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# Estimating Impurities in Surplus Plutonium for Disposition

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## ABSTRACT

The United States holds at least 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. 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. The Savannah River National Laboratory (SRNL) operates a Feed Characterization program for the Office of Fissile Materials Disposition of the National Nuclear Security Administration and the DOE Office of Environmental Management. Many of the items that require disposition are only partially characterized, and SRNL uses a variety of techniques to predict the isotopic and chemical properties that are important for processing through the Mixed Oxide Fuel Fabrication Facility and alternative disposition paths. Recent advances in laboratory tools, including Prompt Gamma Analysis and Peroxide Fusion treatment, provide data on the existing inventories that will enable disposition without additional, costly sampling and destructive analysis.

## BACKGROUND

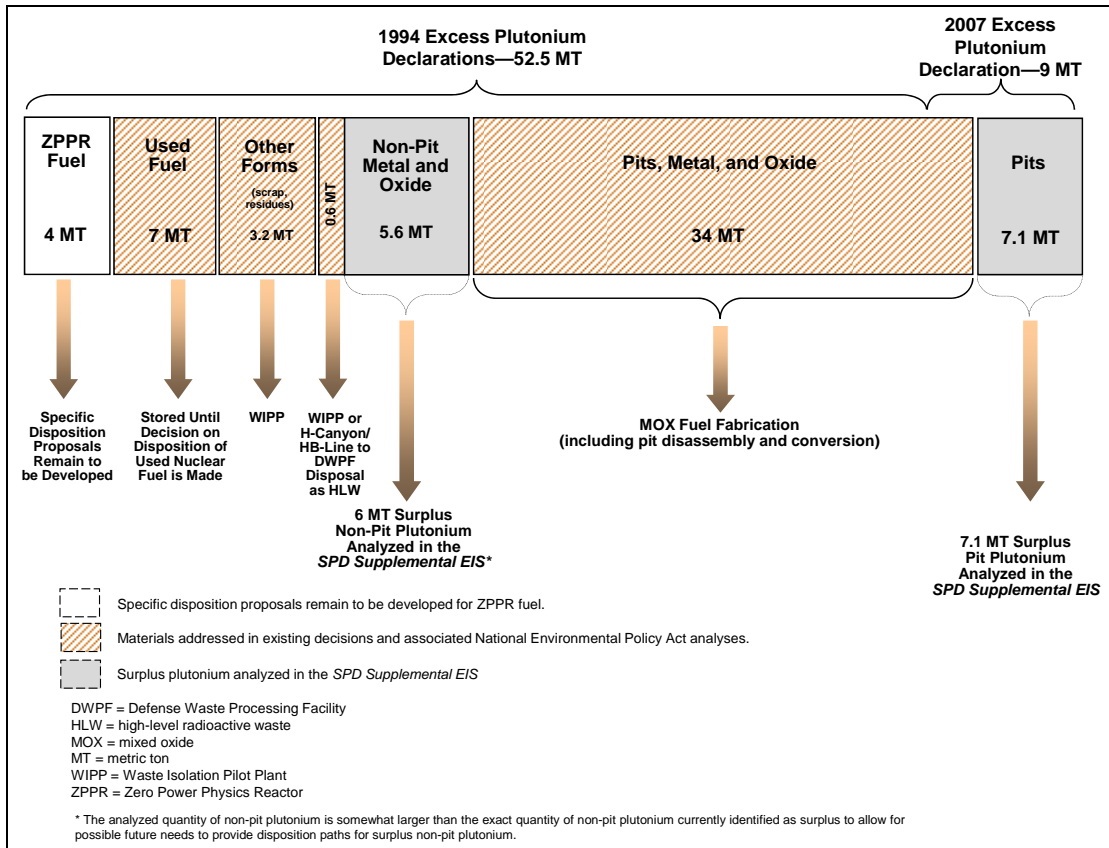
The U.S. has declared 61.5 MT of plutonium to be excess to potential use in nuclear weapons, out of the inventory of 99.5 MT held by the U.S. Government in 1994 after the end of the Cold War.<sup>1</sup> Excess items are stored safely by the DOE and will be transferred to facilities that will prepare the plutonium for permanent disposition. Some plutonium will be used in research or nuclear-energy development programs and others will be disposed with spent fuel. The balance, including more than 50 MT of unirradiated plutonium, is surplus to identified use within DOE.

