
Ce-139									
Ce-141									
Ce-144									
Cs-137									
Pb-212	25.0+/- 0.1e6			2.73+/-0.04e4	2.53+/-0.22e3	6.61+/- 0.08e4	5.85+/- 0.04e4		9.95+/-0.1e4
Pb-212		**5.8+/-0.6e4**		**3.3+/-0.3e4**			**4.0+/- 0.4e4**		
Pr-234m									
Ra-224	nd			nd	nd	nd	nd		nd
Ra-228	nd			nd	nd	nd	nd		nd
Th-234	6.38+/-0.42e6			5.01+/-1.3e3	1.81+/-1.2e3	8.54+/-2.6e3	7.33+/-1.5e3		1.58+/-0.32e4
Th-232	nd			9.11+/- 5.2e4	nd	2.32+/-1.1e5	1.90+/-0.35e5		2.48+/-1.6e5
Th-228	nd			nd	nd	nd	nd		nd
Tl-201						nd			
Tl-208	7.91+/- 0.07e6			1.24+/-0.03e4	7.97+/-2.3e2	2.42+/-0.08e4	1.89+/-0.035e4		3.44+/-0.09e4
(Tl-209)		**1.9+/-0.2e4**		**1.1+/-0.1e4**			**1.3+/- 0.1e4**		
U-235					1.76+/-3.3e2				
I-129									
Total Radium alpha									

		filter press feed slurry BT2-003	supernate TnN+NaOH BT2-004	wet cake BT2-005d	filtrate drum BT2-006a	filtrate drum BT2-006c	dried product BT2-007e	calcined product BT2-008e	condensate water BT2-009c

Permafix results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)								
Antimony (mg/L)	2.1						< 0.2		
Arsenic (mg/L)	5						< 1		
Barium (mg/L)	7.6						0.71		
Beryllium (mg/L)	0.014						< 0.02		
Cadmium (mg/L)	0.19						< 0.03		
Chromium (mg/L)	0.86						< 0.05		
Lead (mg/L)	0.37						< 0.05		
Mercury (mg/L)	0.2						< 0.02		
Nickel (mg/L)	5						< 0.039		
Selenium (mg/L)	0.16						< 0.4		
Silver (mg/L)	0.3						< 0.02		
Thallium (mg/L)	0.078						< 0.02		
Vanadium (mg/L)	0.23						< 0.02		
Zinc (mg/L)	5.3						0.39		
							poorly crystalized ~75% crystalline mainly ThO2	poorly crystalized 90% crystalline from which ~85% ThO2 ~15% NaNO3	

Permafix results are shown in bold

	ThN mother solution BT4-001C	filter press feed slurry BT4-003	superate from slurry BT4-004	solid wet cake BT4-005d	filtrate in holding drum BT4-006	solid dried product BT4-007e	calcined product BT4-008e	condensate water BT4-009c
% moisture	100			25.3				100
% moisture						**14.1**	**<1**	
mercury (mg/L) or (mg/kg)	< 0.02			< 0.2		< **0.0002**	< **0.0002**	< 0.02
Thorium (mg/L) or (mg/kg)	260 000			870 000		27 000	810 000	350
Thorium (mg/L) or (mg/kg)	**168 000**	**186 000**	**10.4**	**360 000**	**234**	**648 000**	**794 000**	**1120**
Sodium (mg/L) or (mg/kg)				7 600		13 900	16 000	40
Sodium (mg/L) or (mg/kg)		**9040**	**58 100**	**7 500**	**3170**	**12 400**		**35**
Nitrate (mg/L) or (mg/kg)	410 000			12 000		22 000	24 000	240
Nitrate (mg/L) or (mg/kg)	**311 000**	**26 800**	**165 200**	**9 000**	**11 200**	**16 500**	**26 500**	**67**
Chloride (mg/kg)							510	
Antimony (mg/L) or (mg/kg)	< 0.2			< 2		< **0.0005**	< **0.0005**	< 0.02
Arsenic (mg/L) or (mg/kg)	< 1			< 10		< **0.001**	< **0.001**	< 0.1
Barium (mg/L) or (mg/Kg)	< 1			< 10		**0.635**	**0.146**	< 0.1
Beryllium (mg/L) or (mg/kg)	< 0.2			< 10		< **0.0002**	< **0.0002**	< 0.02
Cadmium (mg/L) or (mg/kg)	< 0.3			< 3		**0.0002**	< **0.0001**	< 0.03
Chromium (mg/L) or (mg/kg)	< 0.5			< 5		**0.0061**	**0.0041**	< 0.05
Lead (mg/L) or (mg/kg)	< 0.5			< 5		**0.0053**	**0.0006**	< 0.05
Nickel (mg/L) or (mg/kg)	< 5			< 50		**0.0037**	**0.0011**	< 0.5
Selenium (mg/L) or (mg/kg)	< 1			< 10		< **0.002**	< **0.002**	< 0.1
Silver (mg/L) or (mg/kg)	< 0.2			< 2		< **0.0001**	< **0.0001**	< 0.02
Thallium (mg/L) or (mg/kg)	< 0.2			< 2		< **0.0001**	< **0.0001**	< 0.02
Vanadium (mg/L) or (mg/kg)	< 0.2			< 2				< 0.02
Zinc (mg/L) or (mg/kg)	< 2			< 20				< 0.2
Total activity (pCi/L) or (pCi/g)	28.3+/-0.05e7			4.79+/-0.041e5		6.84+/-0.042e5		9.79+/- 0.10e5
Alpha activity (pCi/g)				4.33+/-0.14e5		5.95+/-0.15e5		
Beta activity (pCi/g)				1.57+/-0.062e5		2.38+/-0.064e5		
Isotopes (pCi/L) or (pCi/g)								
Ac-228	2.47+/-0.015e7			3.96+/-0.064e4		7.05+/-0.077e4		8.08+/-0.13e4
Cd-109	7.25+/-0.81e6					4.57+/-0.38e4		1.50+/-0.52e4
Ce-139	4.56+/-4.5e4							
Ce-141	8.38+/-4.2e5							
Ce-144	1.59+/-1.1e5							
Cs-137								
Pb-212	2.4+/-0.01e7			4.12+/-0.037e4		1.57+/-0.022e4		5.02+/-0.08e4
Pr-234m								
Ra-224	2.57+/-0.07e7			nd		nd		nd
Ra-228	nd			nd		nd		nd
Th-234	3.78+/-0.39e6			9.42+/-1.1e3				
Th-232	1.19+/-0.15e8			1.20+/-0.59e5		2.54+/-0.52e5		1.71+/-0.65e5
Th-228	nd			nd		nd		nd
Tl-201	2.96+/-1.8e5							
Tl-208	8.00+/-0.074e6			1.59+/-0.035e4		2.34+/-0.037e4		1.56+/-0.06e4
U-235								
I-129								
Total Radium alpha								

		filter press feed slurry BT4-003	superate from slurry BT4-004	solid wet cake BT4-005d	filtrate in holding drum BT4-006	solid dried product BT4-007e	calcined product BT4-008e	condensate water BT4-009c

Permafix results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)							
Antimony (mg/L)	2.1					< 0.2		
Arsenic (mg/L)	5					< 1		
Barium (mg/L)	7.6					< 0.1		
Beryllium (mg/L)	0.014					< 0.02		
Cadmium (mg/L)	0.19					< 0.03		
Chromium (mg/L)	0.86					< 0.05		
Lead (mg/L)	0.37					< 0.05		
Mercury (mg/L)	0.2					< 0.02		
Nickel (mg/L)	5					< 0.3		
Selenium (mg/L)	0.16					< 0.4		
Silver (mg/L)	0.3					< 0.02		
Thallium (mg/L)	0.078					< 0.02		
Vanadium (mg/L)	0.23					< 0.02		
Zinc (mg/L)	5.3					< 0.2		

Permafix results are shown in bold

	ThN mother solution BT5-001C	filter press slurry feed BT5-003	liquid supernate BT5-004	solid wet cake BT5-005d	filtrate from holding drum BT5-006c	dried product BT5-007e	calcined product BT5-008e	condensate water BT5-009c
% moisture	100			20.9	100			100
% moisture								
mercury (mg/L) or (mg/kg)	< 0.02			< 0.2	0.18	**0.00063**		< 0.02
Thorium (mg/L) or (mg/kg)	260 000			640 000	7	570 000	770 000	250
Thorium (mg/L) or (mg/kg)	**190 000**	**138 000**	**48.5**	**272 000**	**8.85**	**538 000**	**725 000**	**47.5**
Sodium (mg/L) or (mg/kg)				12 300	24 900	29 200	36 200	40
Sodium (mg/L) or (mg/kg)		**20 400**	**78 000**	**13 000**	**24 000**	**27 300**		**14.2**
Nitrate (mg/L) or (mg/kg)	410 000			38 000	80 000	70 000	88 000	1 500
Nitrate (mg/L) or (mg/kg)	**390 000**	**39 000**	**188 000**	**27 400**	**66 500**	**13 300**	**97 000**	**66.4**
Chloride (mg/kg)							570	
Antimony (mg/L) or (mg/kg)	0.29			< 2	< 0.02	**0.0228**		< 0.02
Arsenic (mg/L) or (mg/kg)	< 1			< 10	< 0.1	**0.0032**		< 0.1
Barium (mg/L) or (mg/Kg)	< 1			< 10	< 0.1	**2.77**		< 0.1
Beryllium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	**0.0143**		< 0.02
Cadmium (mg/L) or (mg/kg)	< 0.3			< 3	< 0.03	**0.0009**		< 0.03
Chromium (mg/L) or (mg/kg)	< 0.5			< 5	0.051	**0.0847**		< 0.05
Lead (mg/L) or (mg/kg)	< 0.5			< 5	< 0.05	**0.0237**		< 0.05
Nickel (mg/L) or (mg/kg)	< 5			< 50	< 0.5	**0.0264**		< 0.5
Selenium (mg/L) or (mg/kg)	< 1			< 10	< 0.1	**0.0261**		< 0.1
Silver (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	**0.0004**		0.023
Thallium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02	< **0.0001**		< 0.02
Vanadium (mg/L) or (mg/kg)	< 0.2			< 2	< 0.02			< 0.02
Zinc (mg/L) or (mg/kg)	13			< 20	< 0.2			< 0.2
Total activity (pCi/L) or (pCi/g)	26.8+/-0.05e7			3.35+/-0.034e5	7.07+/-0.30e4	5.11+/-0.035e5		9.97+/- 0.1e5
Alpha activity (pCi/g)				2.59+/-0.11e5		3.80+/- 0.11e5		
Beta activity (pCi/g)				8.72+/-0.46e4		1.55+/-0.05e5		
Isotopes (pCi/L) or (pCi/g)								
Ac-228	2.51+/-0.02e7			2.13+/-0.052e4	5.62+/-0.52e3	4.39+/-0.058e4		9.87+/-0.18e4
Cd-109	6.6+/-0.79e6			1.83+/-0.2e4		2.61+/- 0.27e4		8.04+/-1.0e4
Ce-139	5.74+/-4.2e4							
Ce-141	6.17+/-3.5e5							
Ce-144								
Cs-137					3.50+/-1.6e2			
Pb-212	5.82+/-0.05e6			2.81+/-0.034e4	2.53+/-2.0e2	5.27+/-0.036e4		1.02+/- 0.01e5
Pr-234m	4.31+/-2.8e6							
Ra-224	nd			nd	4.68+/-3.0e3	nd		nd
Ra-228	nd			nd	nd	nd		nd
Th-234	4.12+/-0.38e6			3.18+/-0.9e3	5.18+/-0.91e3	5.32+/-1.2e3		1.43+/-0.45e4
Th-232	1.07+/- 0.14e8			nd	nd	9.63+/-4.3e4		2.37+/-1.3e5
Th-228	nd			nd	nd	nd		nd
Tl-201	2.87+/-2.1e5							
Tl-208	8.12+/-0.07e6			1.24+/- 0.03e4	3.03+/-1.9e2	1.81+/-0.032e4		3.24+/-0.084e4
U-235	3.85+/-1.9e4				2.34+/-1.9e2			
I-129								
Total Radium alpha								

	filter press slurry feed BT5-003	liquid supernate BT5-004	solid wet cake BT5-005d	filtrate from holding drum BT5-006c	dried product BT5-007e	calcined product BT5-008e	condensate water BT5-009c

Permafix results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)							
Antimony (mg/L)	2.1					< 0.2		
Arsenic (mg/L)	5					< 1		
Barium (mg/L)	7.6					0.84		
Beryllium (mg/L)	0.014					< 0.02		
Cadmium (mg/L)	0.19					< 0.05		
Chromium (mg/L)	0.86					< 0.05		
Lead (mg/L)	0.37					< 0.05		
Mercury (mg/L)	0.2					< 0.02		
Nickel (mg/L)	5					< 0.3		
Selenium (mg/L)	0.16					< 0.4		
Silver (mg/L)	0.3					< 0.02		
Thallium (mg/L)	0.078					< 0.02		
Vanadium (mg/L)	0.23					< 0.02		
Zinc (mg/L)	5.3					0.21		
						75.42g extracted in 2000 mL		

Permafix results are shown in bold

	liquid raw condensate CLB1-001c	liquid polished cond. CLB1-002d	liquid raw cond. CLB2-001c	liquid polished cond. CLB2-002d	liquid raw cond. CLB3-001c	liquid polished cond. CLB3-002d
% moisture		100		100		100
% moisture						
mercury (mg/L) or (mg/kg)		< 0.02		< 0.02		0.076
Thorium (mg/L) or (mg/kg)		< 0.1		< 0.1		< 0.1
Thorium (mg/L) or (mg/kg)	**85.4**	**4.66**	**6.36**	**< 0.5**	**2.32**	**< 0.5**
Sodium (mg/L) or (mg/kg)		40		28 500		44 400
Sodium (mg/L) or (mg/kg)	**24.8**	**30**	**25 500**	**25 700**	**38 000**	**40 800**
Nitrate (mg/L) or (mg/kg)		530		90 000		130 000
Nitrate (mg/L) or (mg/kg)	**60.7**	**40.2**	**82 400**	**193 000**	**139 000**	**122 000**
Chloride (mg/kg)						
Antimony (mg/L) or (mg/kg)		< 0.02		< 0.02		< 0.02
Arsenic (mg/L) or (mg/kg)		< 0.1		< 0.1		< 0.1
Barium (mg/L) or (mg/Kg)		< 0.1		< 0.1		< 0.1
Beryllium (mg/L) or (mg/kg)		< 0.02		< 0.02		< 0.02
Cadmium (mg/L) or (mg/kg)		< 0.03		< 0.03		< 0.03
Chromium (mg/L) or (mg/kg)		< 0.05		< 0.05		< 0.05
Lead (mg/L) or (mg/kg)		< 0.05		< 0.05		< 0.05
Nickel (mg/L) or (mg/kg)		< 0.5		< 0.5		< 0.5
Selenium (mg/L) or (mg/kg)		< 0.1		< 0.1		< 0.1
Silver (mg/L) or (mg/kg)		< 0.02		< 0.02		< 0.02
Thallium (mg/L) or (mg/kg)		< 0.02		< 0.02		< 0.02
Vanadium (mg/L) or (mg/kg)				< 0.02		< 0.02
Zinc (mg/L) or (mg/kg)		< 0.2		< 0.1		< 0.2
Total activity (pCi/L) or (pCi/g)		2.60+/-1.7e3		6.87+/-1.8e3		9.84+/-1.9e3
Alpha activity (pCi/g)						
Beta activity (pCi/g)						
Isotopes (pCi/L) or (pCi/g)						
Ac-228		nd		2.01+/-0.56e3		
Cd-109						
Ce-139						
Ce-141						
Ce-144						
Cs-137						3.00+/-0.27e3
Pb-212		nd		nd		nd
Pr-234m						
Ra-224		nd		nd		nd
Ra-228		nd		nd		nd
Th-234						3.91+/-0.92e3
Th-232		nd		nd		nd
Th-228				nd		nd
Tl-201						
Tl-208		nd		nd		nd
U-235						1.91+/-1.6e2
I-129						1.39+/-0.093e3
Total Radium alpha		220 +/- 40		400 +/- 54		900 +/- 110

Permafix results are shown in bold

	liquid ThN liquor E-104A-L1	solid wet filter cake E-108-L1	liquid final waste water E-123-L1	solid Product E-125-L1	liquid wet scrubber sol. E-135-L1
% moisture		37.17			
% moisture		**44.6**			
pH			3.1		7.6
mercury (mg/L) or (mg/kg)	< 0.004	< 0.02	< 0.004		< 0.004
Thorium (mg/L) or (mg/kg)	85 000	300 000	1.6	710 000	54
Thorium (mg/L) or (mg/kg)	**96 000**		**22**		**26**
Sodium (mg/L) or (mg/kg)					
Sodium (mg/L) or (mg/kg)					
Nitrate (mg/L) or (mg/kg)	120 000	27 000	81 000	4700	170
Nitrate (mg/L) or (mg/kg)					
Chloride (mg/kg)				110	
Antimony (mg/L) or (mg/kg)					
Arsenic (mg/L) or (mg/kg)	< 0.1	< 4.5	< 0.1		< 0.1
Barium (mg/L) or (mg/Kg)	39	26	7.3		0.11
Barium (mg/L) or (mg/Kg)			**33**		
Beryllium (mg/L) or (mg/kg)					
Cadmium (mg/L) or (mg/kg)	< 0.03	< 1.4	< 0.03		< 0.03
Chromium (mg/L) or (mg/kg)	0.12	< 2.3	0.24		0.065
Lead (mg/L) or (mg/kg)	0.08	< 4.5	< 0.1		< 0.1
Nickel (mg/L) or (mg/kg)					
Selenium (mg/L) or (mg/kg)	0.1	< 4.5	< 0.1		< 0.1
Silver (mg/L) or (mg/kg)	< 0.02	< 0.9	< 0.02		< 0.02
Thallium (mg/L) or (mg/kg)					
Vanadium (mg/L) or (mg/kg)					
Zinc (mg/L) or (mg/kg)					
Total activity (pCi/L) or (pCi/g)	9.25+/-0.01e7	2.42+/-0.022e5	2.06+/-0.01e6	5.96+/- 0.03e5	
Alpha activity (pCi/g) or (pCi/L)	5.69+/-0.02e7	2.0+/-0.033e5	7.71+/-0.22e5	4.5+/- 0.05e5	1.38+/-0.02e6
Alpha activity (pCi/g) or (pCi/L)			**3.9+/-1.2e4**		
Beta activity (pCi/g) or (pCi/L)	2.97+/-0.009e7	6.74+/- 0.13e4	1.99+/- 0.02e6	1.09+/- 0.02e5	4.18+/-0.07e5
Beta activity (pCi/g) or (pCi/L)			**2.5+/- 0.74e5**		
Isotopes (pCi/L) or (pCi/g)					
Ac-228	9.63+/-0.09e6	4.67+/- 0.52e3	1.11+/-0.007e6	1.09+/- 0.06e4	4.04+/-0.2e4
Ac-228			**3.4+/-0.67e6**		
Ba-133			3.74+/-1.3e3		
Bi-212			5.1+/-16e3		
Cd-109	5.73+/-0.34e6	1.03+/-0.29e4		8.66+/-2.4e3	8.76+/- 0.93e4
Ce-139	2.64+/-2.4e4				
Ce-141	1.78+/-1.2e5		1.04+/-0.29e4		
Cs-137					
Pb-212	6.95+/- 0.05e6	2.52+/-0.05e4	1.05+/- 0.02e5	4.61+/-0.06e4	1.44+/- 0.02e5
Pb-212			**1.0+/- 0.1e5**		
Pr-234m			2.24+/-1.2e5		
Ra-224					
Ra-228			**1.4+/- 0.16e6**		
Th-234	9.48+/-1.6e5				1.84+/-0.47e4
Th-232	3.66+/-0.56e7	5.84+/-5.1e4	2.97+/- 0.33e6		5.77+/-2.7e5
Th-232			**2.2+/- 2.2e3**		
Th-228		2.26+/-0.76e4	**1.4+/- 0.47e5**		
Tl-201	1.41+/-1.3e5				
Tl-208	3.17+/- 0.045e6	1.07+/-0.04e4	3.21+/-0.2e4	2.32+/- 0.05e4	5.76+/- 0.15e4
Tl-208			**2.6+/- 0.31e4**		
U-235			1.44+/- 0.63e3		
Th-230			**2.3+/-3.3e3**		
Total Radium alpha			610+/-18e3		

		solid wet filter cake E-108-L1	liquid final waste water E-123-L1	solid Product E-125-L1	liquid wet scrubber sol. E-135-L1

Recodyne results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)				
Antimony (mg/L)	2.1				
Arsenic (mg/L)	5				
Barium (mg/L)	7.6			< **0.5**	
Beryllium (mg/L)	0.014			< **0.1**	
Cadmium (mg/L)	0.19				
Chromium (mg/L)	0.86			< **0.03**	
Lead (mg/L)	0.37			< **0.1**	
Mercury (mg/L)	0.2			< **0.3**	
Nickel (mg/L)	5			< **0.002**	
Selenium (mg/L)	0.16				
Silver (mg/L)	0.3			< **0.5**	
Thallium (mg/L)	0.078			< **0.05**	
Vanadium (mg/L)	0.23				
Zinc (mg/L)	5.3				

