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Characterization of Surplus Plutonium for Disposition Options

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ABSTRACT

The United States (U.S.) has identified 61.5 metric tons (MT) of plutonium that is permanently excess to use in nuclear weapons programs, including 47.2 MT of weapons-grade plutonium. Except for materials that remain in use for programs outside of national defense, including programs for nuclear-energy development, the surplus inventories will be stored safely by the Department of Energy (DOE) and then transferred to facilities that will prepare the plutonium for permanent disposition. Some items will be disposed as transuranic waste, low-level waste, or spent fuel. The remaining surplus plutonium will be managed through: (1) the Mixed Oxide (MOX) Fuel Fabrication Facility (FFF), to be constructed at the Savannah River Site (SRS), where the plutonium will be converted to fuel that will be irradiated in civilian power reactors and later disposed to a high-level waste (HLW) repository as spent fuel; (2) the SRS H-Area facilities, by dissolving and transfer to HLW systems, also for disposal to the repository; or (3) alternative immobilization techniques that would provide durable and secure disposal.

From the beginning of the U.S. program for surplus plutonium disposition, DOE has sponsored research to characterize the surplus materials and to judge their suitability for planned disposition options. Because many of the items are stored without extensive analyses of their current chemical content, the characterization involves three interacting components: laboratory sample analysis, if available; non-destructive assay data; and rigorous evaluation of records for the processing history for items and inventory groups. This information is collected from subject-matter experts at inventory sites and from materials stabilization and surveillance programs, in cooperation with the design agencies for the disposition facilities. This report describes the operation and status of the characterization program.

INTRODUCTION

Following the end of the Cold War, the U.S. began a program to provide permanent disposal for a large stockpile of special nuclear material (including plutonium and highly enriched uranium). In 1994, 38.2 MT of weapons-grade plutonium was declared to be permanently excess to national defense weapons programs. Another 14.3 MT of government-owned, non-weapons-grade material

was included in the disposition program. The ultimate disposition for these materials is a geologic high-level waste repository.

In 2007, the U.S. declared an additional 9.0 MT of plutonium excess to national defense. A multi-program partnership within the DOE, including the National Nuclear Security Administration, is engaged in managing, stabilizing, storing, and providing permanent disposition for this 61.5 MT.

Disposition of excess material is also important to achieving a transformation of the facilities and sites that previously produced, processed, and recycled materials for weapons and for other programmatic uses. The DOE will continue to reduce the number of facilities required for the storage of plutonium under high safeguards, further improving proliferation resistance and reducing costs.

Multiple pathways are available for disposition of excess plutonium, depending on the character of the existing inventories. These include:

- disposal as high-level waste to a geologic repository, for plutonium contained in irradiated reactor fuel and targets;
- disposal as transuranic waste to the Waste Isolation Pilot Plant (WIPP), for low-grade process residues or scrap; or
- retention and use in development and implementation of advanced nuclear fuel cycles.

However, most of the bulk, high-assay plutonium is unsuitable for any of these pathways. The largest fraction of the excess plutonium is contained in core components from retired nuclear weapons, typically called "pits." About 13 MT is found in non-pit inventories that supported previous production processes. In January 2000, DOE announced a plan to dispose of up to 50 MT of plutonium using three primary facilities, to be built at SRS:¹

- a Pit Disassembly and Conversion Facility (PDCF), to prepare plutonium materials for disposition in the MOX FFF;
- a Mixed Oxide Fuel Fabrication Facility, to convert plutonium oxide from the PDCF; combine it with uranium oxide; and fabricate fuel for irradiation in commercial power reactors; and
- a Plutonium Immobilization Plant (PIP), to convert the remaining non-pit materials into a durable solid, encasing the solid in high-level radioactive waste for disposal.

The properties of pits and the requirements for civilian fuel are relatively straightforward. Therefore, the early characterization programs focused on the varied materials proposed for PIP.

In 2002, the PIP was cancelled so that the U.S. could provide greater attention to the PDCF and MOX FFF programs. These facilities were a cornerstone of a 2000 disposition agreement with the Russian Federation, where each Nation would provide disposition for 34 MT of weapons-grade material.² Studies proceeded to identify alternative pathways for the disposition of the nominal 13 MT of plutonium that would have been disposed through Immobilization. The U.S. developed a "three-prong" approach, which includes these elements:³

- modifying the MOX FFF to accept Alternate Feedstocks (AFS), from sources outside the PDCF, including impure weapons-grade oxides;

- dissolving selected inventories in H-Canyon and HB-Line at SRS, with plutonium disposed through existing HLW systems; and
- implementation a smaller Immobilization concept, based on vitrification technology, that would provide disposition for the very impure materials that are not suitable for the other pathways.

