Characterizing Surplus US Plutonium for Disposition – 13199

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ABSTRACT

The United States (US) 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. 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 (OFMD) of the National Nuclear Security Administration (NNSA) and the DOE Office of Environmental Management (DOE-EM). SRNL manages a broad program of item tracking through process history, laboratory analysis, and non-destructive assay. A combination of analytical techniques allows SRNL to predict the isotopic and chemical properties that qualify materials for disposition through the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF). The research also defines properties that are important for other disposition paths, including disposal to the Waste Isolation Pilot Plant (WIPP) as transuranic waste (TRUW) or to high-level waste (HLW) systems.

INTRODUCTION

The US 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 US Government in 1994 after the end of the Cold War, as shown in Fig. 1.

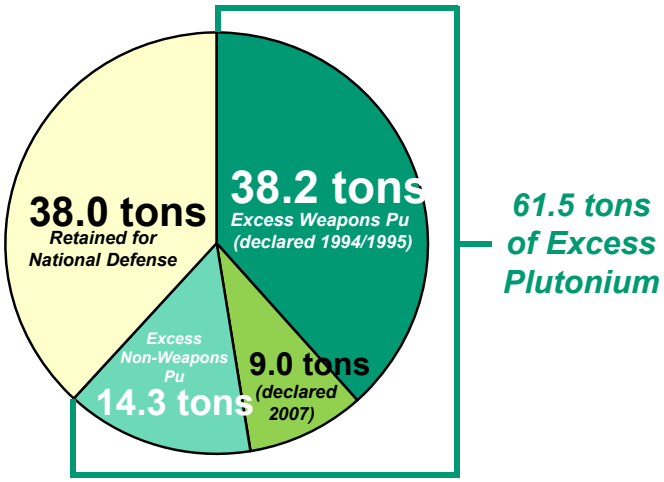

Fig. 1. Excess US Plutonium

Excess items are stored safely by the DOE and will be transferred to facilities that will prepare the plutonium for permanent disposition. A portion will be used in research or nuclear-energy development programs and some items will be disposed as low-level waste or with spent fuel. The remainder, including plutonium removed from retired weapons, is surplus to identified use within DOE. It will be managed in

various ways: (1) using the MFFF, under construction at the Savannah River Site (SRS), where the plutonium will be converted to fuel that will be irradiated in commercial power reactors and later disposed to a HLW repository or future processing facility, as used fuel; (2) packaging to the WIPP acceptance criteria for disposal as TRUW; (3) dissolving at SRS and transfer to HLW systems, also for disposal; or (4) alternative immobilization techniques that would provide durable and secure disposal.

Most of the excess plutonium resides as "pits," components from dismantled weapons, at the Pantex Plant in Amarillo, Texas. Non-pit plutonium includes at least 13 MT of metals, oxides, and lower grade materials, stored primarily by DOE-EM in DOE-STD-3013 containers at SRS, in Aiken, South Carolina, awaiting permanent disposition. DOE developed the "3013" Standard to assure safe storage of plutonium-bearing materials for 50 years or longer, if necessary.[1]

NNSA and DOE are completing a *Surplus Plutonium Disposition Supplemental Environmental Impact Statement* (SPD SEIS) that describes plans for permanent disposition of the pit and non-pit plutonium.[2] The preferred alternative for the bulk of the material is fabrication into MOX fuel in the MFFF. This preferred alternative recognizes the goals of the US-Russian Plutonium Management and Disposition Agreement (PMDA) where each Nation agreed to dispose of 34 MT of weapons-grade plutonium by reactor irradiation to denature plutonium isotopic composition to where weapons use is impractical.[3]

Fig. 2 shows potential disposition paths for the 34 MT and for material that does not qualify for disposal under the PMDA.