Recodyne results are shown in bold

	liquid ThN liquor J-104A-L1	solid wet filter cake J-108-L1	liquid final waste water J-123-L1	solid Product J-125-L1	liquid wet scrubber sol. J-135-L1
% moisture		35.75			
% moisture		**46.1**			
pH			3.4		1.1
mercury (mg/L) or (mg/kg)	< 0.004	< 0.02	< 0.004		< 0.004
Thorium (mg/L) or (mg/kg)	83 000	270 000	1.3	560 000	32
Thorium (mg/L) or (mg/kg)	**93 000**		**16**		**28**
Sodium (mg/L) or (mg/kg)					
Sodium (mg/L) or (mg/kg)					
Nitrate (mg/L) or (mg/kg)	130 000	29 000	74 000	350	4600
Nitrate (mg/L) or (mg/kg)					
Chloride (mg/kg)				170	
Antimony (mg/L) or (mg/kg)					
Arsenic (mg/L) or (mg/kg)	< 0.1	< 4.5	< 0.1		< 0.1
Barium (mg/L) or (mg/Kg)	42	24	24		< 0.1
Barium (mg/L) or (mg/Kg)			**37**		
Cadmium (mg/L) or (mg/kg)	< 0.03	< 1.4	< 0.03		< 0.03
Chromium (mg/L) or (mg/kg)	0.15	< 2.3	0.25		0.13
Lead (mg/L) or (mg/kg)	0.14	< 4.5	< 0.1		< 0.1
Nickel (mg/L) or (mg/kg)					
Selenium (mg/L) or (mg/kg)	< 0.1	< 4.5	< 0.1		< 0.1
Silver (mg/L) or (mg/kg)	< 0.02	< 0.9	< 0.02		< 0.02
Thallium (mg/L) or (mg/kg)					
Vanadium (mg/L) or (mg/kg)					
Zinc (mg/L) or (mg/kg)					
Total activity (pCi/L) or (pCi/g)	9.54+/-0.01e7	2.35+/-0.02e5	1.29+/-0.01e6	6.59+/-0.03e5	
Alpha activity (pCi/g) or (pCi/L)	5.2+/- 0.02e7	1.34+/- 0.03e5	4.75+/- 0.17e5	4.98+/-0.05e5	8.5+/-0.15e5
Alpha activity (pCi/g) or (pCi/L)			**4.6+/-1.3e4**		
Beta activity (pCi/g) or (pCi/L)	2.92+/- 0.01e7	4.68+/- 0.12e4	1.31+/-0.02e6	1.32+/-0.02e5	2.69+/-0.06e5
Beta activity (pCi/g) or (pCi/L)			**3.3+/- 0.94e5**		
Isotopes (pCi/L) or (pCi/g)					
Ac-228	1.14+/-0.01e7	5.26+/-0.58e3	6.94+/-0.05e5	1.44+/-0.07e4	3.39+/-0.18e4
Ac-228			**2.3+/- 0.47e6**		
Ba-133					
Bi-212					
Cd-109				2.68+/-0.31e4	2.74+/-0.86e4
Ce-139					
Ce-141	2.51+/-1.1e5				
Ce-144					
Cs-137	3.74+/-26e3				
K-40	7.69+/-2.0e5		**1.9+/-0.19e5**		
Pb-212	1.06+/-0.005e7	2.32+/-0.05e4	6.73+/-0.15e4	6.15+/-0.07e4	8.24+/- 0.14e4
Pb-212			**1.1+/-0.11e5**		
Pr-234m			1.89+/-1.1e5		
Ra-224					
Ra-228			**1.9+/- 0.21e6**		
Th-234	1.02+/-0.17e6	1.81+/-1.7e3			
Th-232	4.02+/-0.52e7		1.75+/-0.2e6		
Th-228		2.08+/- 0.77e4	**1.9+/- 0.4e5**	7.94+/-0.88e4	9.43+/-2.2e4
Tl-201					
Tl-208	3.39+/-0.046e6	7.7+/- 0.39e3	2.04+/-0.15e4	2.72+/-0.057e4	3.68+/-0.12e4
Tl-208			**2.9+/-0.37e4**		
U-235	6.93+/-19e3				
I-129					
Total Radium alpha			4.0+/-0.16e5		
Th-230			**3.0+/-2.5e3**		

		solid wet filter cake J-108-L1	liquid final waste water J-123-L1	solid Product J-125-L1	liquid wet scrubber sol. J-135-L1

Recodyne results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)					
Antimony (mg/L)	2.1					
Arsenic (mg/L)	5			<	**0.5**	
Barium (mg/L)	7.6			<	**0.1**	
Beryllium (mg/L)	0.014					
Cadmium (mg/L)	0.19			<	**0.03**	
Chromium (mg/L)	0.86			<	**0.1**	
Lead (mg/L)	0.37			<	**0.3**	
Mercury (mg/L)	0.2			<	**0.002**	
Nickel (mg/L)	5					
Selenium (mg/L)	0.16			<	**0.5**	
Silver (mg/L)	0.3			<	**0.05**	
Thallium (mg/L)	0.078					
Vanadium (mg/L)	0.23					
Zinc (mg/L)	5.3					

Recodyne results are shown in bold

	liquid ThN liquor J-104A-L1	solid wet filter cake J-108-L1	liquid final waste water J-123-L1	solid Product J-125-L1	liquid wet scrubber sol. J-135-L1
% moisture		35.75			
% moisture		**46.1**			
pH			3.4		1.1
mercury (mg/L) or (mg/kg)	< 0.004	< 0.02	< 0.004		< 0.004
Thorium (mg/L) or (mg/kg)	83 000	270 000	1.3	560 000	32
Thorium (mg/L) or (mg/kg)	**93 000**		**16**		**28**
Sodium (mg/L) or (mg/kg)					
Sodium (mg/L) or (mg/kg)					
Nitrate (mg/L) or (mg/kg)	130 000	29 000	74 000	350	4600
Nitrate (mg/L) or (mg/kg)					
Chloride (mg/kg)				170	
Antimony (mg/L) or (mg/kg)					
Arsenic (mg/L) or (mg/kg)	< 0.1	< 4.5	< 0.1		< 0.1
Barium (mg/L) or (mg/Kg)	42	24	24		< 0.1
Barium (mg/L) or (mg/Kg)			**37**		
Cadmium (mg/L) or (mg/kg)	< 0.03	< 1.4	< 0.03		< 0.03
Chromium (mg/L) or (mg/kg)	0.15	< 2.3	0.25		0.13
Lead (mg/L) or (mg/kg)	0.14	< 4.5	< 0.1		< 0.1
Nickel (mg/L) or (mg/kg)					
Selenium (mg/L) or (mg/kg)	< 0.1	< 4.5	< 0.1		< 0.1
Silver (mg/L) or (mg/kg)	< 0.02	< 0.9	< 0.02		< 0.02
Thallium (mg/L) or (mg/kg)					
Vanadium (mg/L) or (mg/kg)					
Zinc (mg/L) or (mg/kg)					
Total activity (pCi/L) or (pCi/g)	9.54+/-0.01e7	2.35+/-0.02e5	1.29+/-0.01e6	6.59+/-0.03e5	
Alpha activity (pCi/g) or (pCi/L)	5.2+/- 0.02e7	1.34+/- 0.03e5	4.75+/- 0.17e5	4.98+/-0.05e5	8.5+/-0.15e5
Alpha activity (pCi/g) or (pCi/L)			**4.6+/-1.3e4**		
Beta activity (pCi/g) or (pCi/L)	2.92+/- 0.01e7	4.68+/- 0.12e4	1.31+/-0.02e6	1.32+/-0.02e5	2.69+/-0.06e5
Beta activity (pCi/g) or (pCi/L)			**3.3+/- 0.94e5**		
Isotopes (pCi/L) or (pCi/g)					
Ac-228	1.14+/-0.01e7	5.26+/-0.58e3	6.94+/-0.05e5	1.44+/-0.07e4	3.39+/-0.18e4
Ac-228			**2.3+/- 0.47e6**		
Ba-133					
Bi-212					
Cd-109				2.68+/-0.31e4	2.74+/-0.86e4
Ce-139					
Ce-141	2.51+/-1.1e5				
Ce-144					
Cs-137	3.74+/-26e3				
K-40	7.69+/-2.0e5		**1.9+/-0.19e5**		
Pb-212	1.06+/-0.005e7	2.32+/-0.05e4	6.73+/-0.15e4	6.15+/-0.07e4	8.24+/- 0.14e4
Pb-212			**1.1+/-0.11e5**		
Pr-234m			1.89+/-1.1e5		
Ra-224					
Ra-228			**1.9+/- 0.21e6**		
Th-234	1.02+/-0.17e6	1.81+/-1.7e3			
Th-232	4.02+/-0.52e7		1.75+/-0.2e6		
Th-228		2.08+/- 0.77e4	**1.9+/- 0.4e5**	7.94+/-0.88e4	9.43+/-2.2e4
Tl-201					
Tl-208	3.39+/-0.046e6	7.7+/- 0.39e3	2.04+/-0.15e4	2.72+/-0.057e4	3.68+/-0.12e4
Tl-208			**2.9+/-0.37e4**		
U-235	6.93+/-19e3				
I-129					
Total Radium alpha			4.0+/-0.16e5		
Th-230			**3.0+/-2.5e3**		

		solid wet filter cake J-108-L1	liquid final waste water J-123-L1	solid Product J-125-L1	liquid wet scrubber sol. J-135-L1

Recodyne results are shown in bold

TCLP extract (mg/L)	UTS (mg/L)					
Antimony (mg/L)	2.1					
Arsenic (mg/L)	5			<	**0.5**	
Barium (mg/L)	7.6			<	**0.1**	
Beryllium (mg/L)	0.014					
Cadmium (mg/L)	0.19			<	**0.03**	
Chromium (mg/L)	0.86			<	**0.1**	
Lead (mg/L)	0.37			<	**0.3**	
Mercury (mg/L)	0.2			<	**0.002**	
Nickel (mg/L)	5					
Selenium (mg/L)	0.16			<	**0.5**	
Silver (mg/L)	0.3			<	**0.05**	
Thallium (mg/L)	0.078					
Vanadium (mg/L)	0.23					
Zinc (mg/L)	5.3					

Recodyne results are shown in bold

Investigation of Four DLA Pilot Plant Samples

Investigation of Four DLA Pilot Plant Samples

1.0 Introduction

Two samples from each of the two pilot plant runs were characterized by both x-ray diffraction (XRD) and scanning electron microscopy (SEM). Perma-Fix used a NaOH solution to precipitate $Th(OH)_4$ which was converted to ThO_2, while Recodyne used an oxalic acid solution to precipitate $Th(C_2O_4)_2 \cdot 6H_2O$ which was converted to ThO_2. The two samples from Perma-Fix include BT4-007e and 7A1-5. The BT4-007e sample is from their fourth batch run and is the final product. Sample 7A1-5 is from bench-scale testing and was heated to 1000°F after processing through the equivalent of the pilot plant method. The two Recodyne samples, also final products, are from their fifth run (E-125-L1) and tenth run (J-125-L1) of their pilot plant work.

2.0 Procedures

The samples were prepared for XRD and SEM analyses. Since the samples were radioactive, sample preparation and analysis were carried out under appropriate radiological procedures. Sample preparation for the XRD portion of the analysis was done by coating a tape (Scotch #800) stretched over an open hole aluminum holder with a very thin layer of the sample. The tape and holder were then analyzed by stepping from 5 to 90 degrees two theta at 0.025 degree steps for 10 seconds per step.

XRD data was used to calculate crystallite sizes of the samples. Crystallite size calculations were performed using the Scherrer formula

$$D = \frac{K\lambda}{B\cos\Theta}$$

where D is the crystallite size in nanometers, K is a constant (0.9), λ is the wavelength of the copper radiation (0.15418 nanometers), B is the peak width at one-half the maximum above background in radians, and Θ is the diffracting angle. Crystallite size is a means of determining the crystallinity of the sample, whereas particle size refers to agglomerates of crystallites. Therefore, particles typically are considerably larger than crystallites. The crystallite size is used here to indicate how complete the conversion to ThO_2 was. The larger the size of crystallite, the better the conversion.

Sample preparation for the SEM portion of the analysis followed two methods. The first method consisted of placing as-received sample on double-stick carbon tape. This method of preparation was chosen to look at the samples in an as-received form. The second method consisted of suspending a portion of the bulk sample in acetone and after insuring that the sample was suspended, a portion of the

suspension was pipetted onto a collodion-coated carbon plachette substrate. The resulting SEM mount separates the loosely bound particles of the sample so image analysis can be done on this sample preparation. Carbon or gold coating of the samples was not done.

3.0 Results

XRD

Results of the XRD work are shown as individual x-ray diffractograms in Appendix A. A summary of the diffractograms is shown in Figure 1. The x-ray diffractograms show there is no thorium nitrate hydrate (starting material) above detectable limits left in any of the samples. The detectable limit for the starting material is considered to be less than one weight percent. The two samples from Perma-Fix (BT4-007e and 7A1-5) and the two samples from Recodyne (E-125-L1 and J-125-L1) have different characteristics.

The sample from Perma-Fix from the pilot plant production line (A) shows no crystalline material except ThO_2. This ThO_2 has a calculated crystallite diameter of 3.0 nanometers (based on the Scherrer equation). The other sample from Perma-Fix is from bench-scale testing (B) and shows an additional crystalline phase besides the dominant ThO_2. This second phase is $NaNO_3$, probably from sodium and nitrate left in the filter cake. This ThO_2 has a calculated crystallite diameter of 5.5 nanometers. The results of the calculated crystallite size are tabulated in Table 1.

Plots of the XRD data from Recodyne samples batch E (Figure 1, plot C) and batch J (Figure 1, plot D) are shown in Figure 1. The batch J sample consists of only ThO_2 with a calculated crystallite size of 15. nanometers. The sample from batch E shows two phases; ThO_2 and a minor amount of thorium oxalate hydrate ($ThC_4O_8 \bullet 2H_2O$). The calculated crystallite size of the ThO_2 phase is 7.2 nanometers. The results of the calculated crystallite size are tabulated in Table 1.

Table 1. Calculated Crystallite size of the Four Samples

Sample	Perma-Fix BT4-007e	Perma-Fix 7A1-5	Recodyne E-125-L1	Recodyne J-125-L1
Crystallite Size	3.0 nm	5.5 nm	7.2 nm	15. nm

SEM

SEM photographs and EDS analysis of a few grains of the four samples was performed as well as image analysis of the size of ThO_2 particles of one sample from each of the two pilot plant runs.

Photographs of the Perma-Fix samples are shown in Figures 2 and 4. EDS spectra from some of these areas are shown in Figures 3 and 5. The dominant form of ThO_2 in sample BT4-007e (Figure 2) is of small round grains in groups. These groups can be large (photograph 1729 of Figure 2A) or can be made up of smaller groups as in the other photograph of Figure 2. These photographs illustrate the range of particulates present in the as-received sample, from around 5 micrometers long to grains less than 0.1 micrometer in the long dimension. The EDS spectra of Figure 3 illustrate the thorium-rich nature of the sample.

The dominant form of ThO_2 in sample 7A1-5 (Figure 4) is of small agglomerated round grains (as shown in many grains), photographs 1738 (Figure 4A) and 1747 (Figure 4D). Another morphology is shown in photograph 1744, Figure 4C. This morphology consists of extremely fine grains bound together and looking like dried mud. Photograph 1747 (Figure 4D) shows that the bulk of the sample consists of grains of about 1 micrometer in diameter and grouped together. Photograph 1739 (Figure 4B) shows a grain of $NaNO_3$ exhibiting a lattice-like morphology. These grains of $NaNO_3$ are scattered throughout the sample. The EDS spectra of this $NaNO_3$ and the surrounding grains is shown in the second spectra of Figure 5. The area EDS spectra (Figure 5A) of photograph 1738 (Figure 4A) also contains sodium and oxygen as well as thorium (spectra of Figure 5A). The mud-like area of grains in photograph 1744 (Figure 4C) has a ThO_2 EDS spectra (Figure 5C) with a small amount of Na present (presence of $NaNO_3$).

Photographs of the Recodyne samples are shown in Figures 6 and 8. EDS spectra from some of these areas are shown in Figures 7 and 9. The dominant form of ThO_2 in sample E-125-L1 is small, square tablets with an indented center (Figure 6). $ThC_4O_8 \cdot 2H_2O$ grains were not easily observed in the sample since the EDS spectra for them is almost identical to that of ThO_2. One grain, however, was found as a candidate (Figure 6C). It has a different morphology than the bulk of the sample. The EDS spectra shown in Figure 7 illustrates the average chemistry of the grains in this sample. The dominant element, as with the other samples, is thorium.

The dominant form of ThO_2 in sample J-125-L1 is small, square tablets with less indented center (Figure 8) than in E-125-L1. The bulk of the sample is ThO_2, however, there are a few scattered grains, as shown in Figure 8D, of Ca Cl composition (Figure 9B) material and also some grains of Ca composition,

which was unexpected. This sample was chosen to be used for image analysis to better understand the size of the resulting grains..

The results of the image size analysis from the two samples is summarized in Table 2 and Figures 10 and 11. Figures 10 and 11 use the effective diameter as the basis of the plots. The effective diameter dimension is a calculated diameter based on the area of the particle observed in two dimensions. This essentially assume the particle approximates a disk in outline. Since the Perma-Fix sample particles do approximate a sphere and the Recodyne sample particles, although less spherical, also approximate a sphere, the effective diameter was used as a comparison parameter. The effective diameter is good as an estimation of the ability for these particles to become entrained in the air and become an airborne hazard.

Table 2 Summary of Image Analysis Characterization

Sample	Number of Grains	Median Diameter	Spread Factor	Minimum Diameter	Maximum Diameter
BT4-007e	1009	1.31 μm	2.55	<0.32 μm	11.95 μm
J-125-L1	1080	2.15 μm	3.36	0.34 μm	34.35 μm

Figure 10 shows the distribution in 0.5 micrometer increments over the range 0 to 12 micrometers for both samples. Individual plots may be found in Appendix B. The category of over 12 micrometers contains only particles from Recodyne sample J-125-L1 (98-400). Figure 11 shows the calculated distribution of these two samples. A log-normal distribution is used for these two samples because of the distribution approximates it closer than it does a normal distribution. This can be seen in the plots of the effective diameter in Figure 10. The high number of small particles compared to the long tail toward the larger particles. When plotted on Log-probability charts (Appendix B) these samples can be compared. The Recodyne sample (J-125-L1) is larger in median size as well as having a larger proportion of the larger particles. The spread factor, a measure of the distribution, of the Recodyne sample is also larger than the Perma-Fix sample. From the median size and the spread factor a calculated size distribution can be displayed in a plot (Figure 11). Figure 11 illustrates the larger size spread of the Recodyne sample as well as the high proportion of very small particles present in the Perma-Fix sample.

4.0 Discussion

An assessment of the XRD data for the two Perma-Fix samples indicates that conversion to a well crystallized ThO_2 powder was not achieved for sample BT4-007e and that the sample probably contains

some adhered water on the ThO_2 crystallites. Sample 7A1-5 achieved a slightly higher degree of ThO_2 powder crystallization. However, this sample also contains contaminants ($NaNO_3$) as well as some adhered water on the ThO_2 crystallites.

The XRD data for the two Recodyne samples indicates that sample E-125-L1 achieved a slightly higher degree of ThO_2 powder crystallization than the two Perma-Fix samples. However, this sample also contains contaminants ($ThC_4O_8 \bullet 2H_2O$) as well as some adhered water on the ThO_2 crystallites. Sample J-125-L1 achieved a high degree of ThO_2 powder crystallization. This does not appear to contain adhered water on the ThO_2 crystallites based on the XRD pattern.

Between the four samples, J-125-L1 shows the highest degree of conversion to well crystallized ThO_2 and the cleanest, contaminant-free pattern of the samples.

The morphological difference of the two pilot plant runs can be easily seen in the SEM photographs of the two sample groups. The grains of ThO_2 from the Perma-Fix process were rounded while the grains from the Recodyne process were tabular.

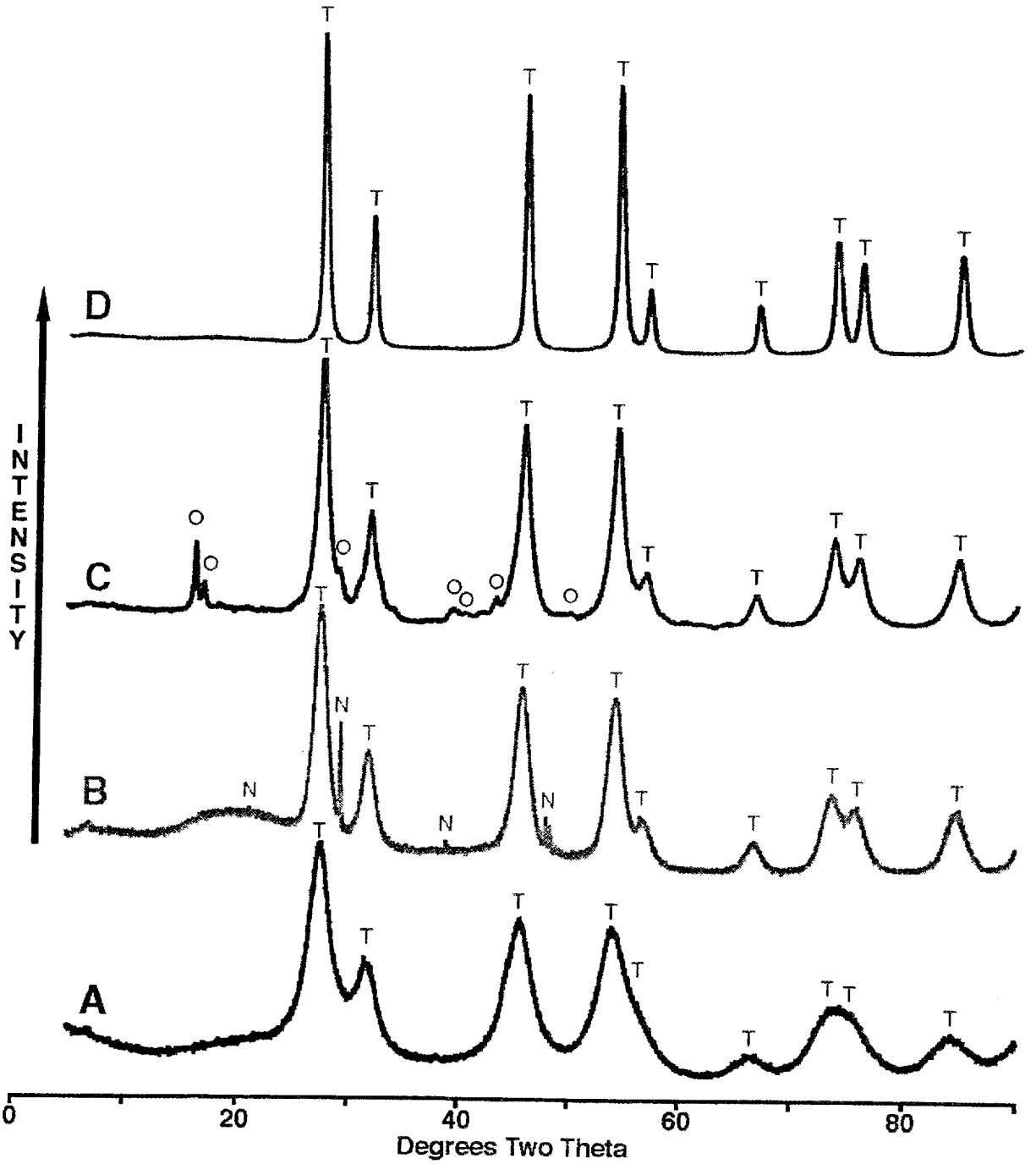
The image analysis of the two pilot plant runs also shows a difference. The sample from Perma-Fix does not contain any particles greater, in effective diameter, than 12 micrometers while the largest size from the Recodyne sample was almost 35 micrometers. The size distributions for both samples follow a log-normal distribution. The sample from Perma-Fix has a smaller median diameter (2.15 micrometers versus 1.31 micrometers) and a smaller spread factor (2.55 versus 3.36) than the sample from Recodyne. These size distribution differences may be due to the larger sized grains present in the Recodyne sample. Of note is the high proportion of very small (less than 2.5 micrometers) sized particles present in both samples.

5.0 Conclusions

The SEM, EDS and size data illustrate the differences between the two processes in the morphology and general size of the resulting products. The oxalate pilot plant product has a higher proportion of larger particles and is more crystalline. The product would seem to be less likely to be a dust problem during processing.