Figure 1 shows a breakdown of key surplus inventories that are subject of a *Supplemental Environmental Impact Statement for Surplus Plutonium Disposition* (SPD SEIS).<sup>2</sup> The largest inventory is retired weapons components ("pits") that would be permanently disposed through fabrication into Mixed Oxide (MOX) fuel in the MOX Fuel Fabrication Facility (MFFF), under construction at the Savannah River Site (SRS). MFFF fuel will be irradiated in commercial power reactors and later disposed to a high-level waste (HLW) repository or future processing facility. Operation of the MFFF is a key component in the U.S. implementation of a Plutonium Management and Disposition Agreement with the Russian Federation, where each Nation agreed to dispose of 34 MT of weapons-grade plutonium by reactor irradiation to denature the plutonium isotopic composition to where weapons use is impractical.<sup>3</sup>

The MFFF will also accept as feed certain non-pit, impure materials. Up to 9 MT of non-weapons-grade and very impure plutonium will be disposed by other methods. Primary alternatives include packaging for disposal as transuranic waste to the Waste Isolation Pilot Plant (WIPP); dissolving at

SRS with transfer to HLW systems; or alternative immobilization techniques that would provide durable and secure disposal.

**Figure 1. U.S. Plutonium Disposition Inventories**



Disposition feeds include metals, including disassembled pits, and oxides resulting from legacy DOE operations. Metals must generally be converted into oxides before disposition. Oxides must be purified before use in MFFF fuel fabrication. The goals of Plutonium Feed Characterization include confirming the isotopic and chemical properties of metals (for conversion processes) and of oxides (for purification and disposal processes).

## PLUTONIUM OXIDE CHARACTERIZATION

From the beginning of the U.S. program for plutonium disposition in the early 1990s, the Office of Fissile Materials Disposition, within the Office of Defense Nuclear Nonproliferation within the National Nuclear Security Administration (NNSA), has sponsored research to characterize the surplus materials and to determine suitability for planned disposition options. The DOE Office of Environmental Management (DOE-EM) has consolidated most of the material that is expected to be unsuitable for the MFFF at SRS and is developing disposition plans.<sup>4</sup> The Office of Defense Programs is managing surplus materials at the Los Alamos National Laboratory (LANL), and the Office of Nuclear Energy is planning the disposition for key materials located at the Idaho National Laboratory. The Feed Characterization program at SRNL evaluates the nature of the potential feeds for reuse or disposal in support of NNSA, DOE-EM, and the other programs.

About 13 MT of non-pit, unirradiated, surplus plutonium is evaluated in the SPD SEIS. Approximately 8-10 MT of this inventory is in the form of oxides, most of which are impure. A goal quantity of 4.1 MT of these oxides is expected to meet the requirements for direct feed to the MFFF in their current form and is stored (or will be stored) at SRS in compliance with the DOE Standard for Long-Term Storage of Plutonium, DOE-STD-3013.<sup>5</sup>

These "Alternate Feedstocks" (AFS) materials were stabilized and packaged at Rocky Flats Environmental Technology Site (RFETS), Hanford, Lawrence Livermore National Laboratory, LANL, and SRS but very few laboratory data were gathered. The program must demonstrate that AFS materials will meet MFFF feed requirements. If the analysis shows that an item will not qualify as feed to the MFFF, the data can be used to qualify items for one of the other pathways.