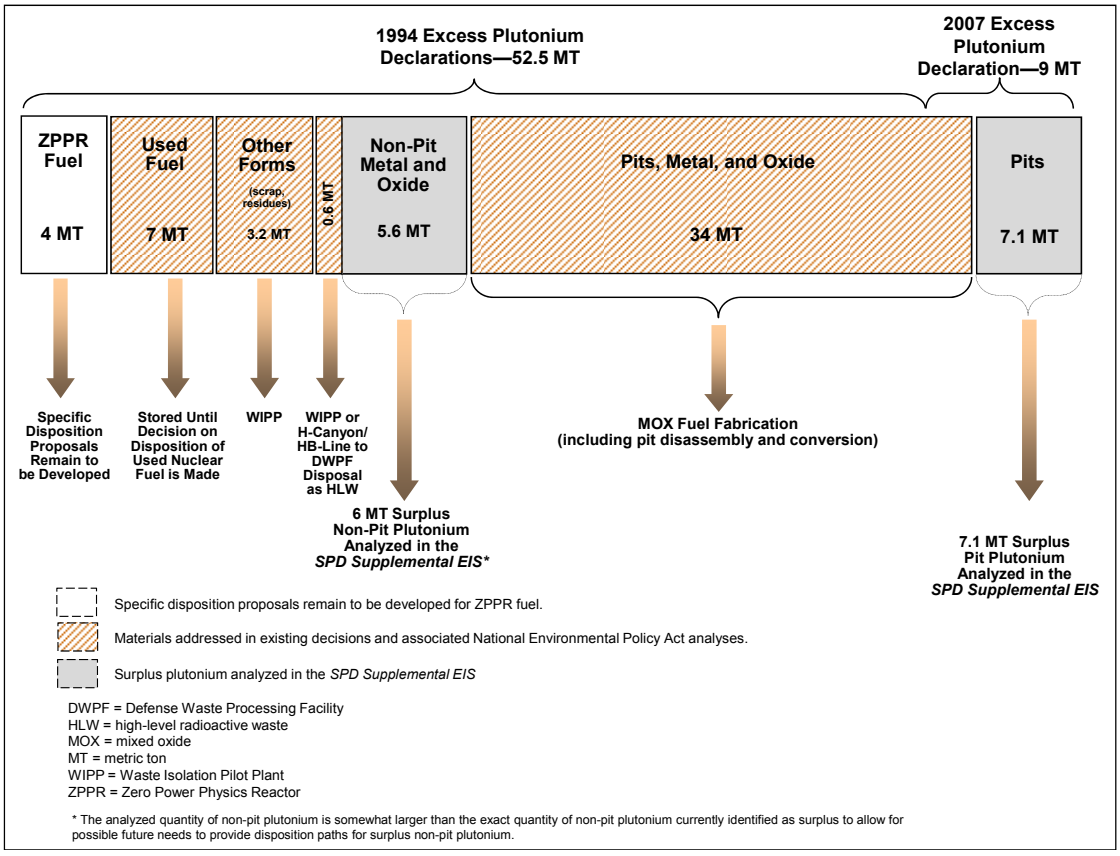

Fig. 2. US Plutonium Disposition Inventories

From the 61.5 MT of excess plutonium, at least 41.1 MT is likely to prove suitable for MOX fuel fabrication. Up to 9 MT of non-weapons-grade plutonium and very impure plutonium will be disposed by other methods, including disposal to WIPP as TRUW or by codisposal with HLW. The SPD SEIS will evaluate optimum pathways for approximately 6 MT of non-pit metal and oxide, which could include processing to meet MFFF requirements or processing for disposal.

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 oxides (for purification and disposal processes).

PLUTONIUM CHARACTERIZATION FOR DISPOSITION

From the beginning of the US program for plutonium disposition in the early 1990s, OFMD has sponsored research to characterize the surplus materials and to determine suitability for planned disposition options. The Feed Characterization program at SRNL evaluates the nature of the potential feeds for reuse or disposal in support of OFMD and DOE-EM.[4] SRNL also provides key support for the storage-container Materials Identification and Surveillance (MIS) program, where characterization data were gathered when items were stabilized for interim storage and continue to be gathered to support safe longer term storage.[5]

Pit Materials and Non-Pit Metals

The chemical properties of pits are important to disassembly and conversion. These items were highly characterized when they were fabricated for the nuclear stockpile. The primary challenge for chemical characterization is to identify which items may contain residual species, such as chlorides, that could complicate purification processing. A portion of the non-pit metals have higher amounts of impurities that would impede purification, and cannot be used by the MFFF.

The isotopic properties are important for fuel fabrication. The pits were fabricated over a time span of nearly 50 years and have different isotopic compositions that are age-dependent. Historical "data mining" for the characteristics and date of fabrication are gathered to support MFFF in its preparation of fuel charges for the commercial reactors. Non-weapons-grade material cannot be used directly by the MFFF, and disposition processes that require conversion to oxide require further chemical data.

Non-Pit Oxide Materials

DOE and MFFF will have the opportunity to analyze the oxides resulting from metal conversion before they are fed to purification processes. This opportunity does not exist for many of the non-pit oxide materials, which will be transferred directly to the MFFF. Therefore, characterization must focus on the interpretation of existing data.