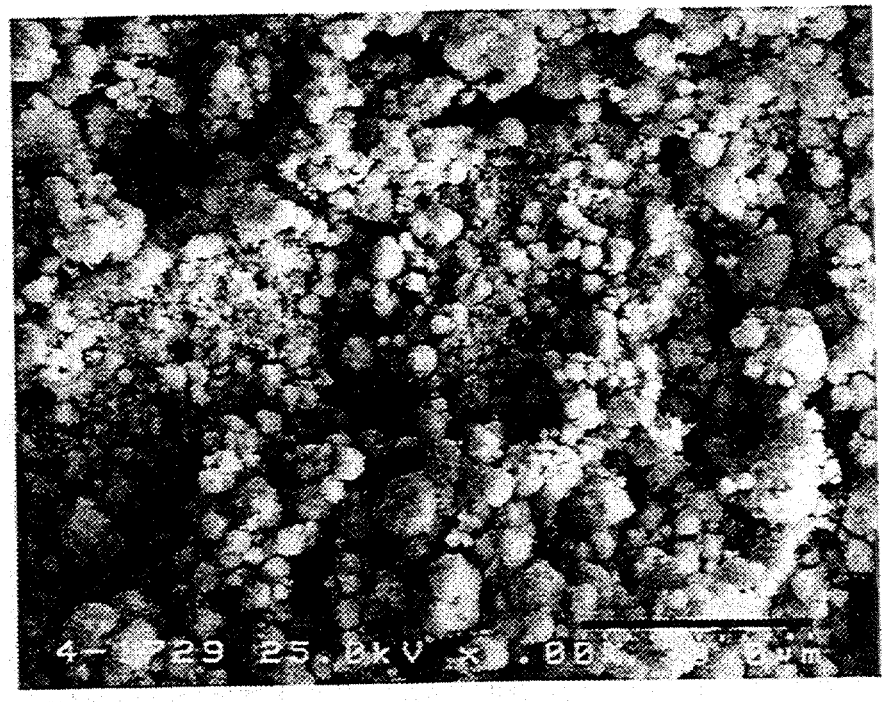
XRD would be very useful as part of production scale product start-up and monitoring. XRD is well suited for the characterization of the end product of the conversion process. XRD can not only indicate the material being produced, but also can identify crystalline contaminants above 1%.

Figure 1. Comparison of X-Ray Diffraction Scans of the Four Samples

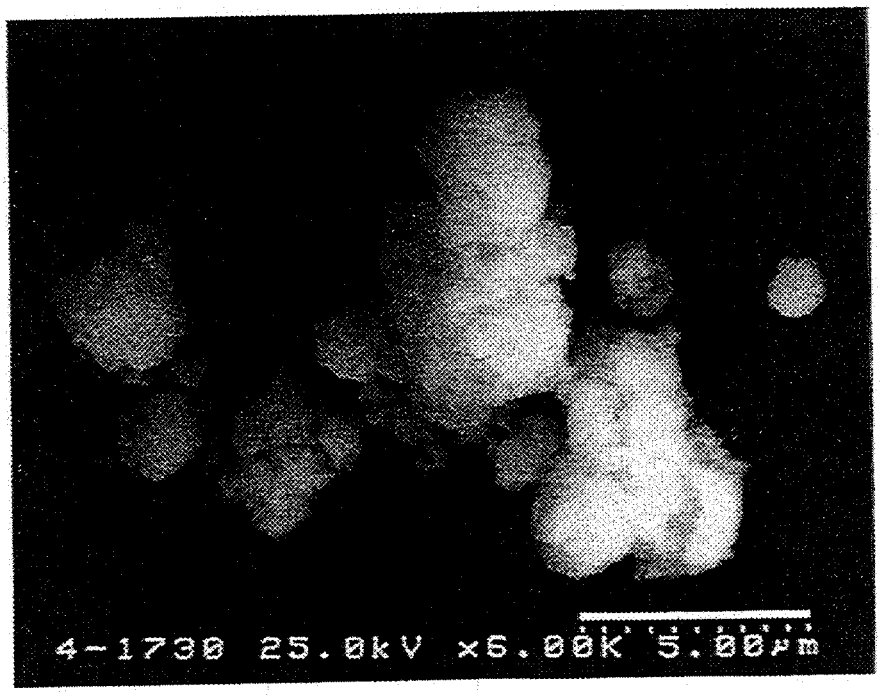


X-Ray diffractograms of four samples of converted thorium nitrate hydrate. The two samples from Perma-Fix are BT4-007e (A) and 7A1-5 (B). The two samples from Recodyne are E-125-L1 (C) and J-125-L1 (D). All samples contain ThO_2. Plot B also shows the presence of $NaNO_3$ and plot C shows the presence of $ThC_4O_8 \bullet 2H_2O$. The marked phases are ThO_2 (T), $NaNO_3$ (N) and $ThC_4O_8 \bullet 2H_2O$ (O).

Figure 2. SEM Photomicrographs of Perma-Fix Sample BT4-007e

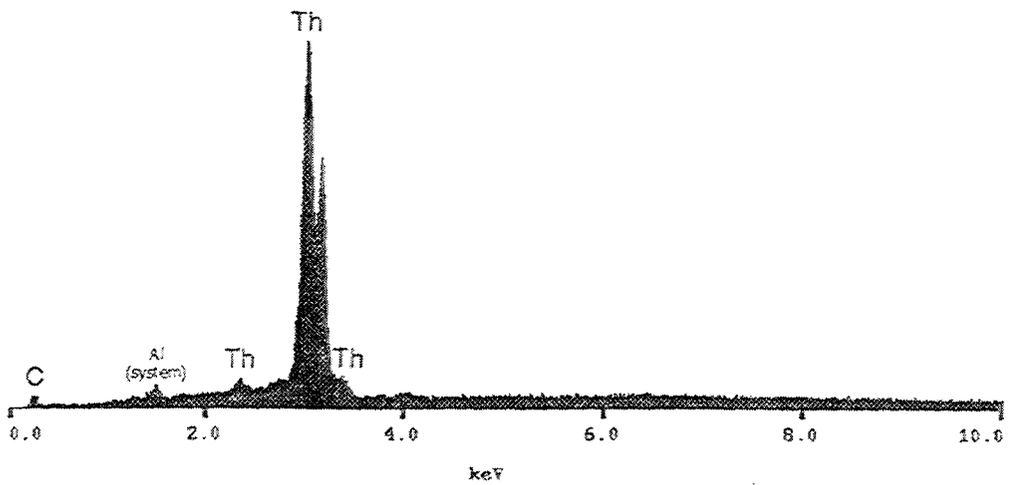


A. Secondary electron image of a representative area of the sample. Figure 3A is the EDS spectra from this area. Bar is 30 micrometers long.

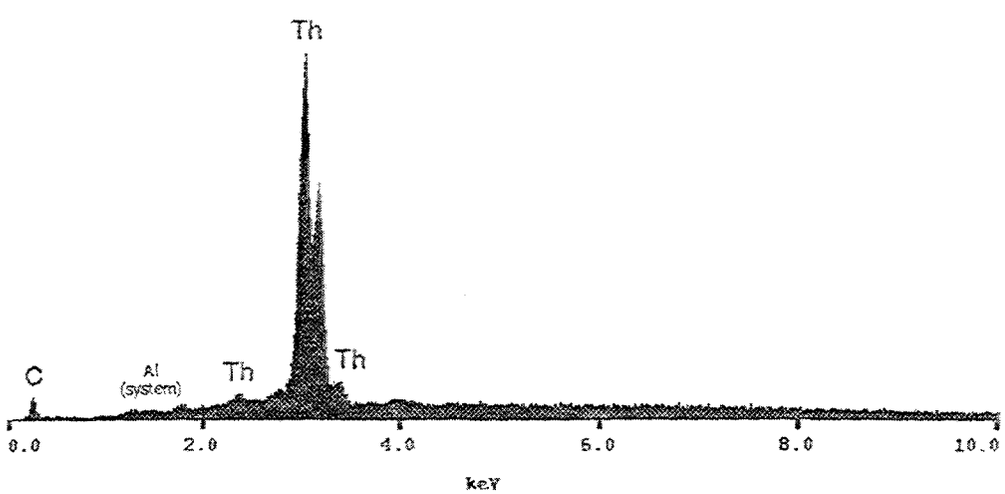


B. Secondary electron image of a representative area of the sample. . Figure 3B is the EDS spectra from this area. Bar is 5 micrometers long.

Figure 3. EDS Spectra of Perma-Fix Sample BT4-007e

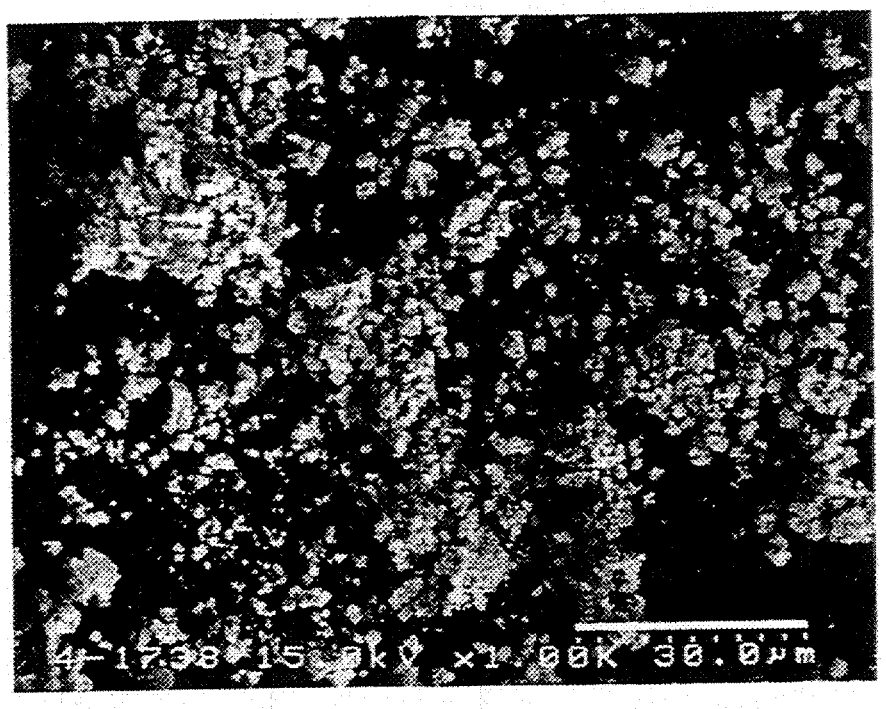


A. Spectra of area shown in photograph 1729, Figure 2A. Note the dominance of the Th peaks. The C peak is from the mounting tape

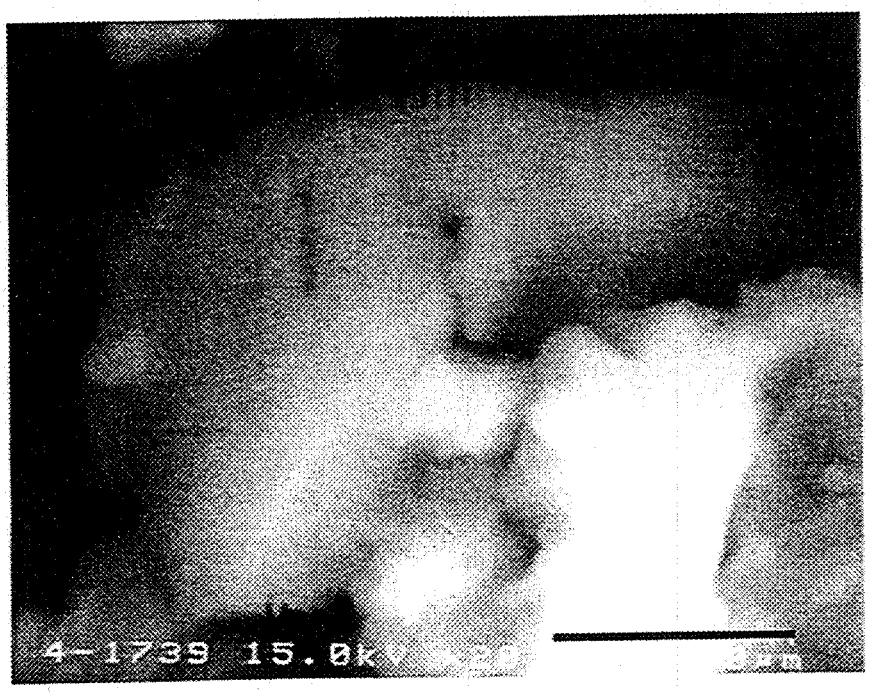


B. Spectra of area shown in photograph 1730, Figure 2B. Note the dominance of the Th peaks. The C peak is from the mounting tape

Figure 4. SEM Photomicrographs of Perma-Fix Sample 7A1-5

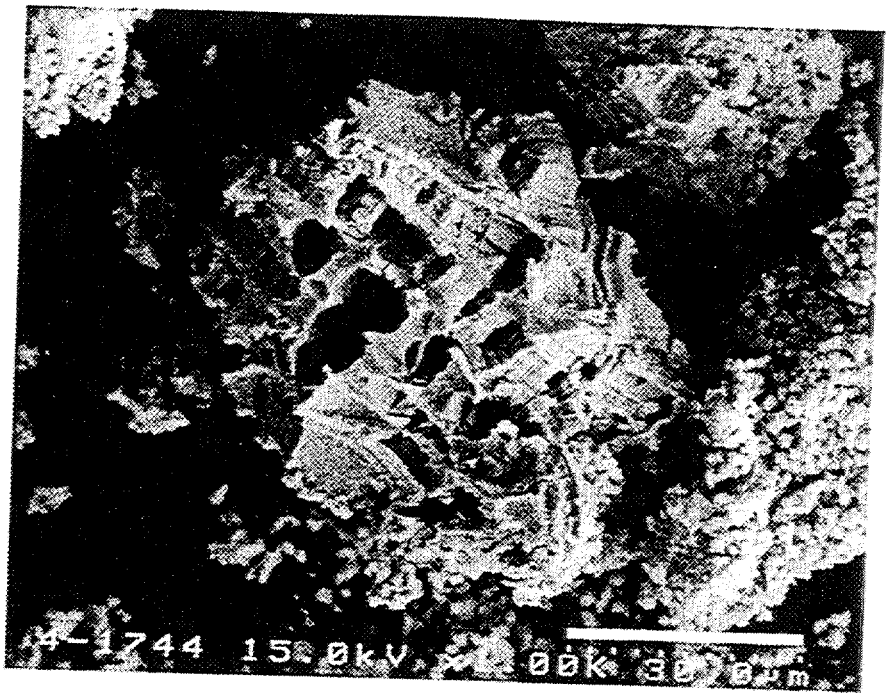


A. Secondary electron image of a representative area of the sample. Figure 5A is the EDS spectra from this area. Bar is 30 micrometers long.

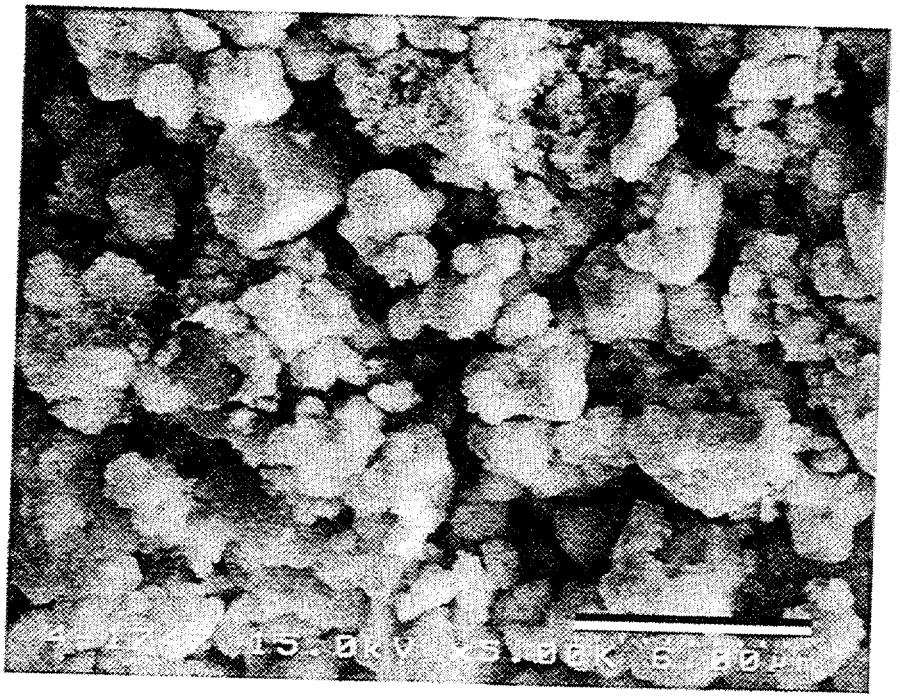


B. Secondary electron image an area of sodium, nitrogen, and oxygen. Figure 5B is the EDS spectra from this area. Note the lattice-like morphology of the $NaNO_3$. Bar is 1.5 micrometers long.

Figure 4 (continued). SEM Photomicrographs of Perma-Fix Sample 7A1-5

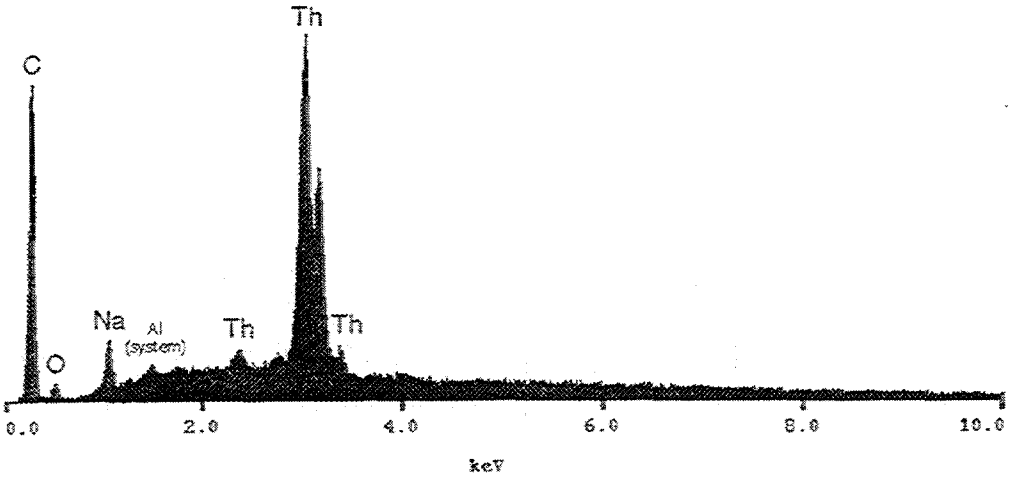


C. Secondary electron image of a representative area of the sample. Figure 5C is the EDS spectra from this area central mud-like material. Bar is 30 micrometers long.

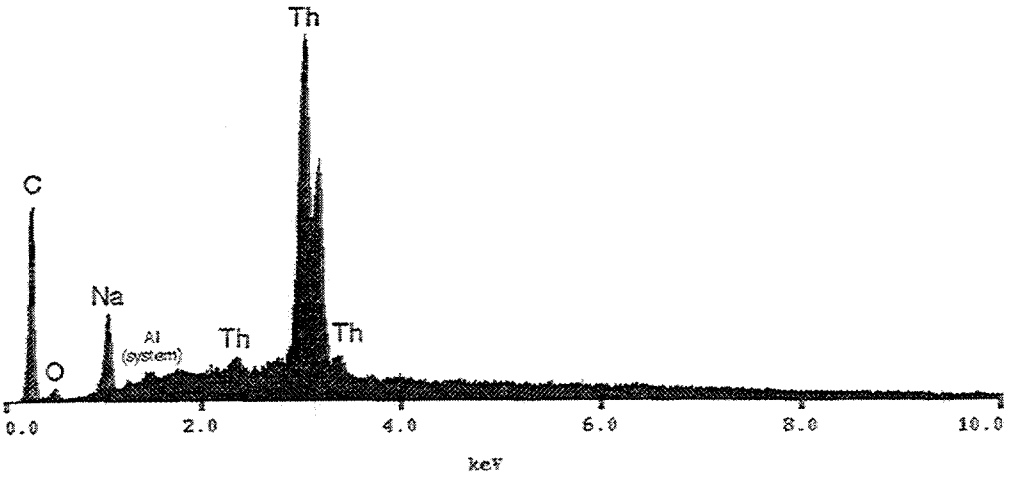


D. Secondary electron image of a representative area of the sample. Bar is 6 micrometers long.

Figure 5. EDS Spectra of Perma-Fix Sample 7A1-5

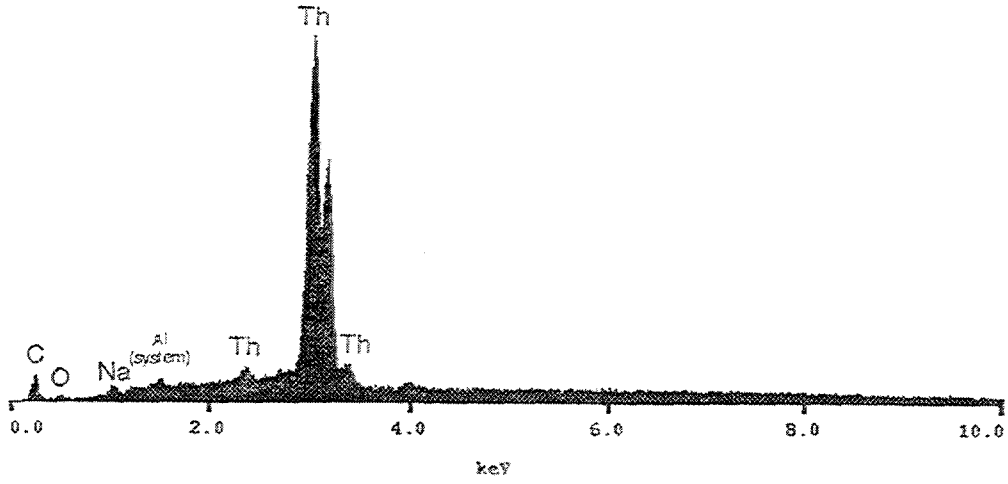


A. Spectra of area shown in photograph 1738, Figure 4A. Note the dominance of the Th peaks and the presence of Na and O peaks. The C peak is from the mounting tape.



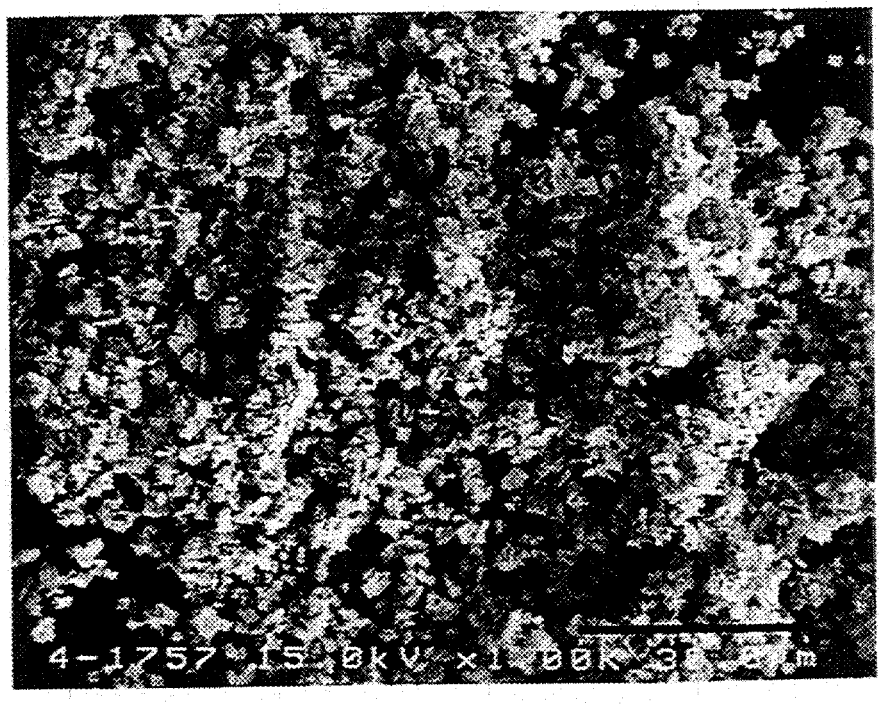
B. Spectra of area shown in photograph 1739, Figure 4B. Note the dominance of the Th peaks and the presence of Na and O peaks. The C peak is from the mounting tape.