In 2006, DOE announced plans to extend the operation of the H-Canyon and HB-Line processes from 2012 through 2019. This extension allowed DOE to consider whether the MOX FFF and H-Area options could be extended further, perhaps allowing for the disposition of the targeted 13 MT solely by a "two-prong" approach. Characterization activities shifted to the development of flow-sheets and evaluation of intermediate steps that would allow this approach to succeed.

Even before formal decisions are made on disposition strategies and facilities, DOE programs continued to stabilize plutonium for interim storage and to evaluate the inventories for compatibility with proposed disposition pathways. Figure 1 shows the processes that have been the subject of detailed study.

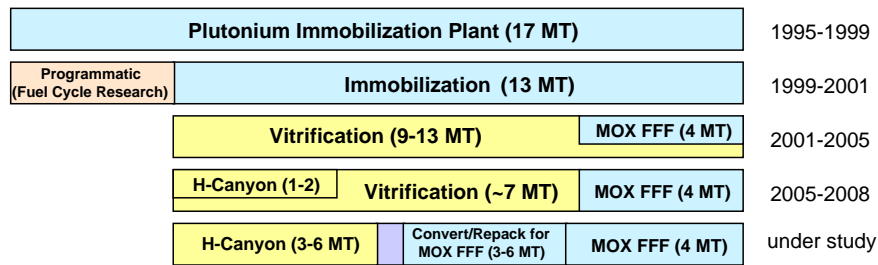


Figure 1. Primary Pathways Evaluated for Plutonium Disposition

Early characterization and evaluation was led by the Immobilization development program at Lawrence Livermore National Laboratory (LLNL), while later work has been managed by Nonproliferation Programs at SRS. All activities are coordinated with subject-matter experts from the sites where the plutonium was produced, processed, stored, or stabilized. Primary sites of origin for the disposition plutonium are the Rocky Flats Environmental Technology Site (RFETS), SRS, Hanford Reservation, Los Alamos National Laboratory (LANL), and LLNL.

REQUIREMENTS FOR DISPOSITION FEEDS

The MOX FFF includes an Aqueous Polishing process to prepare its oxide feeds for fuel fabrication. Originally the process was required to remove americium, gallium, and minor impurities from oxides produced in PDCF. After the Immobilization project was cancelled, the MOX FFF developed specification limits for the chemical, physical, and isotopic characteristics of less-pure AFS.

Surplus plutonium that does not meet the MOX FFF feed requirements is evaluated for alternative disposition, including the Vitrification process or disposal through the SRS H-Area facilities. Items that may not be compatible with the MOX FFF range from highly pure non-weapons-grade material to very impure alloys and mixed oxides (with plutonium isotopic contents ranging from weapons-grade to reactor-grade).

CHARACTERIZATION OF INVENTORIES FOR FEED TO MOX FFF

Detailed laboratory analyses are not available for the bulk of the surplus inventories. The tools available for characterization include:

- **Process knowledge:** The history of the material is inferred from the inventory groupings used by the site that produced or processed the material, including Item Description Codes used at RFETS and similar groupings at other sites. Table 1 shows the primary broad categories for evaluation, based on process knowledge and supplemental data (when available).

C	Pyrochemical Oxides. The oxides contain high chloride and with Mg/Na ratios less than 1 and Na/Cl ratios between 0.125 and 0.4. The most commonly used salt was an equal molar mixture of NaCl and KCl, but sometimes with up to 30 mole percent MgCl ₂ . Materials in RFETS IDCs 086 and 067 are assumed pyrochemical unless ratios indicate otherwise.
X	Foundry Oxides: These oxides may or may not contain chlorine (>500 ppm) and generally have a ratio of Mg/Na>1 and a Na/Cl ratio, outside the range for group C above. Typical IDCs include 057, 061, and 062.
D	These oxides have chloride but low sodium levels with a ratio of Na/Cl generally less than 0.125. This may indicate the presence of Mg or Ca at higher levels.
W	The oxides were originally from Group C but were washed to remove excess chlorides prior to calcination.
A	These oxides are fairly pure and were produced by oxalate or peroxide precipitation of plutonium.
M	The oxides were precipitated using magnesium hydroxide.
U	The oxides contain more than 2% uranium and were processed with uranium streams using either aqueous or pyrochemical operations. Typical IDCs include U61 and Y61.
H	These materials are oxides and residues produced as a byproduct of plutonium processing to an oxide or metal form for production purposes. Often they contain fluoride. Materials which do not easily fit into the other categories are classified as Group H.
S	Screening materials include oxides materials that did not pass through screening operations, heels from dissolving operations, or sweepings. The items have a high potential for contamination with gallium, tantalum, aluminum, or corrosion products.