Early designs for the MOX process included the receipt of "clean" oxide from the conversion of pits. In 2002, NNSA announced the modification of the MFFF design to accept impure oxides as well. Impure materials were stabilized into oxides as part of the 3013 programs at Rocky Flats Environmental Technology Site (RFETS), Hanford, SRS, Los Alamos National Laboratory (LANL), and Lawrence Livermore National Laboratory. In most cases there are no laboratory analyses for these oxides, and data taken during stabilization focused on safety for long-term storage. A major goal for further characterization is to analyze

these materials for their suitability as feed for the MFFF, and if they do not qualify for the MFFF, to compile data that are important to alternative disposition paths.

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 I shows the primary broad categories that are based on process knowledge and supplemental data.

TABLE I. 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.

- **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 MIS program maintains archived samples for each inventory group and performs selected Destructive Evaluation (DE) tests for 3013 packages.

  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 paths.[6]

Fig. 3 shows a typical PGA spectrum. In addition to the elements shown, it identifies other light elements including aluminum, beryllium, and magnesium.

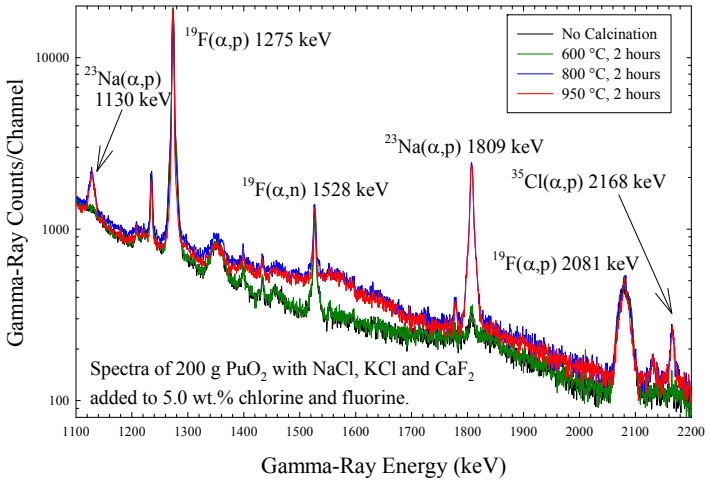

Fig. 3. Prompt Gamma Analysis Spectrum

Using all of these tools, SRNL is able to estimate the chemical composition of each item. Table II shows an early statistical projection of impurities across candidate feeds to the MFFF.[7] 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 II. Statistical Projections of Impurities in Impure Plutonium Oxide Feeds

Element	Specification for 75% of Feed Items	Predicted Percentage of Items Below Stated Concentration (µg/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. Fig. 4 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).

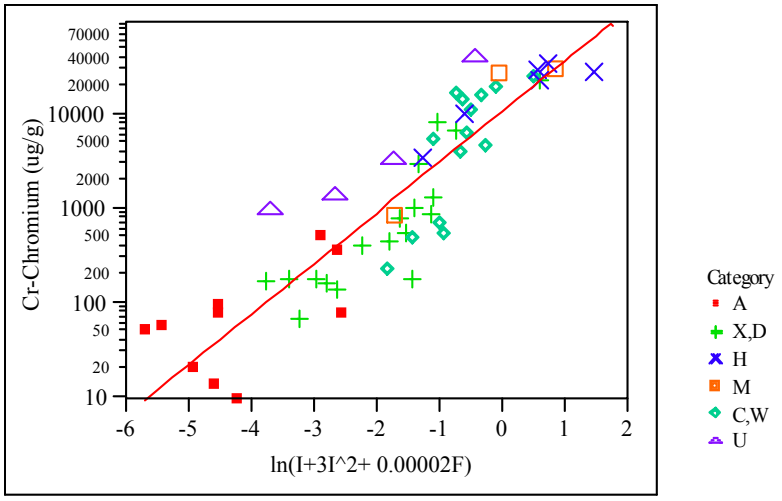

Fig. 4. Correlation of Chromium Measurements

During early characterization, it became evident that there was a component of the total impurity weight that was not fully represented from historical data on the original items or by PGA. SRNL determined that this "missing" material was explained by the introduction of corrosion products during stabilization, where oxides were usually calcined to 950°C. Studies showed that significant iron, nickel, and chromium were introduced through reactions with process equipment. The quantities correlated with the presence of potentially corrosive species (e.g., fluorine and chlorine) and the composition of equipment used at each stabilization site. The 3013 stabilization records reported weight gains and losses for furnace trays and boats, and mining of this data allowed even greater accuracy in predicting the approximate composition of oxide materials as currently packaged. Fig. 5 shows the potential corrosion-product composition for various alloys used in calcination, versus compositions that are typically measured in oxides produced from RFETS foundry metals and from fresh plutonium buttons produced at SRS and Hanford.