Figure 5 (continued). EDS Spectra of Perma-Fix Sample 7A1-5

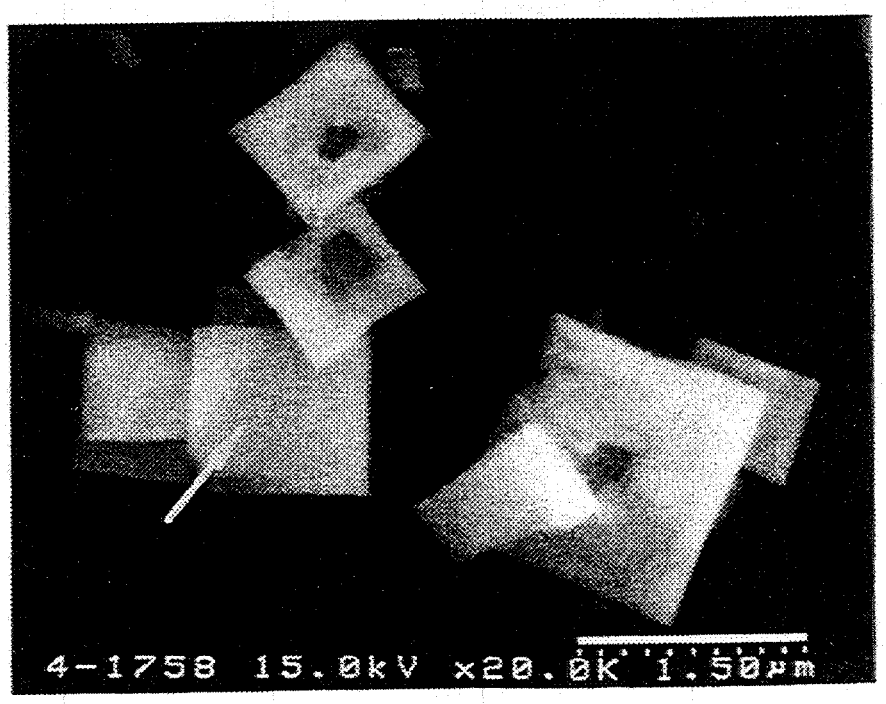


C. Spectra of central area shown in photograph 1744, Figure 4C. Note that this morphology is of extremely fine particles of ThO_2. The C peak is from the mounting tape

Figure 6. SEM Photomicrographs of Recodyne Sample E-125-L1



A. Secondary electron image of a representative area of the sample. Figure 7A is the EDS spectra from this area. The bar is 30 micrometers long.



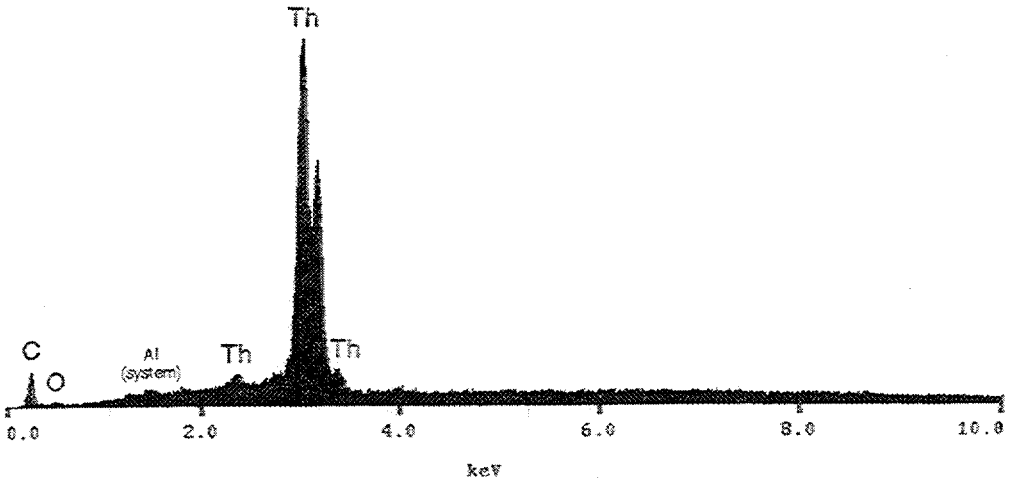
B. Secondary electron image of a representative area of the sample. Figure 7B is the EDS spectra from the grain shown by the arrow. The bar is 1.5 micrometers long.

Figure 6 (continued). SEM Photomicrographs of Recodyne Sample E-125-L1

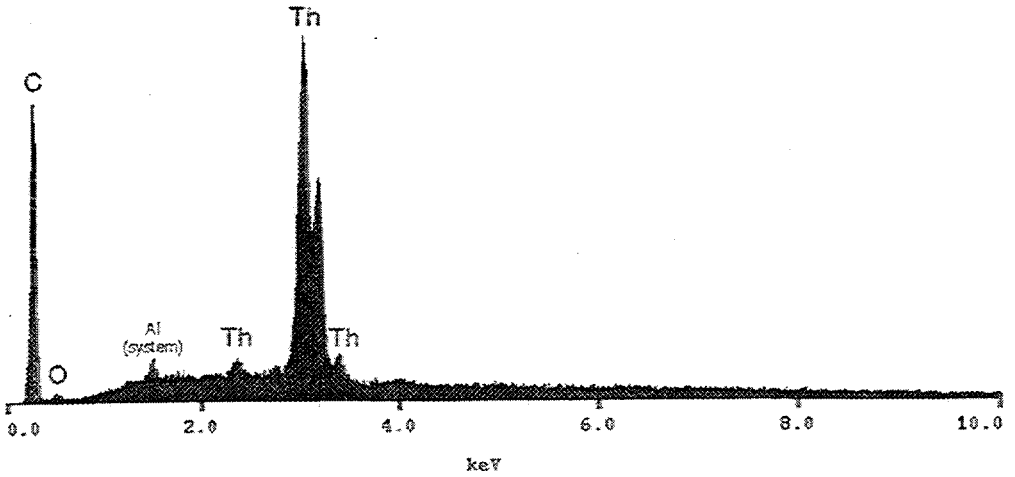
C. Secondary electron image of a representative area of the sample. The bar is 6 micrometers long.

D. Secondary electron image of a representative area of the sample. The arrow indicates a grain that is thought to be thorium oxalate hydrate, based on its morphology. The EDS spectra (Figure 7C) is not conclusive evidence. The bar is 3 micrometers long.

Figure 7. EDS Spectra of Recodyne Sample E-125-L1

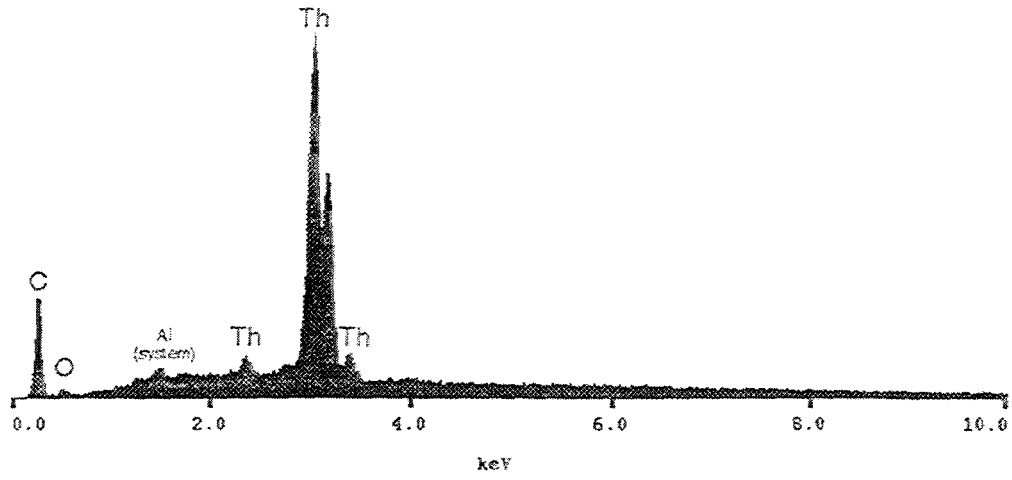


A. Spectra of area shown in photograph 1757, Figure 6A. Note the dominance of the Th peaks. The C peak is from the mounting tape.



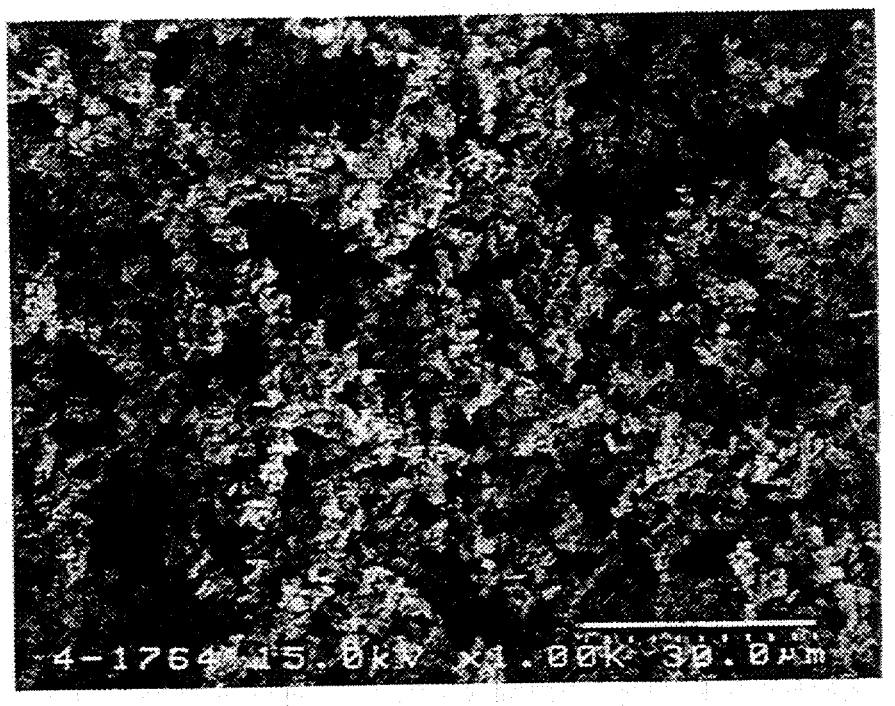
B. Spectra of grain indicated by arrow in photograph 1758, Figure 6B. Note the dominance of the Th peaks. The C peak is from the mounting tape.

Figure 7 (continued). EDS Spectra of Recodyne Sample E-125-L1

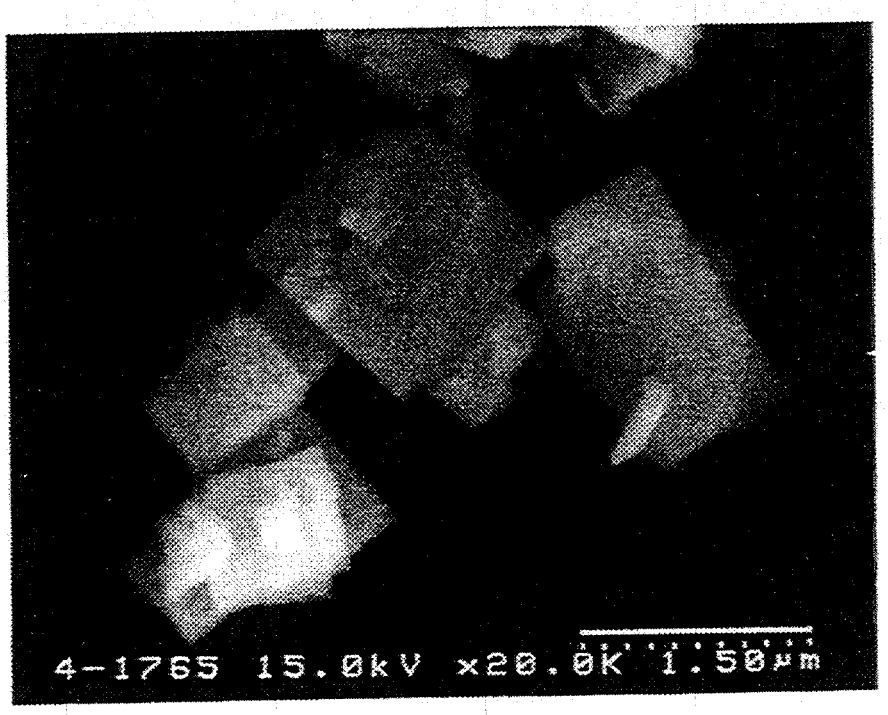


C. Spectra of grain indicated by arrow in photograph 1762, Figure 6D. Note the dominance of the Th peaks. This spectra is probably of the thorium oxalate hydrate, based on morphology. Morphology and especially XRD are the defining criteria for identification of thorium oxalate hydrate. The C peak is from the mounting tape.

Figure 8. SEM Photomicrographs of Recodyne Sample J-125-L1



A. Secondary electron image of a representative area of the sample. Figure 9A is the EDS spectra from this area. Bar is 30 micrometers long.



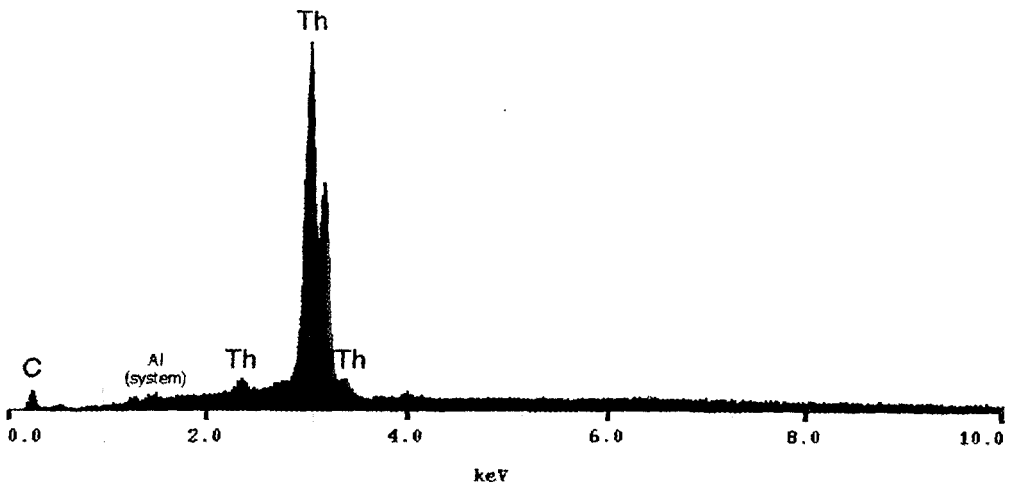
B. Secondary electron image of a representative area of the sample. Bar is 1.5 micrometers long.

Figure 8 (continued). SEM Photomicrographs of Recodyne Sample J-125-L1

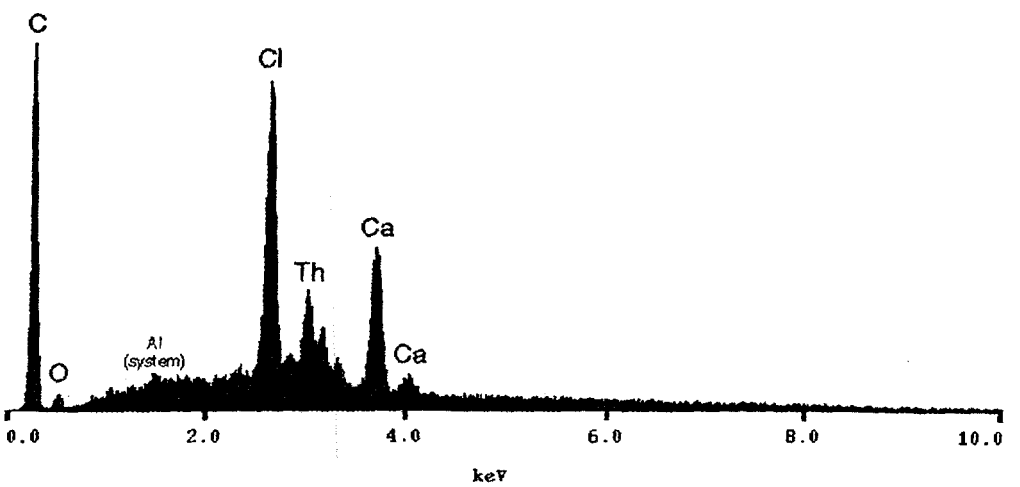
C. Secondary electron image of a representative area of the sample. Bar is 1.5 micrometers long.

D. Secondary electron image of a representative area of the sample. Arrow indicates a grain of Ca and Cl (EDS spectra shown in Figure 9B). Bar is 6 micrometers long.

Figure 9. EDS Spectra of Recodyne Sample J-125-L1

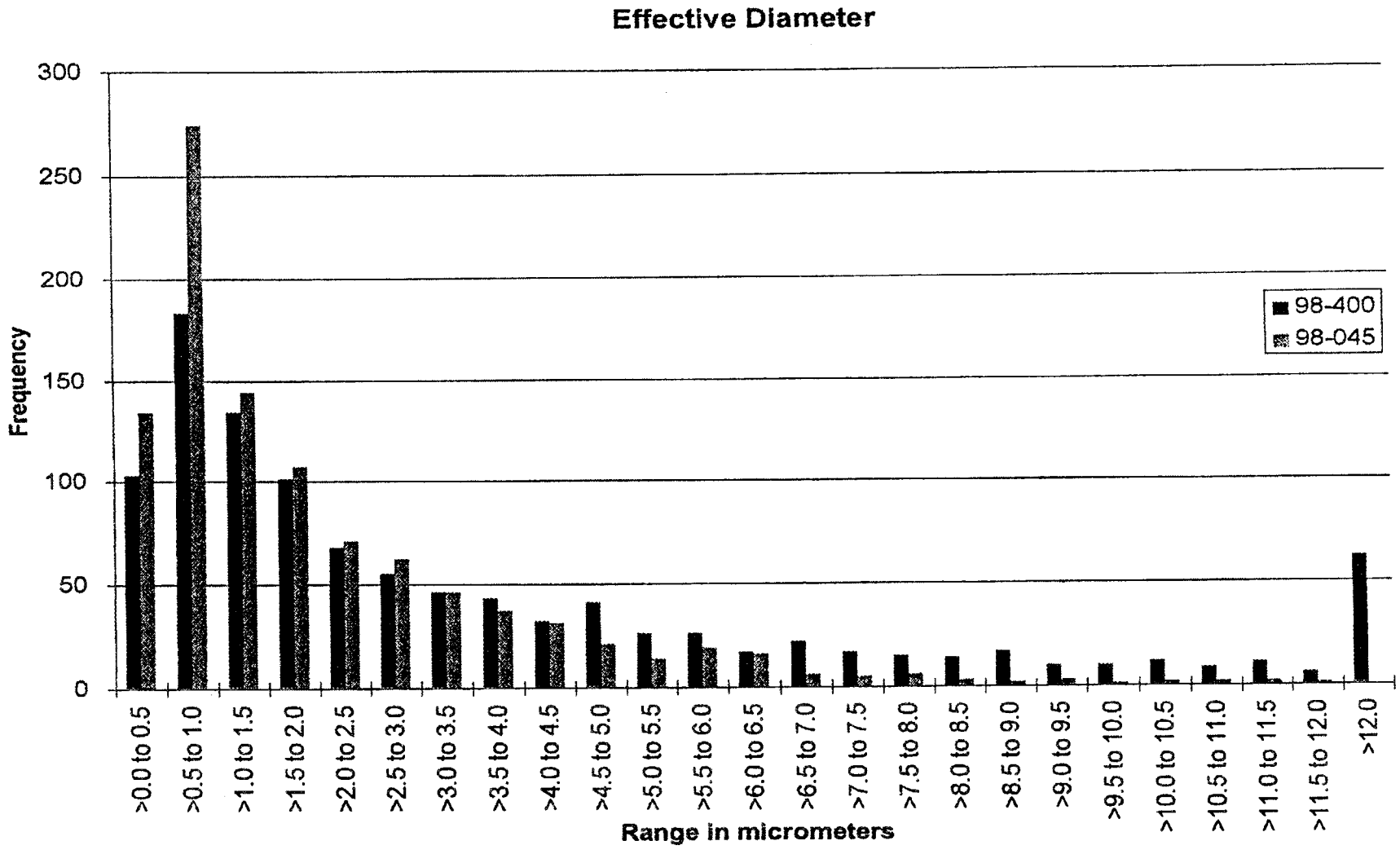


A. Spectra of area shown in photograph 1764, Figure 8A. Note the dominance of the Th peaks. The C peak is from the mounting tape.



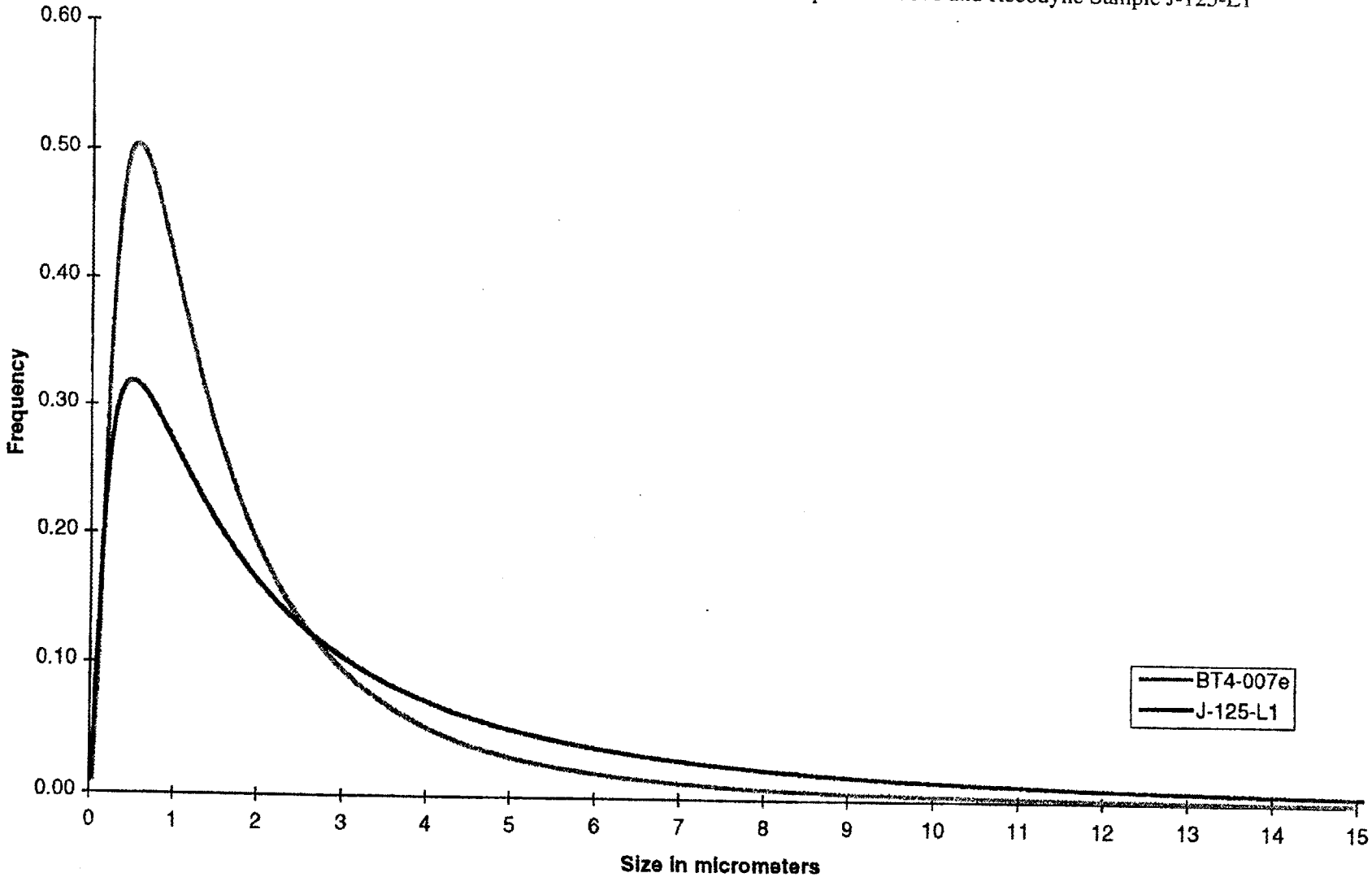
B. Spectra of grain indicated by arrow in photograph 1769, Figure 8D. Note the presence of both Ca and Cl. This material is a very minor phase in the sample. The C peak is from the mounting tape.