Table 1. Primary Inventory Categories for Disposition Feed Evaluation

- **Laboratory analyses:** Chemical data from an inventory group can be used to predict the distribution of impurities for other members of the group. Key information includes historical site data and samples from the Materials Identification and Surveillance (MIS) program that supports the DOE Standard for Long-Term Plutonium Storage (DOE-STD-3013).⁴ Additional data were gathered by Pacific Northwest National Laboratory (PNNL) for items stored at Hanford, including groups of items that originated at RFETS.⁵

Fewer than 400 complete analyses are available for approximately 5300 DOE-STD-3013 containers that comprise the 13 MT of surplus, non-pit plutonium. However, the large majority of the packaged items fall into one of the inventory groups and have similar likelihood for the presence of chemical impurities. Table 2 shows the current coverage of these groups or combined groups by detailed laboratory analyses.

- **Stabilization analyses:** Data on actinide content, net weights, and processing history were reported as part of the documentation of stabilization to DOE-STD-3013.

Source of Sample Data	Inventory Category					
	C,W	D,X	A	U	H	M,S
DOE-STD-3013 MIS Database	5	12	4	4		5
PNNL Evaluation	10		2		6	
Standards for International Atomic Energy Agency		6				
Historical RFETS & Hanford Analyses	13		31			
Los Alamos Oxide from Aqueous Processing			27			
RFETS Metals	4	276				

Table 2. Chemical Sample Analysis Availability

- **Non-destructive assay (NDA):** External data are available from packaged oxides and many packaged metals. Of particular importance is Prompt Gamma Analysis (PGA), which can measure or detect concentrations of certain elements that are important to both the MOX FFF and alternative disposition processes.⁶

Sites performed PGA following stabilization to DOE-STD-3013. PGA measures the production of gamma rays, mostly from light elements, when those elements are activated by the decay of plutonium and americium. Figure 2 shows a typical spectrum. In addition to the elements shown, PGA is effective in identifying aluminum, beryllium, and magnesium. Detection limits for 60-minute counting times range from less than 100 parts per million (ppm) for sodium and beryllium to 7000 ppm for chlorine.

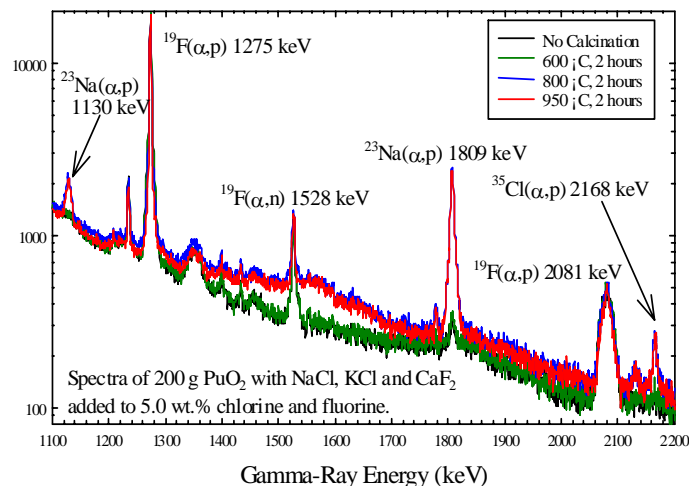


Figure 2. Prompt Gamma Analysis Spectrum

STATISTICAL ANALYSIS

Together with the process history, stabilization data on total impurity content, laboratory data, and NDA, it is possible to predict the distribution of unmeasured impurities. Within each category, many elements show a strong correlation with the total impurity content or a combined relationship that takes into account the total impurities and fluorine (if present). Other elements are less strongly correlated, and their concentrations are estimated from the total weight fraction of unidentified impurities in items proposed for feed to disposition. Figure 3 shows an example plot for chromium.

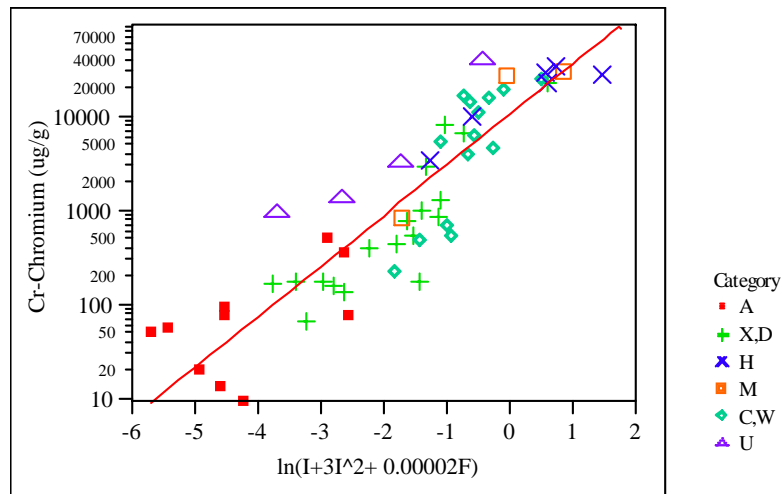


Figure 3. Correlation of Chromium Measurements

Statistical methods may not be able to verify the concentration of a specific impurity in a single inventory item. However, they can predict the average and bounding concentrations that are expected within the inventory group. For disposition processes, these parameters are often more important than the concentrations in individual items. MOX FFF feed specifications are based on impurity distributions: "Most" items (nominally 75%) must fall below an elemental limit, and a "maximum exceptional content" is applied to 98% of the proposed feed inventory. Table 3 shows the results of the statistical analysis for a subset of 2200 impure Alternate Feedstock items, for elements that correlate with total impurity measurements and fluorine.

