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Identifying Impurities in Surplus Non-Pit Plutonium Feeds for MOX or Alternative Disposition

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ABSTRACT

This report provides a technical basis for estimating the level of corrosion products in materials stored in DOE-STD-3013 containers based on extrapolating available chemical sample results. The primary focus is to estimate the levels of nickel, iron, and chromium impurities in plutonium-bearing materials identified for disposition in the United States Mixed Oxide fuel process.

BACKGROUND

A key component of United States program for the disposition of surplus, weapons-usable nuclear materials is the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF), under construction at the Savannah River Site (SRS). This facility, sponsored by the Department of Energy (DOE) Office of Nuclear Nonproliferation, Office of Fissile Materials Disposition (OFMD), will accept plutonium oxides, dissolve and purify them, and fabricate MOX fuel that will be irradiated in civilian power reactors. Many of the early feeds planned for the MFFF were stabilized from materials that remained in inventory at DOE production sites following the end of the Cold War.¹

The feed items have been stabilized to meet the requirements of the DOE Standard for long-term plutonium storage, DOE-STD-3013, and are stored at SRS pending disposition. The DOE Integrated Surveillance Program (ISP),² operated by the Office of Environmental Management, groups items by characteristics that may be important for safe storage, such as the potential for container corrosion or pressurization. However, only limited data are available on other impurities that may be important to MFFF in operating their Aqueous Polishing dissolving and purification process.

When DOE evaluates items against chemical specifications for feed to the MFFF, composition projections must be constructed using "process history" categories; non-destructive data such as Prompt Gamma Analysis taken on stabilized oxides; and results from a limited number of laboratory destructive evaluation (DE) analyses on similar items. The use of the DE analyses is problematic if dissolution was not taken to completeness: Sufficient data were obtained to demonstrate stability for storage, but the character of undissolved solids was unresolved.

The concentrations of many process chemicals are estimated well by prompt gamma techniques³ and by correlations, but legacy materials also contain products from the corrosion of process equipment. Transition metal elements such as iron (Fe), nickel (Ni), and chromium (Cr) are important to Aqueous Polishing flowsheets because they are typically difficult to dissolve, can plug

filters, and can enhance corrosion of MFFF equipment. Estimating their concentrations is complicated by the fact that they can be introduced either in the original process or during stabilization to DOE-STD-3013, e.g., items with the same process origins may differ according to which DOE site performed the high-temperature stabilization.

This paper demonstrates that the use of weight loss data from stabilization furnace pans can be used to approximate corrosion-product impurities. Combined with additional data and correlations with production-process origins, they provide a useful method to estimate the concentration of anticipated impurities. Some of the data used in the analysis are preliminary and unpublished, and therefore results may shift when further and updated data become available.

SUMMARY

Equations to predict the expected levels of nickel, iron, and chromium were developed so that, for a given material category; total impurity level; and prompt gamma impurity fingerprint, the predicted values would match those found based on chemical analysis of more than 200 samples representing materials packaged to DOE-STD-3013. About half of the samples support the ISP and were chosen as bounding for a wide variety of feed materials. The other samples represent historic production activities, principally at Rocky Flats.

Each source of Ni, Fe, and Cr was incorporated into a model that recognizes the fact that the concentrations of Ni, Fe, and Cr found in plutonium materials produced in aqueous processes closely match those of stainless steel or nickel alloys used in the process equipment. As materials are exposed to further processing they are increasingly exposed to Inconel[®] and Hastelloy[®] alloys, resulting in higher levels of nickel. However, the level of corrosion products in the materials found in packaged oxides is much higher than expected based solely on the original process history. The best explanation is that significant levels of impurities were introduced by the corrosion of the Inconel and Hastelloy furnace trays used in stabilization to the Standard. The model assumes the degree of impurity pickup during stabilization can be estimated from tray weight changes during stabilization, when available, and from empirical and theoretical corrosion rates in the presence of corrosives such as chloride, magnesium chloride, and fluoride compounds. The current analysis spans 1366 items packaged at Hanford (RL), Rocky Flats (RF), and SRS that had previously been tagged as potentially MOX-suitable material.

Preliminary results ($\mu\text{g/g Pu}$) are shown in Table 1. Current feed criteria for the MFFF require that fewer than approximately 2% of the items should have Ni, Fe, or Cr levels greater than the "<98%" limit and fewer than 25% of the items should have levels greater than the "<75%" limit. Items outside these guidelines may still be accepted for MOX processing after further analysis. "Predicted Values" are based solely on the least-squares line fit with no correction for the uncertainty of the fit or for the variation of individual items around the fitted line. In reality, each predicted value is an expected or median value from a distribution of possible values. The impact of introducing the variability for individual items is reflected under "Model Predictions."⁴ For instance, 50% of the items are expected to have Ni content below 1,750; 75% fall below 4,650; etc. Predictions using this more-representative method for uncertainties suggests that the MFFF limits could be exceeded. An even more representative approach would be to introduce the uncertainty of the linear fit. The last line of Table 1 illustrates this approach to determine upper limits for the 98th percentiles of Ni, Fe, and Cr with 90% confidence.