Figure 10. SEM Size Analysis of Perma-Fix Sample BT4-007e and Recodyne Sample J-125-L1



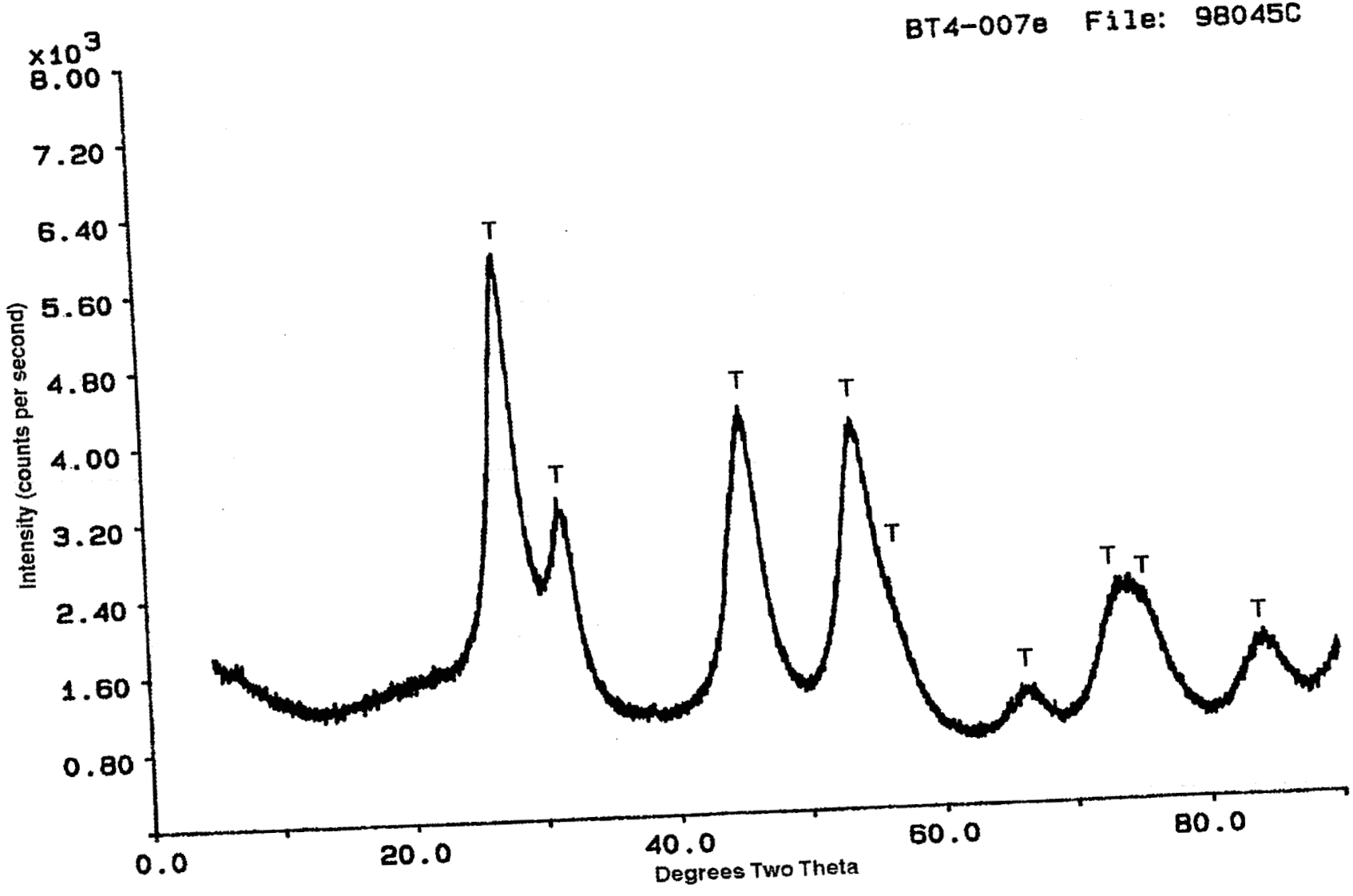
Full range of the number of particles plotted as a function of their effective diameter grouped in ranges of 0.5 micrometers. Perma-Fix Sample BT4-007e is 98-045 and Recodyne Sample J-125-L1 is 98-400.

Figure 11. Calculated Log-normal Size Distribution of Perma-Fix Sample BT4-007e and Recodyne Sample J-125-L1



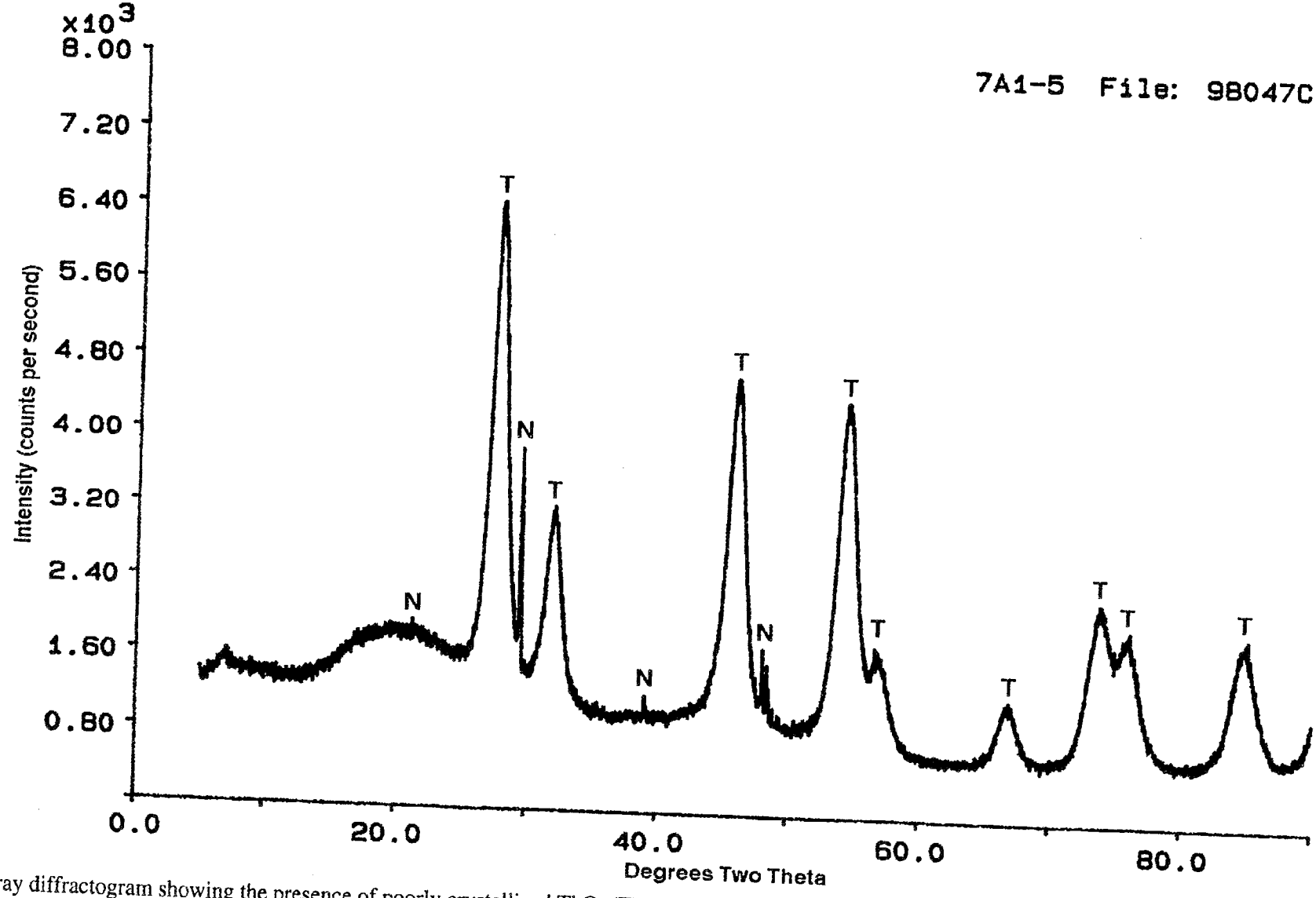
Size distribution as calculated from a log-normal distribution model of the two samples.

X-Ray Diffractogram of Perma-Fix Sample BT4-007e



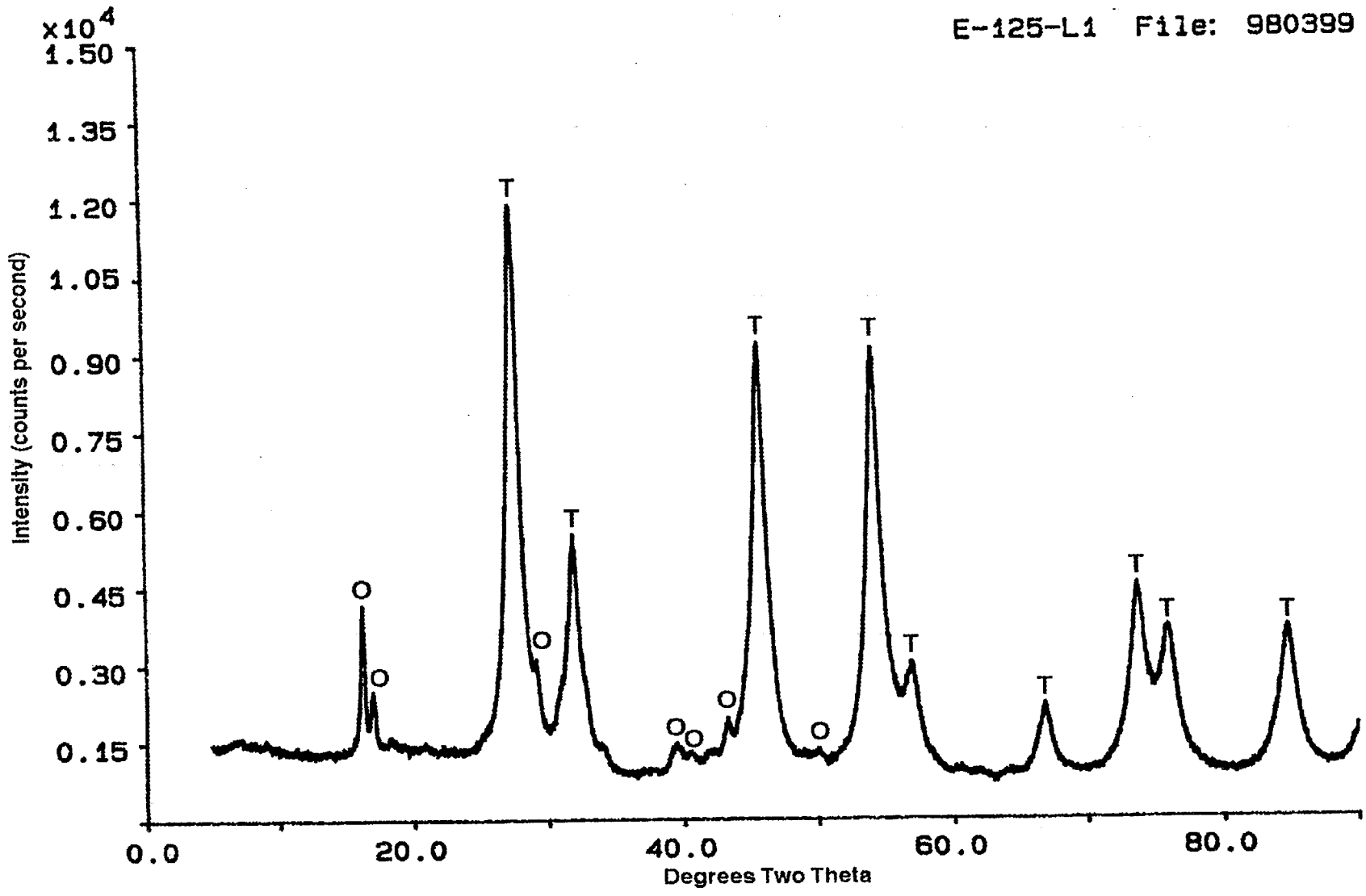
X-ray diffractogram showing the presence of poorly crystallized ThO_2 (T).

X-Ray Diffractogram of Perma-Fix Sample 7A1-5



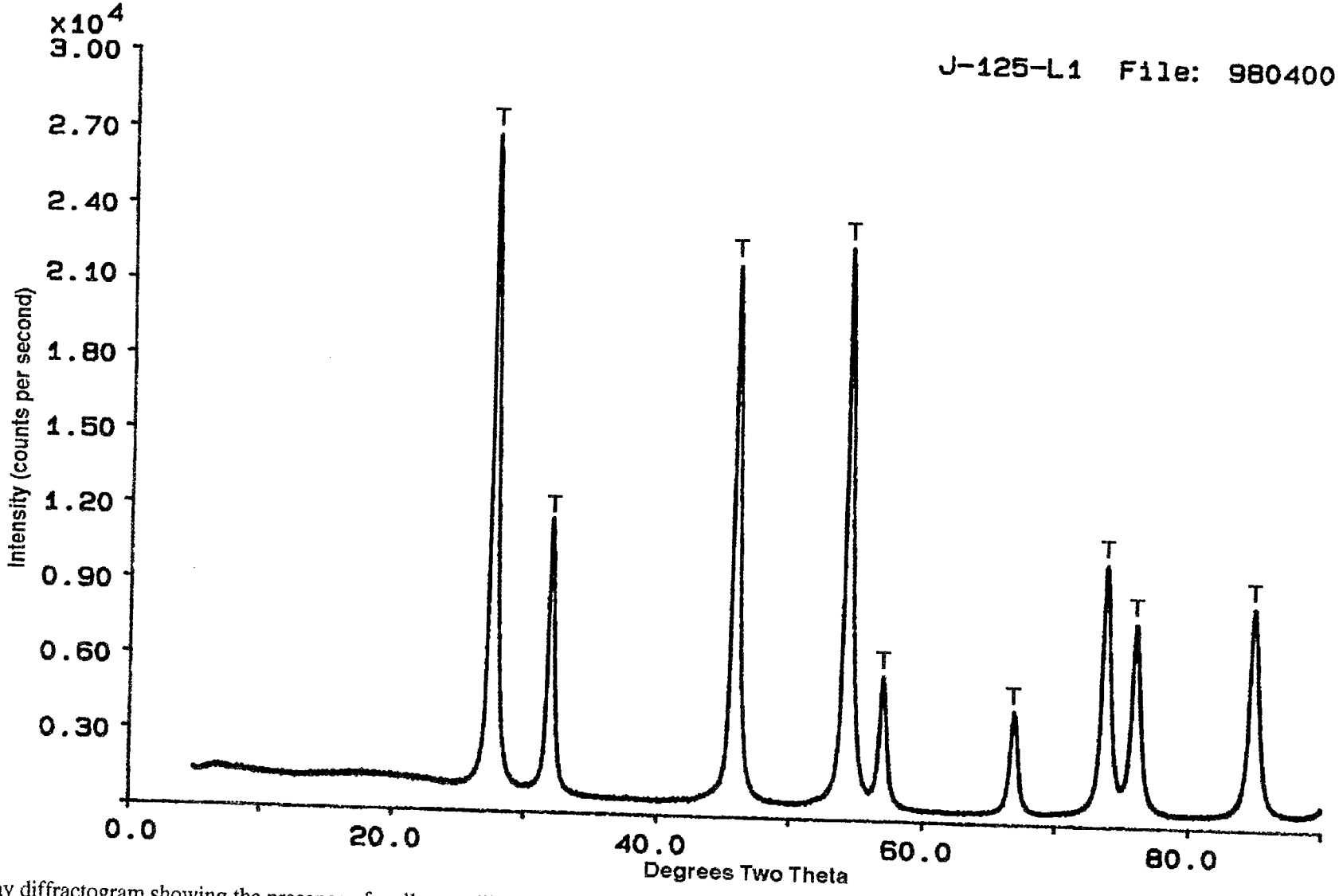
X-ray diffractogram showing the presence of poorly crystallized ThO_2 (T) and well crystallized $NaNO_3$ (N).

X-Ray Diffractogram of Recodyne Sample E-125-L1



X-ray diffractogram showing the presence of ThO_2 (T) and well crystallized $ThC_4O_8 \bullet 2H_2O$ (O).

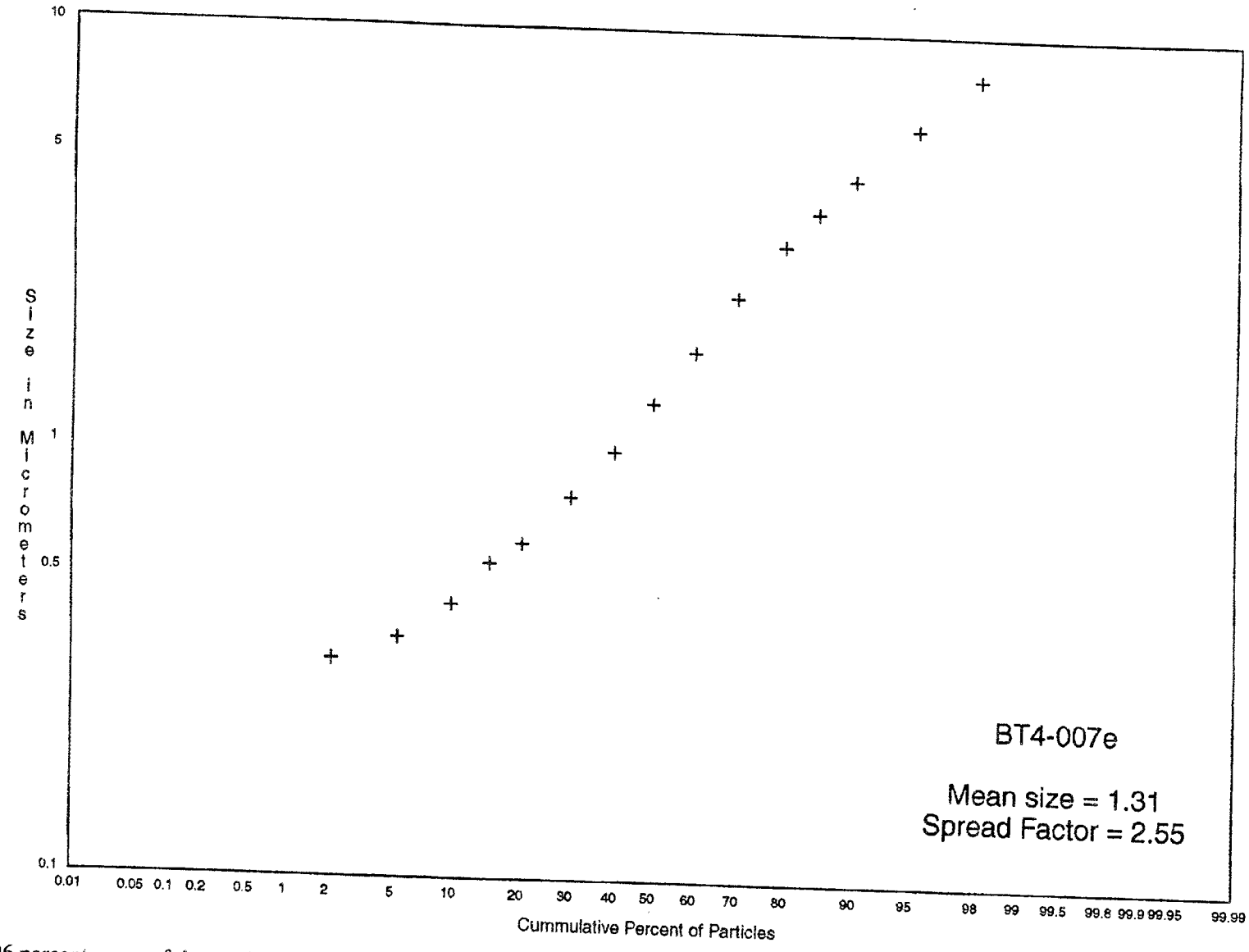
X-Ray Diffractogram of Recodyne Sample J-125-L1



X-ray diffractogram showing the presence of well crystallized ThO_2 (T).