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 that are based on process knowledge and supplemental data.
- **Stabilization analyses:** Actinide content, net weights, and processing history were reported as part of the documentation of 3013 stabilization.
- **Laboratory analyses:** Chemical data from an inventory group can be used to predict the distribution of impurities for other members of the group. The Materials Identification and Surveillance (MIS) program maintains archived samples for each inventory group and performs selected Destructive Evaluation (DE) tests for 3013 packages.<sup>6</sup> Pacific Northwest National Laboratory (PNNL) performed selected tests on candidate AFS oxides.<sup>7</sup>

Fewer than 1000 complete analyses are available for approximately 5300 containers that comprise the 13 MT of surplus, non-pit plutonium. However, almost all packaged items fall into one of the major inventory groups and have similar distributions of chemical impurities.

- **Non-destructive assay (NDA):** Packaged oxides and many packaged metals are measured with NDA techniques, either at the time of packaging or later to support the MIS Surveillance program and material control and accountability. Prompt Gamma Analysis (PGA), refined at LANL, proved to be a valuable tool both for disposition characterization and for assurance of safe storage: PGA can measure or detect concentrations of certain elements that are important to both the MFFF and alternative disposition.<sup>8,9</sup>

**Table 1. Inventory Category Descriptions for Disposition Feed Evaluation**

C	Pyrochemical Oxides. The oxides typically contain high chloride levels with Mg/Na ratios less than 1 and Na/Cl ratios between 0.15 and 0.4.
X	Foundry Oxides: These oxides may or may not contain chlorine (>500 ppm) and generally have a ratio of Mg/Na>1.
D	These oxides have high chloride (>1%) but low sodium levels with a ratio of Na/Cl generally less than 0.15. This may indicate the presence of Mg or Ca at higher levels. Often these items also have high fluoride 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 Item Description Codes include U61 and Y61. UH tagged items were hydride processed.
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.
J	Impure mixed oxide scrap produced in support of various fuel or experimental programs.

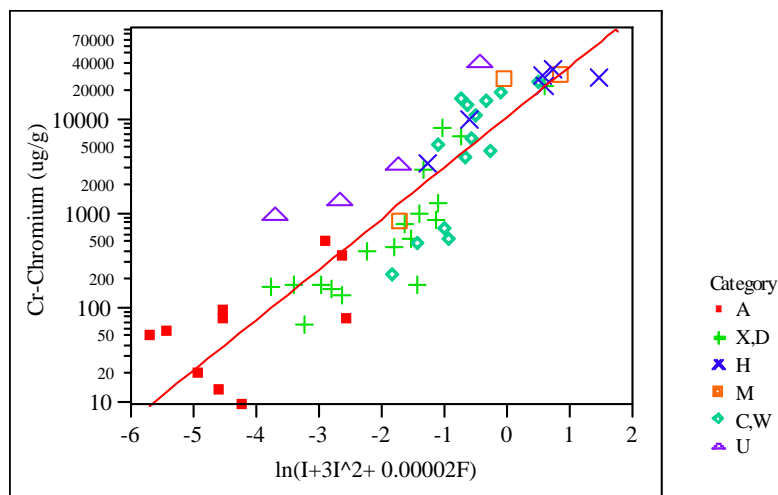
Using all of these tools, SRNL can estimate the chemical composition of each item.<sup>10</sup> Table 2 shows an early statistical projection of impurities across candidate feeds to the MFFF. Because NNSA is aware that laboratory analyses are not available for most items, the primary MFFF impurity limits are based on "most" feed items (i.e., at least 75%) being below a specified limit with "maximum exceptional" (no more than 2%) allowed above a second limit.

**Table 2. Impurities in Impure Plutonium Oxide Feeds**

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

Within each of the process history categories of Table 1, a different distribution is observed. Figure 2 shows a plot for measurements among categories for chromium. The concentration is measured against a factor that is based on the total impurity content (I) and the total fluorine content (F).