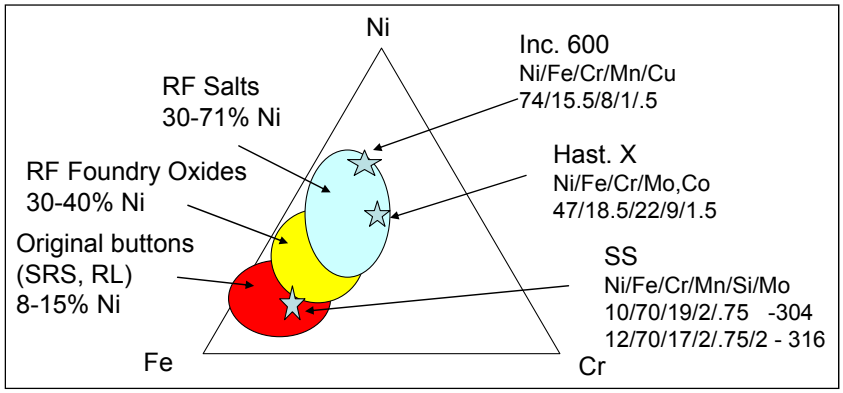

Fig. 5. Corrosion Product Distributions

The MIS DE program provided laboratory analyses for the contents of selected oxide containers. The goals of this program are primarily to assure safe storage, and initially many of the measurements did not analyze stable, undissolved solids. SRNL developed laboratory techniques using sodium peroxide fusion to enable complete dissolution and analysis.[8] Fig. 6 shows that the transition-metal impurities made a significant

contribution to the "stable" impurities, which do not have a significant impact on safe storage but are important to any program that plans to dissolve the material.

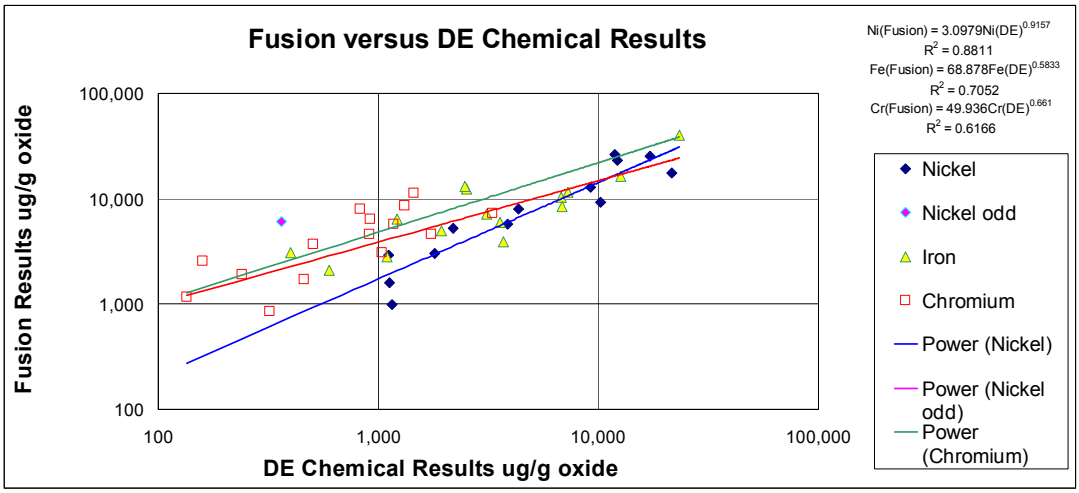

Fig. 6. Analyses of Corrosion Products Before and After Fusion Treatment

Using these tools jointly, SRNL developed a much tighter correlation of measured impurity contents. Fig. 7 shows a plot of chromium content predictions using a correction factor that adds the total corrosion product impurities, concentration of the elements in the containers used by the stabilization site, and weight loss from furnace trays and boats as a fraction of powder mass.

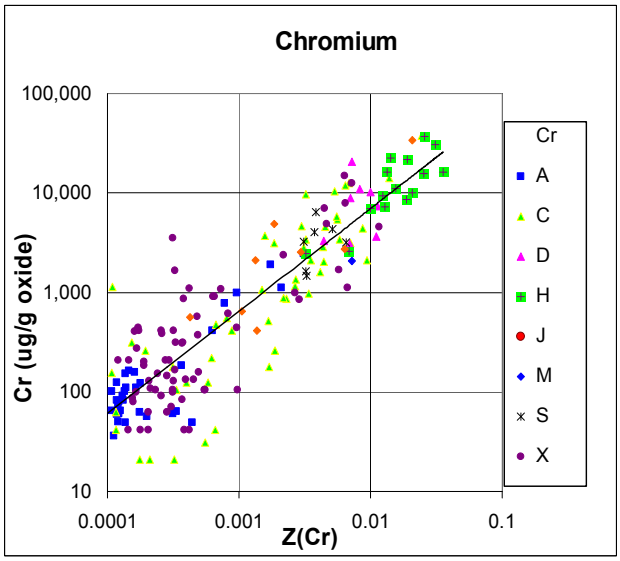

Fig. 7. Chromium Measurements with Corrosion Products

The "Z" factor is based on the following equation; analogous equations apply for Fe, Ni, Mo, Cu, Mn, and Co.