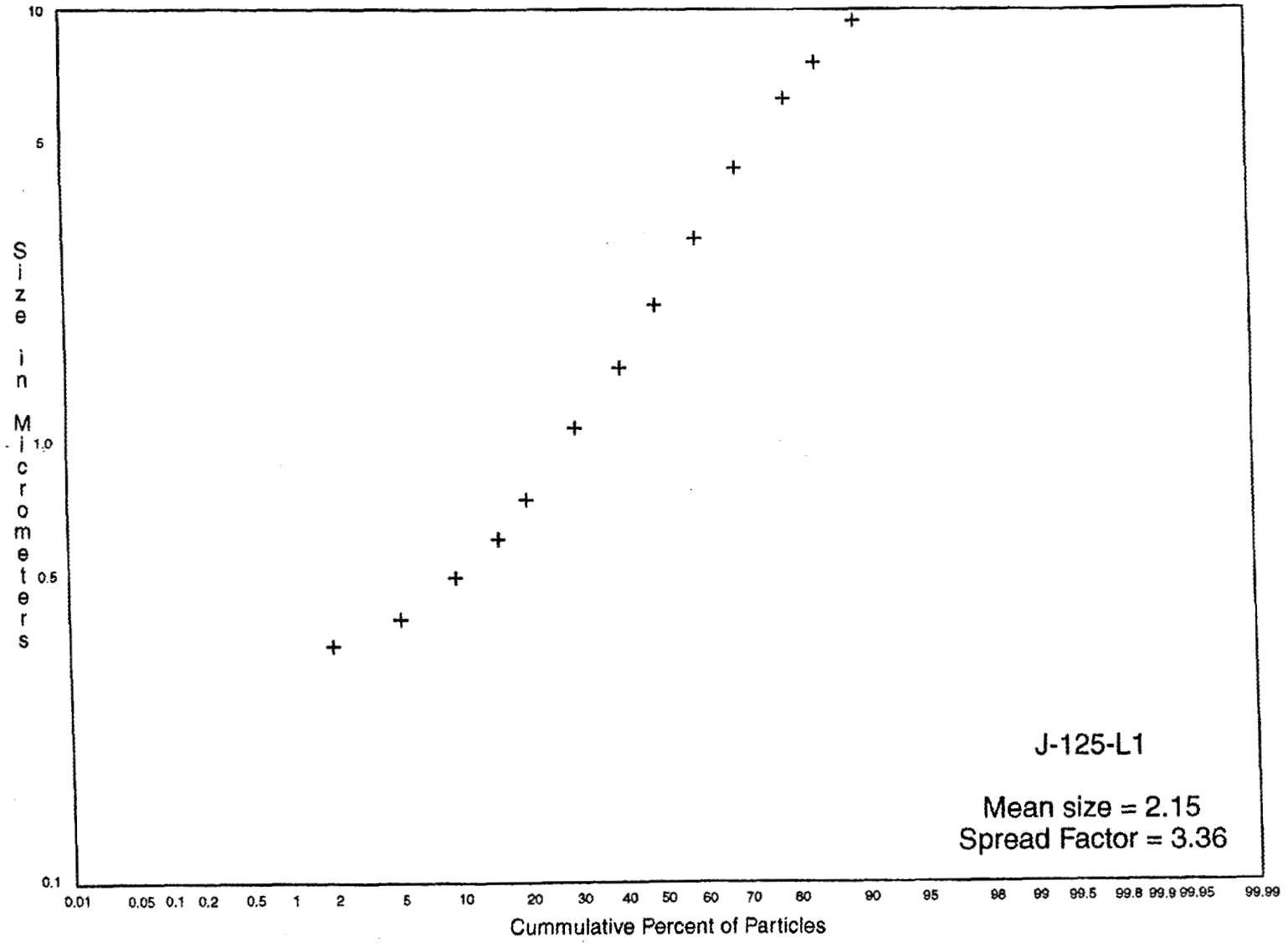
Appendix B

SEM Size Analysis of Perma-Fix Sample BT4-007e



Middle 96 percent range of the particles plotted as cummulative percentage, on a probability scale, versus their effective diameter, on a log scale.

SEM Size Analysis of Perma-Fix Sample BT4-007e



Middle 88 percent range of the particles plotted as cummulative percentage, on a probability scale, versus their effective diameter, on a log scale.

Attachment 5

Analytical and Regulatory Assessment of Metal Concentrations in Thorium Nitrate

LOCKHEED MARTIN

ANALYTICAL AND REGULATORY ASSESSMENT OF METAL CONCENTRATIONS IN THORIUM NITRATE

Date Issued—February 13, 1998

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Analytical and Regulatory Assessment of Metal Concentrations in Thorium Nitrate

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ACRONYMS AND INITIALISMS

AAS	atomic absorption spectroscopy
AEA	Atomic Energy Act
AEC	Atomic Energy Commission
ASO	Analytical Services Organization
CFR	Code of Federal Regulation
CVAAS	Cold vapor atomic absorption spectroscopy
CWA	Clean Air Act
DLA	Defense Logistics Agency
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EC	Environmental Compliance
Energy Systems	Lockheed Martin Energy Systems, Inc.
EPA	U.S. Environmental Protection Agency
GFAAS	graphite furnace atomic absorption spectroscopy
ICP–AES	inductively coupled plasma–atomic emission spectroscopy
ICP–MS	inductively coupled plasma–mass spectroscopy
LDR	Land Disposal Restrictions
NRC	Nuclear Regulatory Agency
RCRA	Resource Conservation and Recovery Act
TC	toxicity characteristic
TCLP	Toxicity Characteristic Leaching Procedure
ThN	thorium nitrate
ThO	thorium oxide
TOC	total organic carbon
TSDF	treatment, storage, or disposal facility

EXECUTIVE SUMMARY

The Defense Logistics Agency (DLA) is evaluating processes that will convert thorium nitrate (ThN) to thorium oxide (ThO). The purpose of the conversion is to improve the marketability of the ThN. This assessment has been prepared to (1) determine metal concentrations in the ThN and ThO; (2) examine the applicability of the Resource Conservation and Recovery Act (RCRA) to ThN, ThO, and the conversion process; and (3) provide the DLA with supporting information (e.g., regulatory citations, literature research, and analytical results) to assist its decision-making process regarding the current and/or future management of ThN and ThO.

Previous analytical data for the ThN indicated the presence of metals at unexpected levels; however, high detection limits were associated with the data. The analytical data was evaluated to determine the cause of the high detection limits. Alternative analytical methods were used to achieve lower detection limits. The results showed that metals are near or below the lower detection limits. This assessment provides information on analytical techniques used to accurately determine metal concentrations in the ThN and ThO. Additional quantitative analytical reference data and technique improvements will be reported in the pilot-scale demonstration reports.

RCRA is the federal law, promulgated in the *Code of Federal Regulation*, Title 40, Parts 260–266, 268, 270–272, 279, 280–282, and 148, which regulates the management of hazardous waste from generation to final disposal. This assessment presents several strategies for determining the regulatory status of the ThN, ThO, and the conversion process relative to RCRA. Generally, the conversion process is not expected to result in a RCRA hazardous waste; however, final determination must be made after a conversion process has been selected.

1. INTRODUCTION

The Defense Logistics Agency (DLA) currently is storing ~20,000 containers of thorium nitrate (ThN). This material has been declared excess and is now available for sale outside the government. DLA is evaluating processes that will convert ThN to thorium oxide (ThO) to improve the marketability of the material. This assessment has been prepared to (1) determine metal concentrations in the ThN and ThO; (2) examine the applicability of the Resource Conservation and Recovery Act (RCRA) to ThN, ThO, and the conversion process; and (3) provide the DLA with supporting information (e.g., regulatory citations, literature research, and analytical results) to assist its decision-making process regarding the current and/or future management of ThN and ThO.

Previous metals data indicated concentrations of some metals were higher than expected (silver @ 4500 mg/kg, lead @ 1050mg/kg, and arsenic @ 1000 mg/kg). The method detection limits for these results were also high, leading to suspicions that actual metal concentrations were much lower than measured. A review of the data by analytical personnel determined interference from the thorium nitrate resulted in the high detection limits. Oak Ridge personnel analyzed the ThN using standard and alternative methods in an effort to improve detection limits. In addition, ThN was converted to ThO (a likely product to be generated during a conversion process) to determine if there were significant changes in metal concentrations as a result of the conversion process.

The complete array of material that could be generated by a product conversion process has not been clearly determined. Therefore, RCRA regulations were reviewed to determine what, if any, impact RCRA could have on the product conversion process. This assessment focused on RCRA applicability; however, DLA should contact the Nuclear Regulatory Commission (NRC) and agreement states, if any, regarding licensing, radiation protection, and waste disposal requirements. Air emissions and/or water discharges from the conversion process(es) may be subject to federal, state, and local regulations. NRC regulations may exempt the thorium from RCRA requirements. NRC regulations are promulgated in the *Code of Federal Regulation* (CFR), Title 10, Chapter I (Parts 0–199).

This assessment is based on information currently available. Generally, the conversion process is not expected to result in a RCRA hazardous waste based on data available to date. Final determination should be made after a conversion process has been identified for product conversion.

2. ANALYSIS OF THORIUM MATERIAL

Solid thorium nitrate [$Th(NO_3)_4 4H_2O$], solid thorium oxide (ThO_2), and the leachate from toxicity characteristic leaching procedure (TCLP) testing of ThO_2 were analyzed by a variety of analytical methods. These methods are inductively coupled plasma–atomic emission spectroscopy (ICP–AES), inductively coupled plasma–mass spectroscopy (ICP–MS), atomic absorption spectroscopy (AAS), and a number of radiochemical techniques. These analytical techniques are available at the Lockheed Martin Energy Systems (Energy Systems) Analytical Services Organization (ASO). A brief description of the instrumentation used in these analyses is included below.

2.1 ANALYTICAL TECHNIQUES

ICP–AES is atomic emission spectroscopy using an inductively coupled plasma. The plasma is formed from argon gas flowing through a radiofrequency field where it is kept in a state of partial ionization. The gas reaches a very high temperature, 10,000°C, in the hottest part. At such high temperatures, most elements emit light at characteristic wavelengths that can be measured and used for determination of the concentrations of elements in a sample. The sample is introduced into the plasma as an aerosol of fine droplets. The light from the different elements is separated into its constituent wavelengths by means of a grating and is directed to light-sensitive detectors. The sensitivity of ICP–AES roughly equals that of flame atomic absorption spectrometry (i.e., detection limits typically are at the < microgram per liter level in aqueous solution).

ICP–MS uses a plasma of the same kind as that in ICP-AES, except that in ICP–MS it is used to convert the elements to ions that are subsequently separated in a mass spectrometer. In this way the different elements in a sample (and their isotopes) are separated and their concentrations can be determined. ICP–MS combines valuable properties of the ICP (simple and rapid sample introduction) and of mass spectrometry (high sensitivity, isotope capability) in one multi-element analytical technique. The detection limits for most elements are much lower than those in ICP–AES; for many elements they are at nanogram per liter levels in aqueous solution.

Radiochemical methods were completed on the thorium nitrate. The radiochemical methods used include alpha spectroscopy on a digested sample, gamma spectroscopy on a solid, and total activity (using alpha and beta emission) by liquid scintillation counting on a digested sample.

Graphite furnace atomic absorption spectroscopy (GFAAS) is used for the determination of mercury (after cold vapor generation) and selenium. Like emission spectroscopy, light emitted from atoms is measured; however, in this case, the emission is brought about by irradiation with light of a characteristic wavelength, which is absorbed by the atom and then re-emitted. The technique has high sensitivity. For mercury in water, detection limits at the low nanogram per liter level can be attained.

2.2 ANALYTICAL RESULTS

In summary, the analyses of the thorium samples indicate that the levels of non-thorium metals in these materials are below single digit mg/kg levels. Table 1 contains results of metals analysis for thorium nitrate and thorium oxide. Mercury was analyzed by cold vapor atomic absorption spectroscopy (CVAAS). The other elements listed in the table were analyzed by ICP–AES and ICP–

Table 1. Metals and analytical results

Analyte	Thorium nitrate results (mg/kg)		Thorium oxide results (mg/kg)		TCLP thorium oxide results (mg/L)	
	ICP–AES	ICP–MS	ICP–AES	ICP–MS	ICP–AES	ICP–MS
Aluminum	<4000	NA	<3000	NA		
Antimony	N/A	<0.60	NA	<0.50		
Arsenic	<2000	<1.9	<2000	<1.5	<40	<1.0
Barium	<80	<1.6	<60	<1.5	2.1	1.7
Beryllium	<20	<0.40	<20	<0.50		
Cadmium	<200	<0.50	<200	<0.50	<2.0	<0.05
Calcium	<10000	NA	<8000	NA		
Chromium	<400	<0.50	<300	<0.50	<4.0	<0.05
Cobalt	<200	<0.50	<200	<0.50		
Copper	<1000	<1.9	<2000	<1.5		
Iron	<4000	NA	<2000	NA		
Lead	<2000	<1.0	<2000	<0.50	<20	<0.05
Magnesium	<10000	NA	<8000	NA		
Manganese	<100	<0.50	<80	<0.50		
Molybdenum	<4000	<1.0	<3000	<0.70		
Nickel	<800	<1.0	<600	1.9	<10	<0.1
Potassium	<200000	NA	<200000	NA		
Selenium	NA	<3.8	NA	<3.0	NA	<1.0
Silver	<400	<0.50	<300	<0.50	<4.0	<0.05
Sodium	<10000	NA	<8000	NA		
Thallium	NA	<0.60	NA	<0.50		
Titanium	<1000	NA	<800	NA		
Uranium	NA	NA	NA	<0.50		
Vanadium	<1000	<0.50	<2000	<0.50		
Zinc	<1000	3.9	<800	<3.0		
Mercury by CVAAS method		0.02		0.02		
Mercury by AAS method					<0.02	
Selenium by GFAAS method					<0.02	

MS. The ICP–AES method follows EPA Method 6010a and the ICP-MS method follows EPA Method 200.8. Both methods are acceptable by a number of regulating authorities. Analytical reports are in Appendix A.

Additionally, the detection limits are discussed in Appendix A. These values illustrate the detection limit difference between ICP–AES and ICP–MS. The dilution factors for ICP–AES for thorium nitrate and thorium oxide are 1890 and 1465, respectively. The dilution factors for ICP–MS for thorium nitrate and thorium oxide are 100. The large dilution factors needed for ICP–AES analyses are a result of the large interferences caused by the high level of thorium in the samples. The only

analyte that is above the reported detection limit (Result column) for both samples is 3.9 mg/kg of zinc in the thorium nitrate. This value is close to the reported detection limit for zinc in the thorium oxide (<3.0 mg/kg). Whether zinc is lost by heating cannot be determined with only these two data points, especially when the values are so close to the reported detection limit. Other methods of analysis are also shown in Table 1. These include GFAAS for selenium and GFAAS for mercury. Mercury is best analyzed by the GFAAS method because it does not lend itself to analysis by either ICP–AES or ICP–MS.

Table 2 contains the results of the radiochemical analyses of the thorium nitrate. The values are given in picocuries per gram of thorium nitrate.

Table 2. Thorium nitrate radiological analyses

Analyte	Result (pCi/g)	Confidence (pCi/g)
Alpha Spectrometry		
Thorium-228	5.46×10^4	5.0×10^3
Thorium-232	1.92×10^5	2.9×10^4
Total U-Alpha activity	0.0	4.4×10^2
Uranium-232	0.0	4.3×10^2
Uranium-234	0.0	4.4×10^2
Uranium-235	0.0	4.4×10^2
Uranium-236	0.0	4.4×10^2
Uranium-238	3.80×10^1	1.4×10^2
Gamma Spectrometry		
Actinium-228	6.00×10^4	5.5×10^2
Lead-212	6.36×10^4	3.72×10^2
Potassium-40	5.04×10^3	1.4×10^3
Radium-224	7.33×10^4	2.3×10^3
Thorium-234	7.72×10^3	9.8×10^2
Thallium-208	2.00×10^4	2.9×10^2
Total Activity[7]	6.08×10^5	2.7×10^3

TLCP testing was performed on a 100-g sample of ThO_2. The sample was produced by thermal denitration of thorium nitrate by members of the Materials and Chemistry Laboratory. The resulting individual vials containing ~15 g of thorium oxide each were transported to ASO for compositing into the TCLP sample. The analytes of TCLP regulatory interest are shown in Table 1.

As can be seen in Table 1 (TCLP of ThO_2), the reported levels of detection of the ICP–AES method are much higher than those for the ICP–MS method. The levels of detection for the ICP–AES method are high because thorium was present in the filtered liquid that was submitted for analysis. The TCLP procedure calls for the liquid to be filtered through a borosilicate filter of 0.6- to 0.8-μm effective pore size. Some of the very fine ThO_2 particles are passing through the filter. This is noteworthy for future filtering regimes.

3. REGULATORY ASSESSMENT

RCRA is the federal law, promulgated in 40 CFR Parts 260–266, 268, 270–272, 279, 280–282, and 148, which regulates the management of hazardous waste from generation to final disposal. States are granted authorization by the U.S. Environmental Protection Agency (EPA) for administering their own hazardous waste programs in lieu of the federal program. A state may be authorized for the entire RCRA program or portions of the program. Consequently, both federal and state agencies may have jurisdiction concurrently in a state under some circumstances. The list and descriptions of authorized state programs are found in 40 CFR 272.

The regulatory agency(ies) having jurisdiction over the RCRA/hazardous waste programs for the state(s) where the conversion process(es) will be conducted should be contacted to resolve any state-specific requirements prior to project implementation.

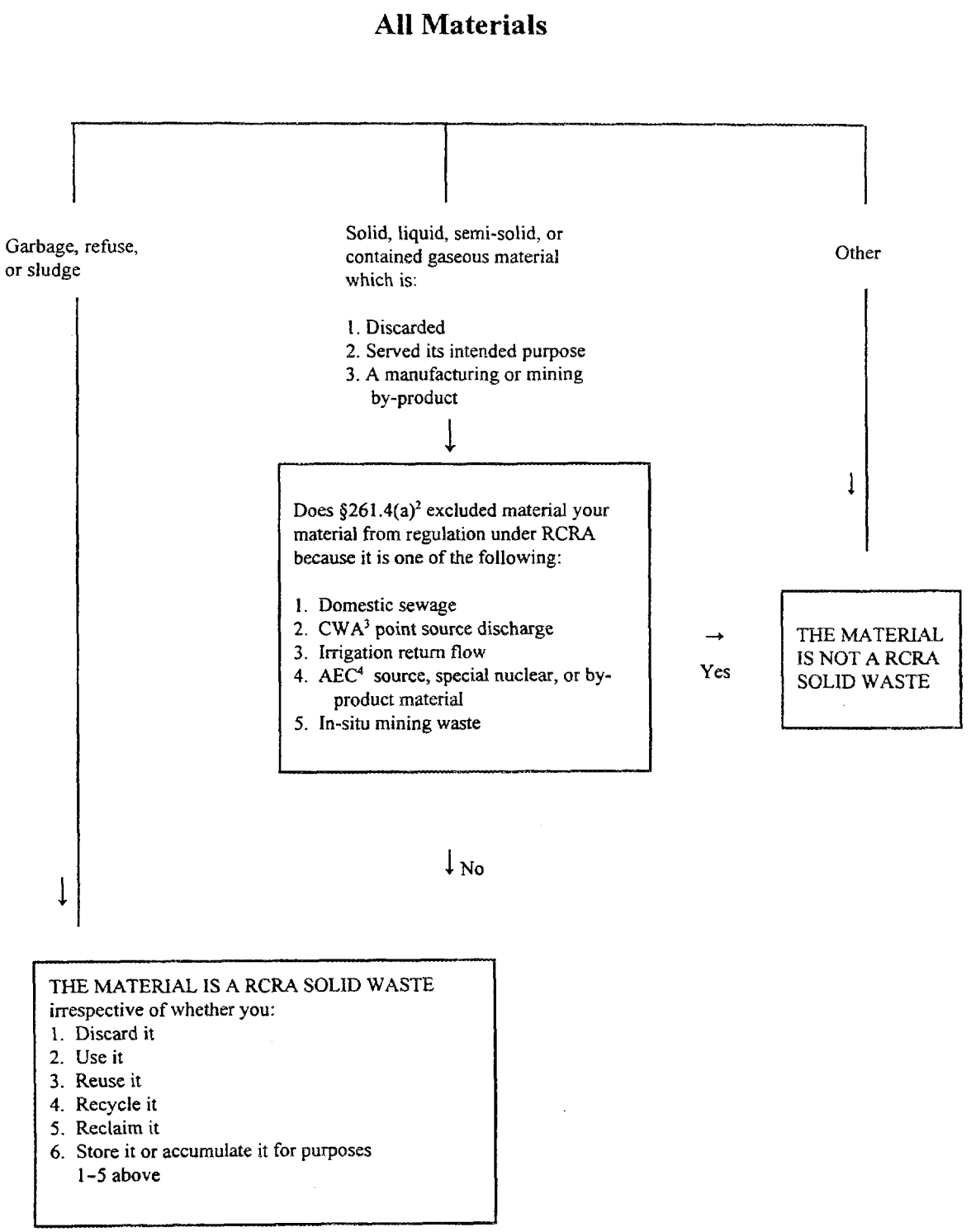
3.1 RCRA HAZARDOUS WASTE DETERMINATION

A generator must determine for each waste, upon generation, whether such waste is a hazardous waste per 40 CFR 262.11. To determine whether a waste is subject to RCRA regulation, the generator should address a series of questions, in the following order:

1. Is the waste a solid waste per 40 CFR 261.2?
2. Is the waste excluded from regulation as a solid waste per 40 CFR 261.4?
3. Does the waste meet one or more hazardous waste listings under 40 CFR 261, Subpart D or a mixture that contains a listed hazardous waste under 40 CFR 261, Subpart D?
4. Does the waste or mixture meet one or more hazardous waste characteristics under 40 CFR 261, Subpart C?

Also, provisions for excluding materials as solid waste when recycled are found in 40 CFR 261.2.

Figures 1 and 2 depict, respectively, how the definitions of solid waste and hazardous waste correlate with the strategy for making a hazardous waste determination per 40 CFR 262.11.



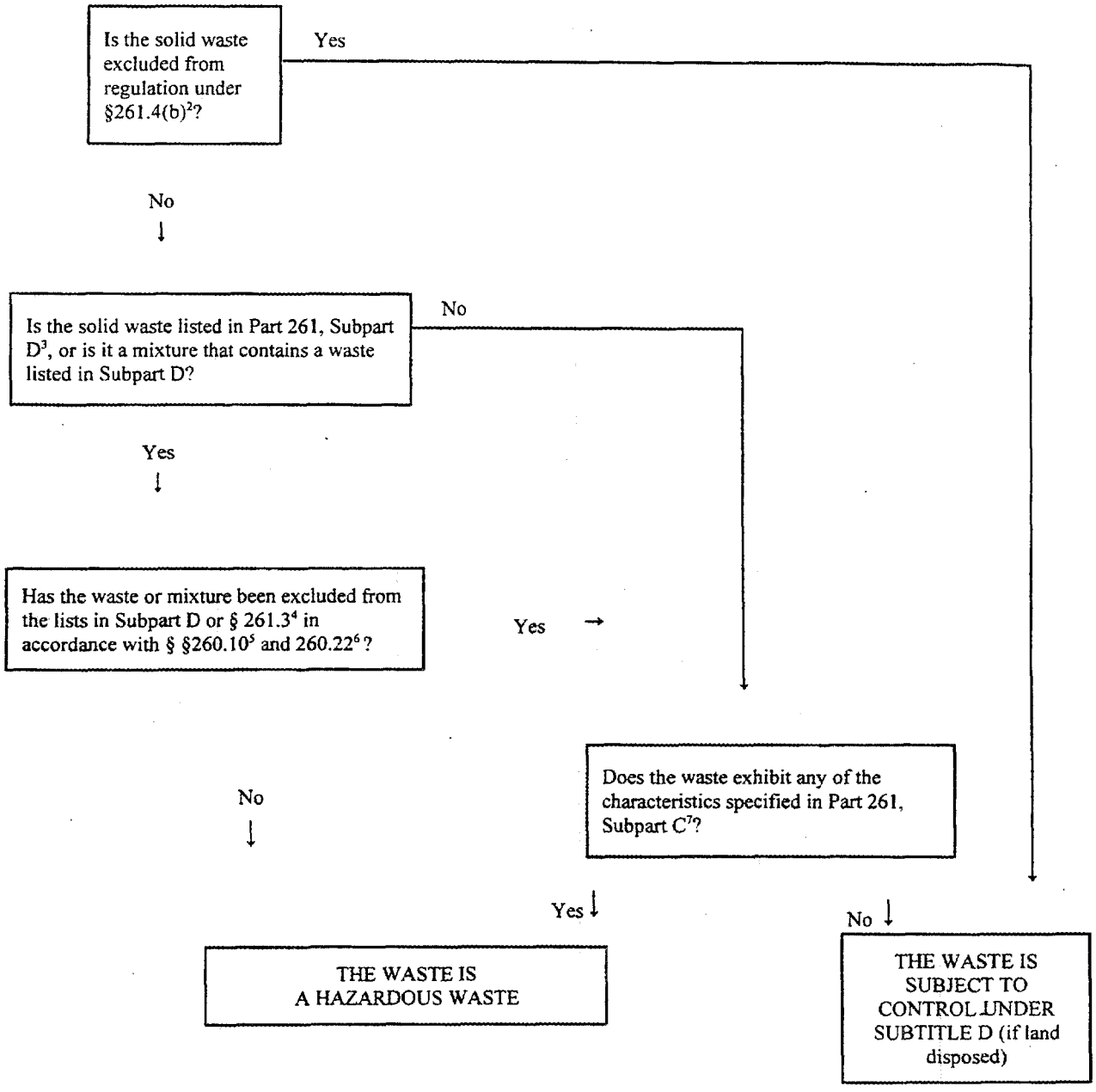
[1] Taken from *RCRA Regulations and Keyword Index: 1997 Edition*, Elservier Science, Inc.