**Figure 2. Correlation of Chromium Measurements**



Key components of the analysis program have been reported previously.<sup>11,12</sup> Process history data and limited analyses were sufficient to show suitability for MOX feeds for most elements. Other elements could be confirmed by bounding estimates obtained with PGA.

Since the initial AFS analysis was completed in 2006, the number of laboratory Destructive Analysis measurements has more than doubled and several process categories are more fully represented, as shown in Table 3. However, each analysis's purpose and the details of the each laboratory's techniques raises issues for interpretation and consistency. SRNL is completing a new statistical evaluation of impurities in the different categories of candidates for AFS, together with an analysis of the data sources.

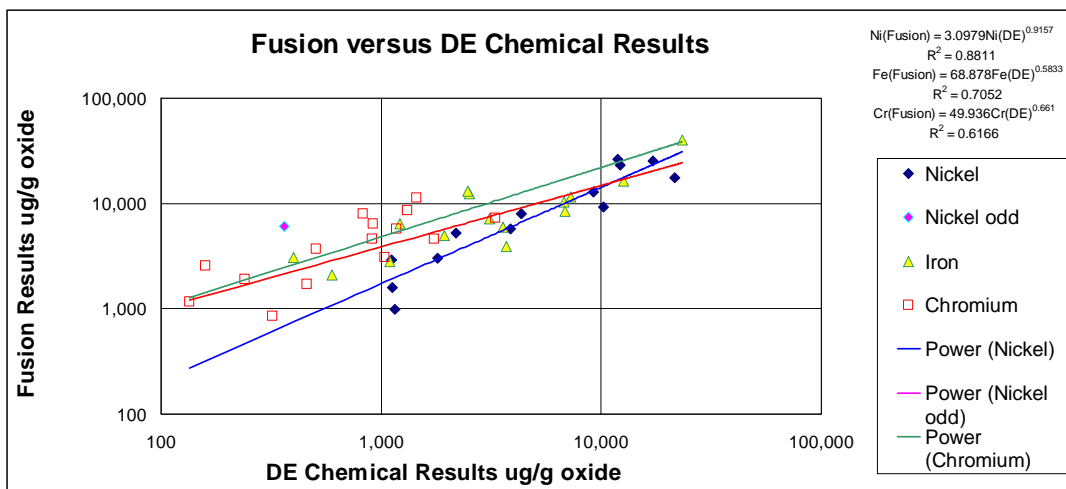
**Table 3. Distribution of Relevant Sample Analyses**

Analysis Source	Process History Category											Sum
	A	C	D	H	J	M	S	U	W	X	New	
Destructive Evaluation	4	26	5	9	3		5	4	5	10	4	75
Field Surveillance	2	6	1	7	2		4	4	2	7		35
MIS Archive	12	5	2	4	4	3	5	4		13	1	53
PNNL		8	2	6		2						18
SRS 772-F Lab					24							24
SRS 772-2F Lab				1	18					2	2	23
Historic	33	26								47	43	149
Basis for 2013 Update	51	71	10	27	51	5	14	12	7	79	50	377
Basis for 2006 Report	37	39	2	6	0	3	4	4	0	59	0	154

An example of the need for interpretation of laboratory data is the varying approaches to the analysis and reporting of undissolved solids. For many studies the "inert" elements in a sample are of lesser importance. The MIS DE program to demonstrate compliance with DOE-STD-3013 initially focused on elements that could lead to corrosion or pressurization that may limit long-term storage.<sup>6</sup> For permanent disposition options such as the MFFF process, the characteristics of the inert residues becomes important. SRNL developed a Peroxide Fusion technique to ensure complete

dissolution.<sup>13</sup> Figure 3 shows how a major component of the initial undissolved solids was explained by oxides of iron, nickel, and chromium.