$$Z_{Cr} = I*K*(C_{CrI600*}N' + C_{CrSS*}(1-N')) + (C_{Crtray})*W^{1.2} \quad \text{(Eq. 1)}$$

Where:

- Z_{Cr} is the expected Cr content as a fraction of the oxide feed mass.
- I is the non-actinide impurity content as a fraction of the oxide feed mass.
- K= (Fe+Cr+Ni), the ratio of corrosion products to total impurity in the feed category.
- N= Cr/(Fe+Cr+Ni), the ratio of Cr to Fe+Cr+Ni for the feed category.
- N' is the fraction of Inconel® 600 mixed with stainless steel to obtain N.
- W= weight loss from tray (Hastelloy® X or Inconel 600) as fraction of powder mass.
- C = Concentration of chromium in various alloys.

Fig. 7 shows improvements over Fig. 4 in three ways: (1) The data set is more than two-fold larger, including new analyses from the 3013 DE program; (2) Chemical data are adjusted for complete dissolution using fusion, which in the case of chromium increased the estimated concentration by up to a factor of four; and (3) The more sophisticated scalar takes into account total impurities, historical tray-weight changes, and prompt gamma data, with calibration factors that are unique for each feed category. Used together with the factors for other elements; radioisotope and mass measurements; PGA; and category assignments based on process history data, all major contributors to impurity mass are identified.

Fig. 8 shows how the modified predictions are used to estimate the chromium content for a variety of items that are expected to be suitable as feed for the MOX process.

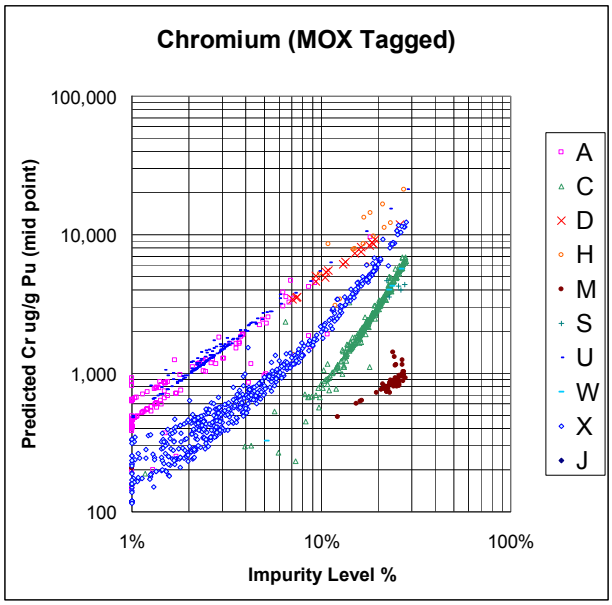

Fig. 8. Predicted Chromium Impurity versus Total Impurities

Other Disposition Paths

Although the boundaries for the characterization program focused on evaluating items for disposition through the MOX cycle, different criteria are used for the evaluation of materials for other disposition pathways. In particular:

- Chemical predictions support Acceptable Knowledge documentation for disposal of selected materials for disposal to WIPP as TRUW. 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 materials in air during 3013 stabilization). Priorities for processing material for disposal also depend on optimizing storage efficiency and on the potential for container degradation.[9]

- 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. Fluorine is measurable at very low levels by PGA and a combination of process knowledge and measurements determines chlorine content. SRNL is developing processes, including Vacuum Salt Distillation, that would remove halides prior to processing or to assure complete dissolution of candidate feeds.

- Plutonium isotopic composition governs suitability for the MOX cycle and also affects options for other disposition paths. The MFFF places limits on the uncertainties in isotopic measurements to enable it to manage the isotopic content of fabricated fuel. Existing or new NDA measurements are used to improve the data on packaged materials and historical data are used to characterize pit feeds to PDC.

- Existing data are used to evaluate potential recovery of byproduct isotopes, including enriched uranium; americium; and neptunium.

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 US 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 treatments) 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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