[2] Refers to materials excluded from the definition of solid waste under RCRA.

[3] CWA = Clean Water Act.

[4] AEC = Atomic Energy Commission.

Fig. 1. Definition of a solid waste.[1]



[1]Taken from *RCRA Regulations and Keyword Index: 1997 Edition*, Elservier Science, Inc.
[2]Refers to materials excluded from the definition of hazardous waste under RCRA.
[3]Refers to the listed hazardous wastes (F, K, P, U).
[4]Refers to mixtures of hazardous wastes excluded from RCRA which consist primarily of wastewaters the discharge of which is regulated under the Clean Water Act.
[5]Refers to general rulemaking petitions for modification or revocation of provisions under RCRA.
[6]Refers to petitions to exclude a waste produced at a particular facility (delisting petitions).
[7]Refers to characteristic (D-code) hazardous wastes.

Fig. 2. Definition of a hazardous waste.[1]

3.2 RCRA APPLICABILITY ASSESSMENT

The information presented in this assessment was provided by the Energy Systems Environmental Compliance (EC) organization, at the request of the Energy Systems Project Manager.

ThN is classified as an oxidizer per U.S. Department of Transportation (DOT) regulations 49 CFR 173.151. Such a designation would subject a waste to the D001 ignitability characteristic category under RCRA (40 CFR 261, Subpart C). Three scenarios may apply to the current ThN inventory: (1) exclusion as a solid waste under RCRA, (2) management as a recyclable material under RCRA, and (3) management as a hazardous waste under RCRA.

3.2.1 Scenario 1: ThN Excluded as a RCRA Solid Waste

Under this scenario, it should be demonstrated that the ThN is source material per the Atomic Energy Act [(AEA), U.S. Code, Title 42, Sect. 2011–Sect. 2259]. Source material, as defined under Sect. 11(z) of the AEA, is excluded from regulation as a solid waste under RCRA per 40 CFR 261.4(a)(4). Source material is defined as:

> *(1) Uranium or thorium, or any combination thereof, in any physical or chemical form or (2) ores which contain by weight one-twentieth* [1/20] *of one percent (0.05%) or more or: (i) Uranium, (ii) thorium or, (iii) any combination thereof. Source material does not include special nuclear material.*

Per guidance provided by the NRC, thorium nitrate meets the definition of 'source material.'

A final rule promulgated in 10 CFR 962.3 limits the AEA exemption for certain Department of Energy (DOE) –owned or –produced radioactive materials. Specifically, this rule states that, for a byproduct material regulated under the AEA, the exemption applies only to the radionuclides in the material, not the nonradioactive hazardous portion. The nonradioactive hazardous portion of the material would be subject to regulation under RCRA. Department of Defense (DOD) –owned or –produced materials are not addressed in this Rule. The DLA may wish to obtain clarification from the NRC to determine whether the limitation under 10 CFR 962.3 (1) encompasses source material and (2) has any implications on DOD materials.

Because the ThN would be excluded from regulation as a solid waste under RCRA, the ThN would not be subject to a hazardous waste determination and would not be required to be managed in accordance with RCRA standards. Additionally, conversion of the thorium nitrate to another product form does not remove the source material properties.

3.2.2 Scenario 2: ThN Managed as Recyclable Material

The second scenario addresses how to handle the ThN if it does not qualify for the AEA exemption. Under the second scenario, it should be demonstrated that the ThN is being recycled by the conversion process and, as such, it is not a solid waste when recycled, per 40 CFR 261.2(e). In essence, the ThN would be considered 'excess materials' and not declared as waste at this point. Specifically, it must be demonstrated that the ThN is being used or reused as either (1) an ingredient in the conversion process to make a product and is not being reclaimed or (2) an effective substitute for a commercial product [40 CFR 261.3(3)(1)(i) and (ii), respectively]. To qualify under this exemption, the ThN cannot be processed to recover a usable product or be regenerated for use in the

conversion process; the ThN must be substituted in the process 'as-is.' [See 40 CFR 261.1(c)(4), (5), and (7) for the definition of terms 'reclaimed,' 'used or reused,' and 'recycled.']

Materials that are (a) being abandoned, discarded, or disposed of (b) cannot be used for their intended purpose, (c) cannot be recycled, or (d) are speculatively accumulated are examples of materials considered to be solid waste under RCRA per 40 CFR 261.2. An issue of concern is whether the ThN is being stored or accumulated before or in lieu of being abandoned [40 CFR 261.2(b)(3)]. Management of the ThN in this manner would deem the material to be a solid waste, subject to hazardous waste regulation. It is imperative to maintain thorough documentation to support claims of materials being exempt as solid waste. The generator, at a minimum, must demonstrate that a known market exists for the material; facilities claiming to be recycling materials must have the necessary equipment to do so. Additional requirements for such documentation can be found in 40 CFR 261.2(f).

3.2.3 Scenario 3: Management of ThN as RCRA Hazardous Waste

Should the ThN fail to meet the conditions under the two scenarios above, the ThN would be required to be managed as D001 hazardous waste in accordance with all applicable RCRA requirements [due to meeting the ignitability characteristic as a DOT oxidizer. Also, it should be determined whether the ThN is subject to other hazardous waste characteristics under 40 CFR 261, Subpart C. Of particular importance would be certain heavy metals above the RCRA regulatory thresholds found in 40 CFR 261.24, Table 1. At a minimum, until such time as the ThN can be shipped off-site to a treatment, storage, or disposal facility (TSDF) authorized under RCRA to manage this hazardous waste stream, the DLA would be required to:

1. Obtain a permit from the EPA (or authorized state) in accordance with 40 CFR 270 (or applicable authorized state regulations) for the design, construction, and operation of a container storage area in accordance with 40 CFR 264 TSDF standards (or applicable authorized state regulations) to store hazardous waste longer than 90 days, or;
2. Accumulate, for 90 days or less, the ThN in compatible, structurally sound containers in accordance with 40 CFR 262 generator standards (or applicable authorized state regulations) without a TSDF permit, and;
3. Comply with applicable 40 CFR 268 Land Disposal Restrictions (LDR) requirements while storing the ThN on-site. This includes, but is not limited to (1) identification of all underlying hazardous constituents found in 40 CFR 268.48, "Table UTS–Universal Treatment Standards," as required by 40 CFR 268.40(e), and (2) compliance with the storage requirements found in 40 CFR 268, Subpart E.

3.3 RCRA APPLICABILITY TO ThN/ThO CONVERSION PROCESS

The applicability of 'treatment' as defined under RCRA is addressed relative to the ThN/ThO conversion process. 'Treatment' per 40 CFR 260.10 is defined as:

> *Any method, technique, or process, including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to neutralize such waste, or so as to recover energy or material resources from the waste, or so as to render such waste as non-hazardous, or less hazardous; safer to transport, store, or dispose of; or amenable for recovery, amenable for storage, or reduced in volume.*

In the conversion process, the ThN loses the ignitability characteristic as ThO. Consequently, the conversion could satisfy the first part of the treatment definition—the chemical nature of the ThN is changed by the process. It must be determined whether the result of the conversion process (1) changes the nature of the ThN in such a manner to satisfy (intentionally or unintentionally) one of the conditions in the second part of the treatment definition or (2) produces a usable, marketable product.

Under Scenario 1 in Sect. 3.2.1, the definition of treatment would not be applicable since the ThN is excluded from RCRA.

Under Scenario 2 in Sect 3.2.2, it must be demonstrated that the conversion process is a legitimate recycling activity that is generally accepted and/or used by industry, or achieved results similar to those activities generally accepted and/or used by industry. Also, if the activity produces a material for which there is no market and is intended to be discarded, or disposed of, abandoned, or otherwise managed per 40 CFR 261.2 as solid waste, such activity is considered 'sham recycling.' Such activity would be deemed as treatment under RCRA.

Under Scenario 3 in Sect. 3.2.3, the conversion process would be deemed treatment under RCRA regardless of whether a usable material is produced. The process changes the chemical character of the ThN (i.e., in this instance, D001 ignitable hazardous waste) by rendering it nonhazardous. Based on current regulations, the thorium nitrate would be classified as a D001 nonwaste water ignitable characteristic waste other than high total organic carbon (TOC) subcategory. The treatment technology standard code for this classification is DEACT (deactivation to remove the hazardous characteristics) and includes the requirement to meet 40 CFR 268.48, underlying hazardous constituents (metal levels must be less than those specified by Universal Treatment Standards).

Should the conversion process be deemed treatment of hazardous waste under RCRA (Scenario 2 or 3 above) and such activity was conducted on-site, the DLA would be required either to:

1. obtain a permit issued from the EPA (or authorized state) in accordance with 40 CFR 270 (or applicable authorized state regulations) for the design, construction, and operation of the process in accordance with 40 CFR 264 TSDF standards (or applicable authorized state regulations); or

2. treat, in 90 days or less, the ThN in accordance with 40 CFR 262 generator standards or exclusion under 40 CFR 270.1(c) (or applicable authorized state regulations) without a TSDF permit. Additionally, if the DLA is treating its hazardous waste in containers to meet the applicable D001 hazardous waste treatment standards under 40 CFR 268 LDR requirements, a

written waste analysis plan must be developed, implemented, and maintained on-site in its records in accordance with 40 CFR 268.7(a)(5).

If the vendor(s) proposed to perform the process(es) on-site, the EPA or authorized state agency may require that the vendor(s) and/or DLA obtain the necessary permits. The appropriate authority should be contacted to determine whether the owner and/or operator would be required to obtain the permit. At government-owned, contractor-operated facilities, the government agency and contractor(s) are considered co-operators, and therefore co-signatories on permit applications and other compliance documents.

If the DLA chooses to ship the ThN off-site to a TSDF-permitted facility under RCRA, the ThN would be required to be managed on-site as outlined in Sect. 3.2.3.

3.4 RCRA APPLICABILITY TO ThO

It should be noted that the hazardous waste criteria in 40 CFR 261 attaches to wastes at the point of generation. Consequently, the ThO must be deemed a solid waste as defined under RCRA in order to be subject to hazardous waste characterization. The ThO would be subject to hazardous waste criteria if:

1. the product fails to meet the exclusion under RCRA as a source material under the AEA;
2. no market exists for this end product, or the end product cannot be used for its intended purpose, and consequently the material will ultimately be disposed; or
3. the conversion process is deemed under RCRA as treatment of hazardous waste, and consequently the material would be considered to be a treatment residue subject to hazardous waste characterization.

3.5 TOXICITY CHARACTERISTIC CRITERIA APPLICABILITY

Following a thorium nitrate laboratory-scale production study conducted by Energy Systems for the DLA, several chemical analyses were performed on the ThN and ThO. Of particular interest were the ThN total metals results and the ThO TCLP results given in Table 1. Under RCRA, the TCLP is the required EPA method to analyze hazardous wastes for toxicity characteristics (TC) under 40 CFR 261.24 (see 40 CFR 261, Appendix II regarding the TCLP). A hazardous waste exhibiting one or more TC constituents equal to or above the regulatory limit (in 40 CFR 261.24, Table 1) is considered to be a characteristic hazardous waste for the constituent(s). Only TC metals were evaluated since the remaining TC constituents would not be expected in the ThN or ThO above their respective TC regulatory levels.

In reviewing the TCLP results for the ThO, some of the metals appear to exceed the TC regulatory thresholds using the ICP–AES method. This is a result of the detection limit being at a higher level than the concentration specified by TC regulatory criteria. When comparing metals data from the ICP–MS method, all metal concentrations are below TC regulatory criteria. Comparisons of the TC regulatory criteria for the metals and metal concentrations in the ThO are presented in Table 3.

Based on the comparison in Table 3, it can generally be concluded that the ThO does not exceed TC regulatory criteria for metals. Given the inconsistency of the results of the methods used, the DLA may choose to discuss these results with the appropriate regulatory agency(ies) to obtain agreement that use of ICP–MS is acceptable for determining TCLP metal concentrations in the ThO.

Table 3. Comparison of ThO results

Metal	TC regulatory criteria (mg/L)	Universal treatment standards (mg/L)	ICP-MS method[a] (mg/L)	ICP-AES method (mg/L)
Arsenic	5.0	5.0	<1.0	<40
Barium	100.0	7.6	1.7	2.1
Cadmium	1.0	0.19	<0.05	<2.0
Chromium	5.0	0.86	<0.05	<4.0
Lead	5.0	0.37	<0.05	<20
Silver	5.0	0.30	<0.05	<4.0
Selenium	1.0	0.16	<1.0	<0.02 (GFAAS method)
Mercury	0.2	0.025	NA	<0.02 (CVAAS method)

[a]Analytical results in μg/L, reported in mg/L; conversion factor used 0.001.

4. REGULATORY ASSESSMENT CONCLUSIONS

This assessment presents the results of metals analyses of ThN and ThO, several strategies for determining the regulatory status of the ThN, and the conversion process for ThO relative to RCRA. Key issues that may need to be discussed with the regulators include:

1. **Determination of the regulatory status of the ThN.** This issue is pivotal to the ultimate status of the conversion process and the ThO. Should it be deemed that the ThN is excluded from RCRA as a source material as defined in the AEA, the conversion process would also be exempt from RCRA. Exempting the material from RCRA could eliminate sampling and analysis costs that may be required if the exemption determination is not made prior to processing the ThN.

2. **Applicability of source material definition to ThO.** Again, if the ThO can be determined to be source material as defined in the AEA, this material would be excluded from further regulation under RCRA. It is important to determine whether the source material definition applies to derivatives and similar compounds from source material.

APPENDIX A

Analytical Data Reports

Customer Smpl Id: DEMO-01 Project: K-WM-K116 52P K116-52P

Customer: F R VAN RYN JR BLDG 1037, MS 7349 (423)574-1907

Matrix: SOLID
Sample Description: THORIUM NITRATE
Location: ETTP
Chain of Custody No: 103303
Protocol: NONE
Charge Number: PN892605
Sampler(s): STEVENSON

Date/Time Sampled: 08/01/97 00:00:00
Date/Time Received: 08/29/97 11:00:59
Date/Time Needed: 09/25/97 23:59:59
Date/Time Completed: 10/23/97 07:37:29
Date/Time Approved: 10/23/97 07:37:29
Sample Status: APPROVED
Sample Approver:

Customer Comments: The ThN is a very fine hygroscopic powder.
Lab Comments:

<<<<< Inorganic >>>>>

Test: HG7471
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-7471
Approver: T T ADAMS
QC Batch/File:

Test Name: Mercury in Solid Waste/Soil/Sludge by CVAAS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 08/29/97 00:00:00
Date/Time Analyzed: 09/05/97 07:00:00
Lab Group: MYWST1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7439976	Mercury	L			1		0.02	U		ug/g

Test: ICP6010
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-6010A
Approver: R M WILKES
QC Batch/File: QC97279034/30501N1

Test Name: Elements by EPA 6010A ICP-AES
Prep Method/Date: ASO-Y/P65-0027 09/26/97 09:00:00
Test Status: APPROVED
HT Deadline: 03/25/98 23:59:59
Date/Time Analyzed: 10/04/97 17:09:00
Lab Group: IYICP2

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7429905	Aluminum				18904		<4000			mg/kg
7440382	Arsenic				18904		<2000			mg/kg
7440393	Barium				18904		<80			mg/kg
7440417	Beryllium				18904		<20			mg/kg
7440439	Cadmium				18904		<200			mg/kg
7440702	Calcium				18904		<10000			mg/kg
7440473	Chromium				18904		<400			mg/kg
7440484	Cobalt				18904		<200			mg/kg
7440508	Copper				18904		<1000			mg/kg
7439896	Iron				18904		<4000			mg/kg
7439921	Lead				18904		<2000			mg/kg
7439954	Magnesium				18904		<10000			mg/kg
7439965	Manganese				18904		<100			mg/kg
7439987	Molybdenum				18904		<4000			mg/kg
7440020	Nickel				18904		<800			mg/kg
7440097	Potassium				18904		<200000			mg/kg
7440224	Silver				18904		<400			mg/kg
7440235	Sodium				18904		<10000			mg/kg
7440326	Titanium				18904		<1000			mg/kg
7440622	Vanadium				18904		<1000			mg/kg
7440666	Zinc				18904		<1000			mg/kg

Comments: TRACE METALS IN THORIUM
Secondary 100 fold dilution prior to analysis due to spectral interferences caused by thorium. Results should be considered estimated because of the significant interferences from thorium. Digested spike recoveries were low for most elements reported (60-80%). QC limit for digested spikes: 75-125%.

Test: ICPMS2008
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: EPA-200.8 R4.4
Approver: D G AILEY
QC Batch/File: QC97275035/C970930B

Test Name: Elements by EPA 200.8 ICPMS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 01/28/98 00:00:00
Date/Time Analyzed: 09/26/97 09:00:00
Lab Group: IYPMS1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7440360	Antimony				10		<0.60			ug/g
7440382	Arsenic				10		<1.9			ug/g
7440393	Barium				10		<1.6			ug/g
7440417	Beryllium				10		<0.40			ug/g
7440439	Cadmium				10		<0.50			ug/g
7440473	Chromium				10		<0.50			ug/g
7440484	Cobalt				10		<0.50			ug/g
7440508	Copper				10		<1.9			ug/g
7439921	Lead				10		<1.0			ug/g
7439965	Manganese				10		<0.50			ug/g
7439987	Molybdenum				10		<1.0			ug/g
7440020	Nickel				10		<1.0			ug/g
7782492	Selenium				10		<3.8			ug/g
7440224	Silver				10		<0.50			ug/g
7440280	Thallium				10		<0.60			ug/g
7440291	Thorium				1		NA			ug/g
7440611	Uranium				10		<0.60			ug/g
7440622	Vanadium				10		<0.50			ug/g
7440666	Zinc				10		3.9			ug/g

Comments: METALS IN THORIUM.
Due to the unusual nature of this matrix, this samples was prepared for analysis according to a technical directive prepared on 9/26/97.

Test: PREPHOTPLATE
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: ASO-Y/P65-0027
Approver: D G AILEY
QC Batch/File:

Test Name: Hot plate prep (non-regulatory) for AA/ICP/ICPMS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 01/28/98 23:59:59
Date/Time Analyzed: 09/26/97 09:00:00
Lab Group: IYICP2

EPA Qualifiers:
U - Analyte analyzed for but undetected. Analyte result was below the instrument detection limit (IDL).

Test: TOTALACT-WP
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: ASO-ACD-160063
Approver: E E CLARK
QC Batch/File: QC97275052/WP-5199

Test Name: Total Activity using LSC by 160063
Prep Method/Date: ASO-ACD-160084 10/08/97 06:00:00
Test Status: APPROVED
HT Deadline: 04/06/98 23:59:59
Date/Time Analyzed: 10/14/97 08:00:00
Lab Group: RKRAD1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	MDA	Detection Limit	Result	EPA Qual	Confidence	Unit
N931	Total Activity			d			6.08E5		2.7e3	pCi/g

Footnotes:
d - Spike control limits do not apply, sample activity exceeds the activity of the spike
g - Gamma photopeak is near MDA, resulting in a poor curve fit
h - Daughter of uranium isotopes, reported for comparison purposes only
l - Duplicate control limits do not apply, duplicate and sample results are near MDA
m - Duplicate results are outside of control limits
v - Result is less than MDA, confidence level is less than 95%
w - Result is less than background

***** END OF REPORT *****
UNCLASSIFIED

Customer Smpl Id: DEMO-01 Project: K-WM-K116 52P K11652P-R

Customer: F R VAN RYN JR BLDG 1037, MS 7349 (423)574-1907

Matrix: SOLID
Sample Description: THORIUM NITRATE
Location: ETTP
Chain of Custody No: 103303
Protocol: NONE
Charge Number: PN892605
Sampler(s): STEVENSON

Date/Time Sampled: 08/01/97 00:00:00
Date/Time Received: 08/29/97 11:00:56
Date/Time Needed: 12/10/97 23:59:59
Date/Time Completed: 01/20/98 15:15:57
Date/Time Approved: 01/20/98 15:15:57
Sample Status: APPROVED
Sample Approver:

Customer Comments: Radiological analysis rerun of thorium nitrate sample
Lab Comments:

<<<<< Radiochemical >>>>>

Test: ASPECU-WP
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: ASO-ACD-160083
Approver: E E CLARK/Lab Supervisor
QC Batch/File: QC98020047/WP-5267

Test Name: Isotopic Uranium Act. by 160083
Prep Method/Date: ASO-ACD-160080 12/19/97 11:05:00
Test Status: APPROVED
HT Deadline: 06/17/98 23:59:59
Date/Time Analyzed: 12/21/97 21:48:00
Lab Group: RKRAD1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	MDA	Detection Limit	Result	EPA Qual	Confidence	Unit
N1763	Total U Alpha Activity						0.00E0		4.4E2	pCi/g
14158293	Uranium-232			1			0.00E0		4.3E2	pCi/g
13966295	Uranium-234						0.00E0		4.4e2	pCi/g
15117961	Uranium-235						0.00E0		4.4e2	pCi/g
13982702	Uranium-236						0.00E0		4.4e2	pCi/g
24678828	Uranium-238			1			3.80E1		1.4e2	pCi/g

Comments: This sample was analyzed for Uranium using a modified method. The tracer recoveries are lower than normal, but still acceptable for the mo
dified method. Method was modified to remove excess Thorium from Uran
ium ROI at customer request.