**Figure 3. Identifying Undissolved Solids from Initial Analyses**



Only 54 of the current analyses are considered "Fusion Quality," i.e., where complete dissolution or its equivalent was achieved. These samples are distributed across the process history categories, as shown in Table 4, which will allow better calibration of the less-complete analysis methods. Calibration is required even for the complete dissolutions to account for reagents added during analysis and impurities present in laboratory equipment, together with the timing impacts of element reprecipitation.

**Table 4. Distribution of Fusion-Quality Sample Analyses**

Analysis Source	Process History Category											Sum
	A	C	D	H	J	M	S	U	W	X	New	
SRNL Fusion	1	3	3	3	1		2	1	2	5		21
MIS X-Ray Diffraction	1	3	1	3		2	2	2			1	15
PNNL		8	2	6		2						18
Basis for 2013 Report	2	14	6	12	1	4	4	3	2	5	1	54

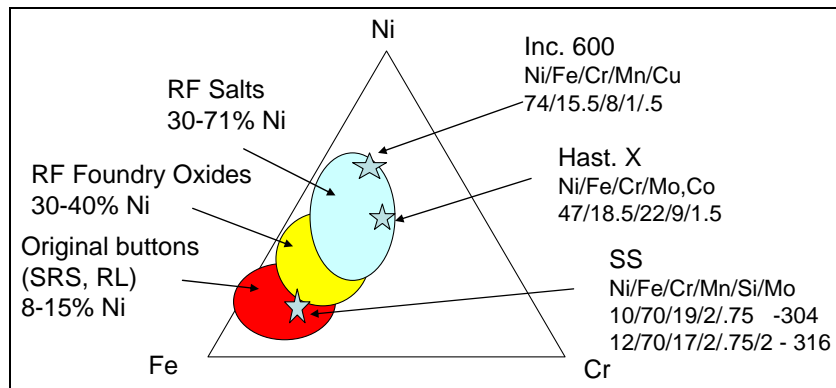
**IMPURITIES RESULTING FROM STABILIZATION AND HANDLING**

For successful flowsheet development and feed screening, it is necessary to estimate the average or individual contribution from the material to complete the material balance on a candidate feed item: The measured actinide contents as oxides, measured impurities, and inferred impurities should represent 100% of the oxide mass. Early in the characterization program, it became apparent that a portion of the impurity mass could not be explained solely from process history estimates, historical data, and NDA. Significant mass had been added to the oxides after they were removed from process lines, handled, stored, and stabilized.<sup>12</sup> During stabilization to DOE-STD-3013, oxides were usually calcined to 950°C. Significant amounts of corrosion products could be introduced through reactions with process equipment, especially if potentially corrosive species were present in the

oxide (e.g., fluorine or chlorine). Up to 3 wt.% of the final oxide mass can consist of the added material.

Stabilization sites used different alloys for equipment used in calcination, as shown in Figure 4. Elemental ratios reported in Fusion-aided analyses are consistent with the ratios predicted for the alloy used at the stabilization site. Table 5 compares the pre-stabilization and post-stabilization analyses for an RFETS item. Other studies show that impurities were picked up during both extended storage (up to 0.5 wt.% from stainless steel). Additional correlations are under study for prior processing in refractory oxides.

**Figure 4. Identifying Undissolved Solids from Initial Analyses**



**Table 5. Corrosion Product Introduction During Stabilization**

	Elemental Composition (ppm)				
	Ni	Fe	Cr	Mn	Mo
Pre-Stabilization	1,269	4,882	1,467	139	49
Post-Stabilization	7,553	5,589	2,930	852	84
Change	6,284	707	1,463	713	35
Composition % for Change	68.3%	7.7%	15.9%	7.7%	0.4%
Composition of Inconel® 600	72.0%	8.0%	15.5%	1.0%	NA