Element	Specification for 75% of Feed Items	Predicted Percentage of Items Below Stated Concentration ($\mu\text{g/g Pu}$)				Statistical Correlation Coefficient
		98%	75%	50%	Mean	
Aluminum	4,000	20,000	1,850	500	820	0.73
Chromium	3,000	13,250	1,700	500	1,050	0.90
Copper	500	5,600	450	110	220	0.78
Iron	5,000	38,000	5,000	1,750	3,000	0.87
Manganese	1,000	2,100	180	50	90	0.79
Molybdenum	100	2,200	180	50	80	0.76
Nickel	5,000	18,250	1,800	450	1,030	0.86
Silicon	5,000	16,500	1,850	600	970	0.79
Lead	200	1,270	90	50	116	0.64
Tungsten	4,000	5,500	330	80	130	0.67
Zinc	1,000	4,600	280	80	120	0.69

Table 3. Statistical Projections of Impurities in Impure Plutonium Oxide Feeds

Other methods determine the distribution of concentrations of other elements, within specific inventory groups and over the complete inventory of disposition feeds. Separate criteria are used to measure isotopic content and the presence of actinide impurities that could affect the quality of fabricated fuel. Using these tools, more than 4 MT of current oxide materials was verified as suitable AFS feed to the MOX FFF. Table 4 shows the approximate distribution of oxide items that are judged to be suitable for the MOX FFF as AFS, versus non-qualifying items.

MOX Suitable (AFS) Oxides

Category	A	C	D	H	M	U	W	X	S	Overall
% in Category	4.2%	24.5%	3.4%	1.3%	5.7%	17.9%	0.4%	42.6%		100.0%
% with Low Chloride	71.4%	0.0%	0.0%	38.5%	91.1%	89.3%	0.0%	81.3%		59.3%
Average Impurity Level	2.6%	17.9%	13.4%	5.4%	2.7%	3.8%	16.8%	5.3%		8.8%

Non-MOX Suitable Oxides

Category	A	C	D	H	M	U	W	X	S	Overall
% in Category	16.2%	10.5%	1.7%	9.3%	4.1%	34.4%	1.3%	14.0%	8.4%	100.0%
% with Low Chloride	70.9%	0.0%	0.0%	15.9%	84.0%	65.1%	12.5%	54.4%	12.7%	47.7%
Average Impurity Level	5.1%	28.5%	26.3%	27.4%	19.6%	9.2%	40.7%	18.0%	31.4%	22.0%

Table 4. Distribution of MOX FFF and Non-Qualifying Oxides by Process Category

EVALUATION FOR OTHER DISPOSITION OPTIONS

Once items are characterized for potential feed to MOX FFF, the same methods are used to estimate the chemical composition of proposed feeds for processing in the SRS H-Area or for Vitrification. Different elements can be important for process design and flowsheet development.

One new category that is proposed for MOX FFF, identified in Figure 1, are materials that do not currently meet the MOX FFF specifications but that can be converted to meet those specifications without reprocessing. Up to 4 MT of additional AFS can be produced at SRS by oxidation of metals, repackaging, further calcination, or removal of excess halides through a washing process. Potential changes to the chemical or isotopic specifications may allow additional items to qualify as AFS. Work continues to establish equipment requirements and process flowsheets that may allow DOE to pursue the "two-prong" approach to disposition by using H-Area for all items that are not suitable for the MOX FFF cycle.

FUTURE WORK

Considerable feed characterization is possible through a combination of process history tracking, statistical analysis, and limited measurements. Additional "hard" data would add confidence to process plans. Process throughputs and operating plans can be estimated less conservatively if more measurements can supplement calculated or inferred compositions.

Further measurements will be taken during the stabilization of additional items at LANL and LLNL, during the conversion and repackaging of items at SRS, and from the Destructive Evaluation of selected items for the DOE-STD-3013 surveillance program. Recharacterization is in progress to take advantage of recent PGA data and to develop correlations for new disposition pathways.

The characterization methods described above focus on the chemical nature of the impure surplus plutonium. Separate studies continue for the isotopic and chemical composition of pit feeds to PDCF and for other oxides to be produced from pits.

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