Test: GAMSPEC-WP
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: ASO-ACD-160067
Approver: E E CLARK/Lab Supervisor
QC Batch/File: QC98020048/WP-5267

Test Name: Gamma Spectrometry by 160067
Prep Method/Date: ASO-ACD-160092 12/05/97 08:02:00
Test Status: APPROVED
HT Deadline: 06/03/98 23:59:59
Date/Time Analyzed: 12/10/97 11:51:00
Lab Group: RKRAD1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	MDA	Detection Limit	Result	EPA Qual	Confidence	Unit
14952400	Actinium-227						NA			pCi/g
13967709	Cesium-134						NA			pCi/g
10045973	Cesium-137						NA			pCi/g
13981505	Cobalt-57						NA			pCi/g
10198400	Cobalt-60						NA			pCi/g
13966002	Potassium-40						5.04E3		1.4e3	pCi/g
N2006	Protactinium-234m						NA			pCi/g
15065108	Thorium-234						7.72E3		9.8e2	pCi/g
15117961	Uranium-235						NA			pCi/g

Comments: Gamma was analyzed under a special library designed specifically for t
his customer. Other analytes identified:

Th-232:	1.92e5	+/-	2.9e4	pCi/g
Pb-212:	6.36e4	+/-	3.7e2	pCi/g
Ra-224:	7.33e4	+/-	2.3e3	pCi/g
Th-228:	5.46e4	+/-	5.0e3	pCi/g
Tl-208:	2.00e4	+/-	2.9e2	pCi/g
Ac-228:	6.00e4	+/-	5.5e2	pCi/g

Analytes with an "NA" were not identified in the gamma scan.

Footnotes:
1 - Duplicate control limits do not apply, duplicate and sample results are near MDA

***** END OF REPORT *****

Customer Smpl Id: TH1 Project: K-WM-K116 52P K116-52P

Customer: F R VAN RYN JR BLDG 1037, MS 7349 (423)574-1907

Matrix: SOLID
Sample Description: THORIUM OXIDE - TOTAL METALS
Location: ETTP
Chain of Custody No: 103303
Protocol: NONE
Charge Number: PN892605
Sampler(s): STEVENSON

Date/Time Sampled: 08/01/97 00:00:00
Date/Time Received: 08/29/97 11:00:59
Date/Time Needed: 09/25/97 23:59:59
Date/Time Completed: 10/06/97 15:16:08
Date/Time Approved: 10/06/97 15:16:08
Sample Status: APPROVED
Sample Approver:

Customer Comments: The ThN is a very fine hygroscopic powder.
Lab Comments:

<<<<< Inorganic >>>>>

Test: HG7471
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-7471
Approver: T T ADAMS
QC Batch/File:

Test Name: Mercury in Solid Waste/Soil/Sludge by CVAAS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 08/29/97 00:00:00
Date/Time Analyzed: 09/05/97 07:00:00
Lab Group: MYWST1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7439976	Mercury	L			1		0.02	U		ug/g

Test: ICP6010
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-6010A
Approver: R M WILKES
QC Batch/File: QC97279034/30501N1

Test Name: Elements by EPA 6010A ICP-AES
Prep Method/Date: ASO-Y/P65-0027 09/26/97 09:00:00
Test Status: APPROVED
HT Deadline: 03/25/98 23:59:59
Date/Time Analyzed: 10/04/97 17:09:00
Lab Group: IYICP2

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7429905	Aluminum				14652		<3000			mg/kg
7440382	Arsenic				14652		<2000			mg/kg
7440393	Barium				14652		<60			mg/kg
7440417	Beryllium				14652		<20			mg/kg
7440439	Cadmium				14652		<200			mg/kg
7440702	Calcium				14652		<8000			mg/kg
7440473	Chromium				14652		<300			mg/kg
7440484	Cobalt				14652		<200			mg/kg
7440508	Copper				14652		<2000			mg/kg
7439896	Iron				14652		<2000			mg/kg
7439921	Lead				14652		<2000			mg/kg
7439954	Magnesium				14652		<8000			mg/kg
7439965	Manganese				14652		<80			mg/kg
7439987	Molybdenum				14652		<3000			mg/kg
7440020	Nickel				14652		<600			mg/kg
7440097	Potassium				14652		<200000			mg/kg
7440224	Silver				14652		<300			mg/kg
7440235	Sodium				14652		<8000			mg/kg
7440326	Titanium				14652		<800			mg/kg
7440622	Vanadium				14652		<2000			mg/kg
7440666	Zinc				14652		<800			mg/kg

Comments: TRACE METALS IN THORIUM
Secondary 100 fold dilution prior to analysis due to spectral interferences caused by thorium. Results should be considered estimated because of the significant interferences from thorium. Digested spike recoveries were low for most elements reported (60-80%). QC limit for digested spikes: 75-125%.

Test: ICPMS2008
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: EPA-200.8 R4.4
Approver: D G AILEY
QC Batch/File: QC97275035/C970930B

Test Name: Elements by EPA 200.8 ICPMS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 01/28/98 00:00:00
Date/Time Analyzed: 09/26/97 09:00:00
Lab Group: IYPMS1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7440360	Antimony				10		<0.50			ug/g
7440382	Arsenic				10		<1.5			ug/g
7440393	Barium				10		<1.5			ug/g
7440417	Beryllium				10		<0.50			ug/g
7440439	Cadmium				10		<0.50			ug/g
7440473	Chromium				10		<0.50			ug/g
7440484	Cobalt				10		<0.50			ug/g
7440508	Copper				10		<1.5			ug/g
7439921	Lead				10		<0.50			ug/g
7439965	Manganese				10		<0.50			ug/g
7439987	Molybdenum				10		<0.70			ug/g
7440020	Nickel				10		1.9			ug/g
7782492	Selenium				10		<3.0			ug/g
7440224	Silver				10		<0.50			ug/g
7440280	Thallium				10		<0.50			ug/g
7440291	Thorium				1		NA			ug/g
7440611	Uranium				10		<0.50			ug/g
7440622	Vanadium				10		<0.50			ug/g
7440666	Zinc				10		<3.0			ug/g

Comments: Due to the unusual nature of this matrix sample was prepared for analysis according to a technical directive prepared on 9/26/97.

Test: PREPHOTPLATE
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: ASO-Y/P65-0027
Approver: D G AILEY
QC Batch/File:

Test Name: Hot plate prep (non-regulatory) for AA/ICP/ICPMS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 01/28/98 23:59:59
Date/Time Analyzed: 09/26/97 09:00:00
Lab Group: IYICP2

EPA Qualifiers:
U - Analyte analyzed for but undetected. Analyte result was below the instrument detection limit (IDL).

***** END OF REPORT *****
UNCLASSIFIED

Customer Smpl Id: TH-TCLP Project: K-WM-K116 52P K116-52P-2

Customer: F R VAN RYN JR BLDG 1037, MS 7349 (423)574-1907

Matrix: SOIL
Sample Description: THORIUM OXIDE-TCLP
Location: ETTP
Chain of Custody No: 103305
Protocol: NONE
Charge Number: PN892605
Sampler(s): STEVENSON

Date/Time Sampled: 09/10/97 12:00:00
Date/Time Received: 09/10/97 12:00:20
Date/Time Needed: 09/25/97 23:59:59
Date/Time Completed: 09/29/97 16:49:25
Date/Time Approved: 09/29/97 16:49:25
Sample Status: APPROVED
Sample Approver:

Customer Comments: The ThN is a very fine hygroscopic powder. CUSNUMS= Th2,3,6,7,8,9,11,12,13
Lab Comments:

<<<<< Inorganic >>>>>

Test: ICPMSTCLP
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-6020
Approver: D G AILEY
QC Batch/File: QC97272053/C970922A

Test Name: Elements in TCLP Extracts by ICPMS
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 03/15/98 07:00:00
Date/Time Analyzed: 09/23/97 13:16:00
Lab Group: IYPMS1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7440382	Arsenic				100		<1000			ug/L
7440393	Barium				100		1700			ug/L
7440439	Cadmium				100		<50			ug/L
7440473	Chromium				100		<50			ug/L
7439921	Lead				100		<50			ug/L
7440020	Nickel				100		<100			ug/L
7782492	Selenium				100		<1000			ug/L
7440224	Silver				100		<50			ug/L

Test: ICPTCLP
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-6010A
Approver: D G AILEY
QC Batch/File: QC97260047

Test Name: Elements in TCLP Extracts by ICPAES
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 03/15/98 07:00:00
Date/Time Analyzed: 09/17/97 14:15:00
Lab Group: IYICP2

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7440382	Arsenic				100		<40			mg/L
7440393	Barium				100		2.1			mg/L
7440439	Cadmium				100		<2.0			mg/L
7440473	Chromium				100		<4.0			mg/L
7439921	Lead				100		<20			mg/L
7440020	Nickel				100		<10			mg/L
7440224	Silver				100		<4.0			mg/L

Comments: SAMPLE PREPARED FOR ANALYSIS ACCORDING TO SW8463010A
SAMPLE REQUIRED A 100 FOLD DILUTION FOR ANALYSIS DUE TO INTERFERENCE
EFFECTS FROM THORIUM. TCLP SPIKE RECOVERY FOR AS WAS 19%. QC
LIMIT: >50%.

Test: TCLPHG
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-7470
Approver: T T ADAMS
QC Batch/File:

Test Name: Mercury In TCLP Extract by Cold Vapor AA
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 10/14/97 07:00:00
Date/Time Analyzed: 09/17/97 07:00:00
Lab Group: MYWST1

Analyte Id	Analyte Name	HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
7439976	Mercury				1		<0.02			mg/L

UNCLASSIFIED
ASO Operating ESLIMS
P. O. Box 2009 Oak Ridge,TN 37831
Official Report

Lab Smpl Id: A972530168

Test: TCLPSE
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-7740
Approver: E K SEDMAN
QC Batch/File:

Analyte Id	Analyte Name
7782492	Selenium

Test Name: Selenium In TCLP Extract by GFAA
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 03/15/98 07:00:00
Date/Time Analyzed: 09/22/97 07:00:00
Lab Group: MYWST1

HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
			10		<20			ug/L

<<<<< None >>>>>
Test: TCLPEXN-NV
Rpt Basis: As-Received
Test Req Cnt: 01
Analysis Meth: SW846-1311
Approver: C A HUBBUCH
QC Batch/File:

Analyte Id	Analyte Name
N3112	Extraction fluid number
N679	Percent Solids
N8957	Sample Weight
N704	pH

Test Name: TCLP Extn for NonVolatiles
Prep Method/Date:
Test Status: APPROVED
HT Deadline: 09/24/97 12:00:00
Date/Time Analyzed: 09/15/97 14:30:00
Lab Group: MYWST1

HT	Cust Lim	Fn	Dilution Factor	Detection Limit	Result	EPA Qual	Confidence	Unit
			1		1			none
			1		100			%
			1		100.04			g
			1		4.18			none

***** END OF REPORT *****
UNCLASSIFIED

To: Bob Stevenson

I have reviewed the information you put together on the analysis of the thorium materials you submitted in September. I decided that I would provide you with both the practical quantitation limits (PQL) and the instrument detection limits (IDL) that apply to those analyses. You can still use the IDL values in your table, but the PQL will give you a better understanding of how the samples were handled. A PQL will sometimes vary with the preparation and analysis method used. As you can see different PQLs were used in the total and TCLP analyses of your thorium samples. I have also included the instrument detection limits for both techniques. These will also vary somewhat depending on the acid matrix analyzed. An instrument detection limit is a good basis for comparing two techniques. However, it can not be used as a quantitation limit. The limit to which one can reliably quantitate is dependent on the preparation method used and the dilution required due to sample matrix, in addition to the instrument detection limit.

If you multiply the appropriate PQL by the total dilution factor for a sample analysis you will obtain the reporting limit for each element before any rounding and signficant figures rules are inacted. Additionally, reporting limits will sometimes be increased for certain elements because of specific sample matrix interferences. Some of the dilution factors you have quoted in your report need to be changed. I checked the dilution factors for the sample analyses associated with ESLIMS samples A972530168, A972410094 and A972410095. The dilution factors included in the ESLIMS report for the TCLP sample A972530168 are correct. The prepared solution of the TCLP extract was in fact diluted 100 fold in both the ICPAES and ICPMS analysis. The dilution factors included in the ESLIMS report for the total analyses A972410094 and A972410095 are correct for the ICPAES analysis. They include the subsequent 100 fold dilution mentioned in the comment section of the ICPAES data report. However, only the dilution of the sample after preparation was included in the ESLIMS report for ICPMS data. This is due to a difference in the software programs presently used for data crunching. The complete dilution factors for samples A972410094 and A972410095 for the ICPMS analysis were 1465 and 1890, respectively. Please note that the units in the ICPAES report are in mg/L, so the PQL below should be converted to mg/L to make any comparison with the results in the ESLIMS report.

The < symbol in the analytical reports indicates that the value was below the ASO practical quantitation limit." Let me know if you have questions.

Debbie Ailey

DETECTION LIMITS AND QUANTITATION LIMTS FOR TCLP ANALYSES (ug/L)				
	ICPAES PQL (ug/L)	ICPAES IDL (ug/L)	ICPMS PQL (ug/L)	ICPMS IDL (ug/L)
Arsenic (As)	400	10	10	0.10
Barium (Ba)	1000	1	10	0.20
Cadmium (Cd)	20	2	0.50	0.020
Chromium (Cr)	40	4	0.50	0.060
Lead (Pb)	200	30	0.50	0.020
Nickel (Ni)	100	10	1.0	0.40
Selenium (Se)	NA	NA	10	0.20
Silver (Ag)	40	2	0.50	0.010

DETECTION LIMITS AND QUANTITATION LIMTS FOR TOTAL ANALYSES (ug/L)				
	ICPAES PQL (ug/L)	ICPAES IDL (ug/L)	ICPMS PQL (ug/L)	ICPMS IDL (ug/L)
Silver (Ag)	20	2	0.40	0.010
Antimony (Sb)	NA	NA	0.40	0.010
Aluminum (Al)	200	10	NA	NA
Arsenic (As)	100	10	1.0	0.10
Barium (Ba)	4	1	1.0	0.20
Beryllium (Be)	1	0.1	0.40	0.030
Calcium (Ca)	500	4	NA	NA
Cadmium (Cd)	10	2	0.40	0.020
Cobalt (Co)	10	2	0.40	0.010
Copper (Cu)	40	2	1.0	0.20
Chromium (Cr)	20	4	0.40	0.060
Iron (Fe)	200	4	NA	NA
Lead (Pb)	100	30	0.40	0.020
Magnesium (Mg)	500	20	NA	NA
Manganese (Mn)	5	0.5	0.40	0.020
Molybdenum (Mo)	200	6	0.50	0.010
Nickel (Ni)	40	10	0.60	0.40
Potassium (K)	10000	50	NA	NA
Sodium (Na)	500	100	NA	NA
Selenium (Se)	NA	NA	2.0	0.2
Titanium (Ti)	50	2	NA	NA
Thallium (Tl)	NA	NA	0.40	0.010
Uranium (U)	NA	NA	0.40	0.010
Vanadium (V)	50	2	0.40	0.020
Zinc (Zn)	50	2	1.5	0.3

Attachment 6

NEPA Supplemental Data

CURTISBAYBULLSEYEOUTPUT

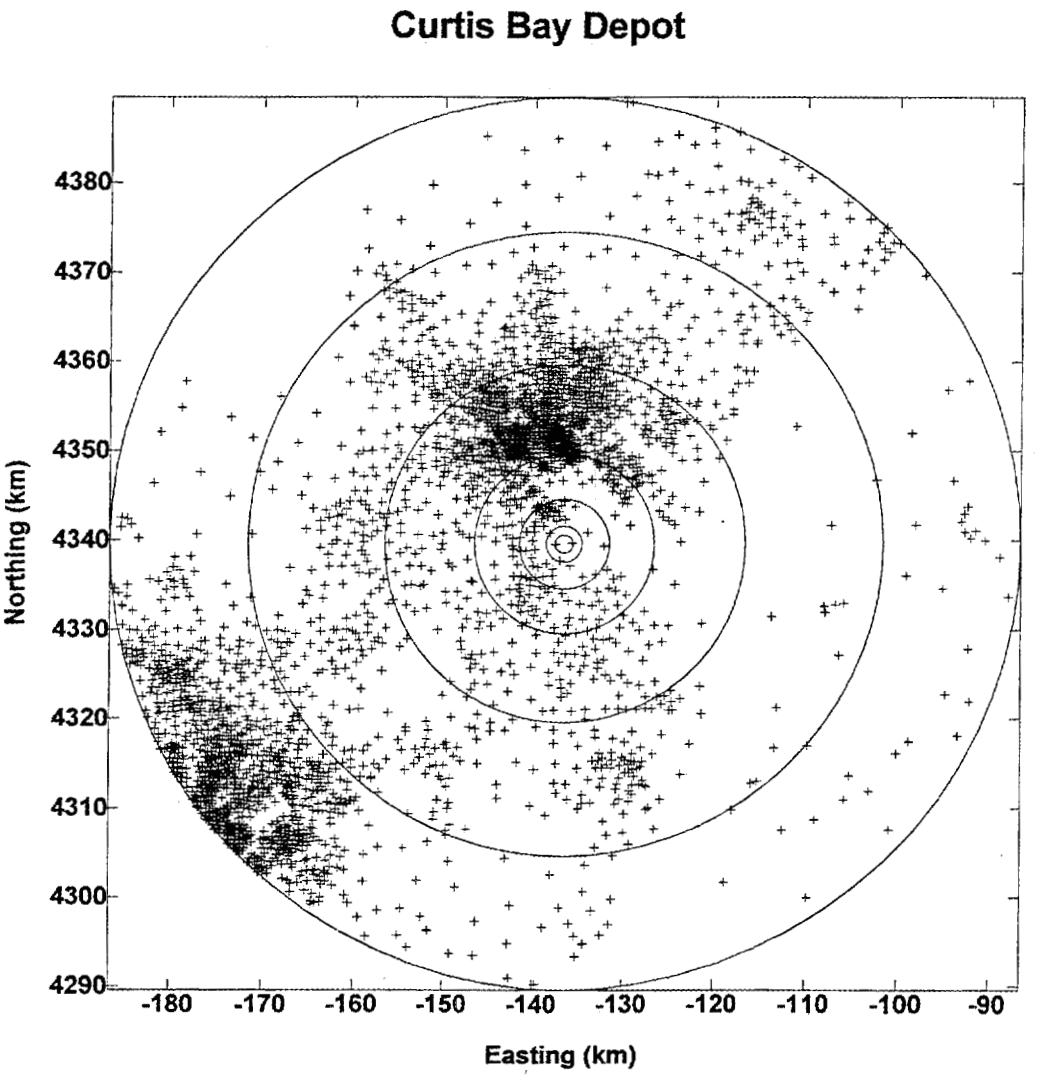
07/27/98

People	One Km	Two Km	Five Km	Ten Km	Twenty Km	Thirtyfive	Fifty Km
Total	42	666	49,216	210,688	1,038,741	879,591	1,357,920
White	33	638	43,480	175,795	557,918	712,481	652,954
Black	7	17	4,498	30,526	459,272	130,703	613,113
Hispanic	2	9	529	2,713	12,173	16,372	77,506
Amerindian	0	2	221	784	3,285	1,859	3,640
Asian	0	4	876	2,887	15,131	30,298	51,405
Other	2	5	141	696	3,135	4,250	36,808

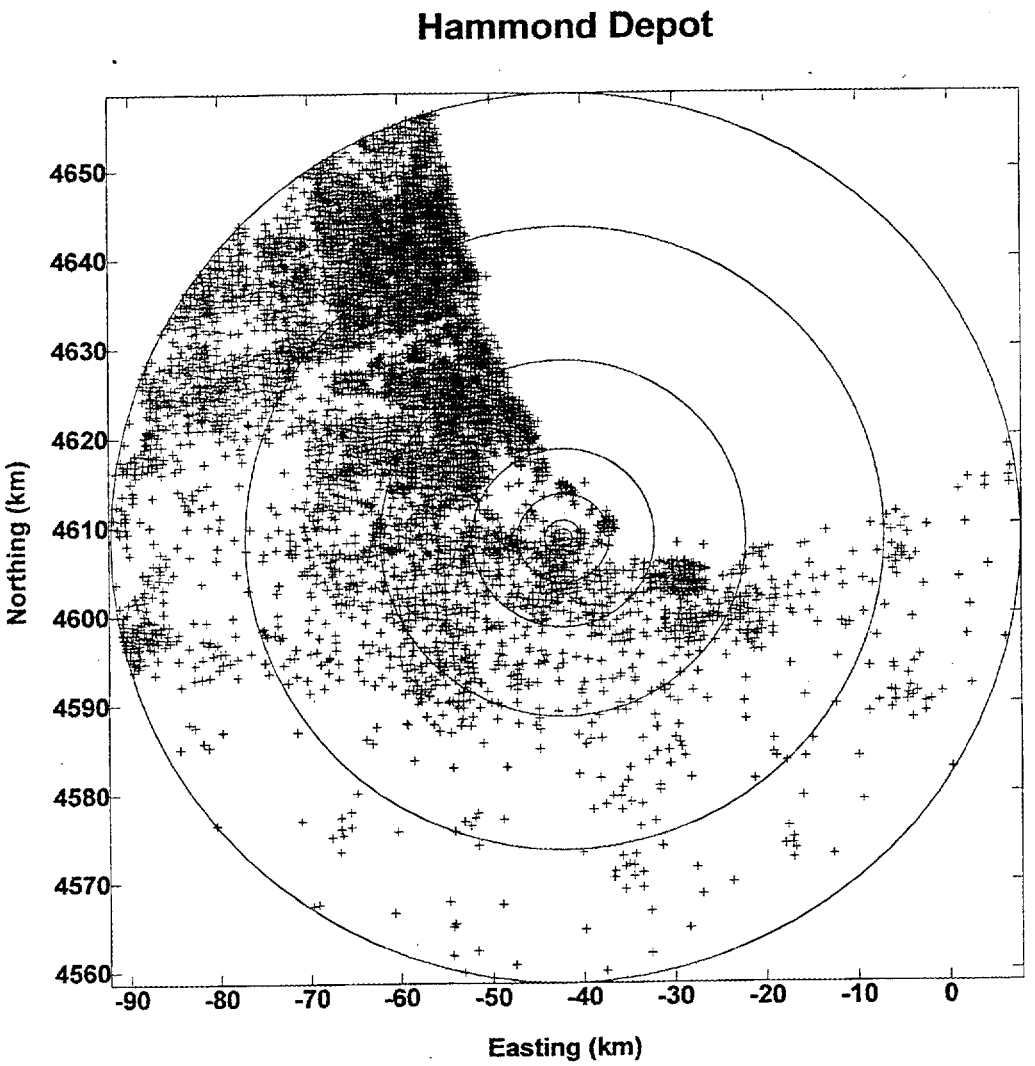
HAMMONDBULLSEYEOUTPUT

07/28/98

People	One Km	Two Km	Five Km	Ten Km	Twenty Km	Thirtyfive	Fifty Km
Total	6,326	17,085	78,427	226,072	1,067,462	1,823,439	2,154,804
White	5,444	12,639	55,328	166,987	361,942	1,122,682	1,616,608
Black	53	1,519	14,133	45,586	669,967	468,784	258,981
Hispanic	1,620	5,263	15,746	23,411	53,994	314,810	307,247
Amerindian	17	18	180	360	1,498	3,572	5,517
Asian	23	62	354	1,765	6,955	33,041	118,061
Other	789	2,847	8,432	11,374	27,100	195,360	155,637



Population distribution within 50 km of Curtis Bay Depot



Population distribution within 50 km of Hammond Depot