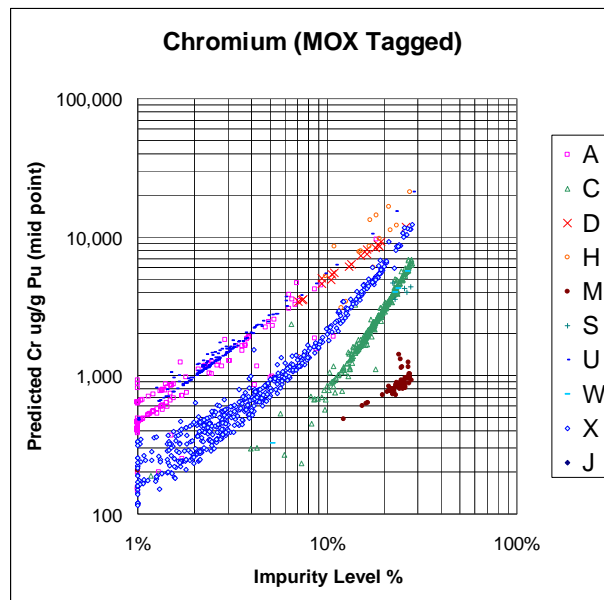
For the rest of the items that did not have laboratory analyses, the 3013 program reported weight gains and losses for furnace trays and boats. The data could not always be associated with a single stabilization run. However, the stabilization records have proven to be valuable in identifying the "missing mass" after the actinide oxides and NDA-measured elements and components are subtracted from the total mass.

Using these tools jointly, SRNL developed a much tighter correlation of measured impurity contents, using a relationship that takes into account the total non-actinide impurity content; the amount of key elements expected in the uncalcined oxide from the feed category; the composition of the alloy used at the stabilization site; and the weight loss from furnace trays and boats.

Figure 5 shows how one element's composition is predicted for items in each oxide category as a function of the total non-actinide impurity level for AFS candidates under current specifications.



**Figure 5. Predicted Chromium Impurity versus Total Impurities**



These predictions are not "proof" for the composition of unmeasured oxides, but the consistent behavior within each category will allow greater statistical certainty in predicting average and abnormal concentrations for proposed feeds.

### **OTHER DISPOSITION PATHS**

The first target for the characterization program was to evaluate oxide items for feed to MFFF. As oxides are produced at LANL from the conversion of pit metal, similar methods have been used, and the specifications for maximum concentrations of transition metals were raised to account for the oxidation of equipment during high-temperature calcination.

The evaluation extends to items that contains even more impurities than the levels allowed for MFFF feed. Different elements may be important for different disposition options.

- Chemical predictions support Acceptable Knowledge documentation for disposal of selected materials for disposal to WIPP as transuranic waste. Elements of importance to the WIPP Waste Acceptance Criteria include beryllium (readily measured by PGA) and carbon (measured or determined following high-temperature calcination of oxide).<sup>14</sup>
- Halide content is important for oxides and metals considered for disposal or processing by dissolving in H Canyon for disposal to HLW or for purification into feed for MFFF.<sup>9</sup> Fluorine is measurable at very low levels by PGA and a combination of process knowledge and measurements determines chlorine content. In some cases, better knowledge of impurities at levels beyond the MFFF limits can support methods for partial purification, allowing greater leeway in choosing the most effective disposition pathway.

## CONCLUSIONS

A wide range of techniques are needed when DOE evaluates surplus plutonium for its suitability for different disposition paths. These techniques benefit not only the MOX program but also the processes that will be used for plutonium that is not suited for that program. Expertise at SRNL, LANL, and other sites is key to the success of disposition for up to 61.5 MT of U.S. plutonium that will be removed permanently from the potential use in weapons programs and for other plutonium that will be disposed worldwide in international nonproliferation programs.

Advances in laboratory tools (including Prompt Gamma Analysis and Peroxide Fusion) provide much tighter characterization of stored plutonium, demonstrating compatibility of more excess items with the disposition paths and avoiding additional, costly sampling and destructive analysis.

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