	Concentration ($\mu\text{g/g Pu}$)		
	Ni	Fe	Cr
MOX Limits			
<75%	5,000	5,000	3,000
<98%	15,000	18,000	8,000
Descriptive Statistics of Predicted Values			
Median	1,491	2,152	869
Mean	2,439	3,402	1,331
<75%	2,913	4,106	1,620
<98%	11,505	15,450	5,831
Model predictions			
<50%	1,750	2,600	1,050
<75%	4,750	6,250	2,750
<90%	11,000	13,250	6,250
<95%	17,500	20,500	10,000
<98%	27,500	31,500	17,000
Model predictions at 90% confidence			
<98%	36,000	38,500	22,500

Table 1. Preliminary Results

CATEGORIES

Tables 2 and 3 show how materials were grouped into ten category bins. Binning was primarily based on site-specific categories, generally referred to as IDCs (Item Description Codes), but used other information such as the prompt gamma results, which provide an indication of total content for some impurities (Al, Be, Cl, F, Mg, Na, and K). Hanford materials originally from Rocky Flats were classified by prompt gamma because the direct traceability to the original Rocky Flats IDCs has been lost. Additional categories or sub-categories may be developed as analysis proceeds.

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 IDCs 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.

Table 2. Category Definitions

Category	RF IDCs	RL MIS	SRS MIS
A	080, 081, 082	1B, 1C, 2D(300)	1C
AG or AH		1G, 2A	
C	067, 086 (not D)	IE (Cl>1, Na/Cl>15)*	
H		2B	without U(2B)
M	54	1F, 2F	
S	062, 065, 289		
SC	159		
U	Y61, U61, 256	2E	1B
X	057, 060, 061, 145, 653	IE (Cl<1), 1A, 1D	without U(3,1A,1D,1E)
D	X or C with Na/Cl<0.15, Cl>1	IE (Cl>1, Na/Cl<.15)	
W		IE (Washed)	
JA, JD, JU		2D(not 300)	without U(3,2A,1F,1D, 2B)

Table 3. Category Mapping

DATA

Chemical analysis results are available for a limited number of DOE-STD-3013 items from four principal sources. These sources include the ISP DE program, Pacific Northwest National Laboratory (PNNL) analyses performed for OFMD,⁵ Materials Identification and Surveillance (MIS) analyses performed at Los Alamos National Laboratory (LANL), and historic sample results from similar items processed at Rocky Flats. Another source, sample results on items packaged at SRS, will be analyzed separately because few of the sampled materials were MOX-tagged. With the exception of fifteen DE samples where sodium peroxide fusion was performed and the PNNL samples where caustic fusion was performed, the results reflect incomplete dissolution of the feeds. Table 4 provides a summary showing what categories are represented by the sample sources.

Category	Data Set				Total
	DE	PNNL	MIS	RF Old	
A	5		4	34	43
C	17	6	5	26	54
D	4	2	2		8
H	8	6	1		15
M		2	1		3
S	3		4		7
U	4		4		8
X	8		12	48	68
Total	49	16	33	108	206

Table 4. Sample Sources Versus Categories

ESTIMATING UNDISSOLVED SOLIDS

There is substantial evidence (e.g., material balance, Scanning Electron Microscopy and X-Ray Diffraction results, reported undissolved solids) that the chemical results reported by the MIS and DE programs under-report some elements, including Cr, F, Fe, Ni, Si, Ta, and W. In fact, complete dissolution is rare. This conclusion is supported by dissolutions aided by sodium peroxide fusion treatments following fifteen DE runs. A simple equation compares the reported DE results with the

better fusion results: $C_{\text{fusion}} = C_{\text{solution}} / ((1-u)e)$, where C_{fusion} equals the concentration found via fusion, C_{solution} equals the reported DE chemical concentration, u equals the fraction of undissolved solids, and e equals the dissolution efficiency. The efficiency factor e would equal 0.5 if twice as much of an element's mass was left behind in the heel. The most-difficult-to-dissolve element would have the lowest the value of e . Average values found for e for Ni, Fe, and Cr are, respectively, 0.88, 0.52, and 0.24. Figure 1 show the results of a least squares fit comparing the DE solution results for iron, nickel, and chromium with the fusion results.

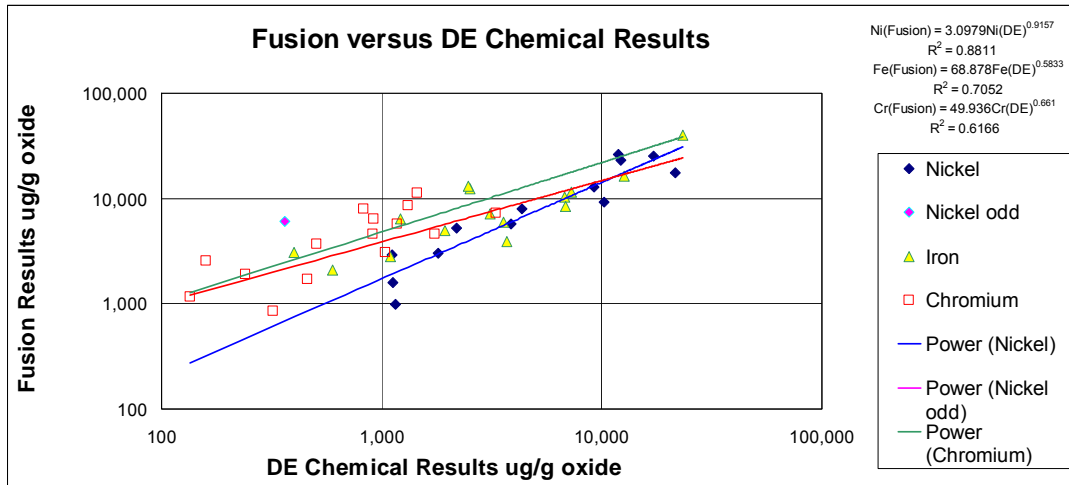


Figure 1. Fusion Versus DE Results for Nickel, Iron, and Chromium

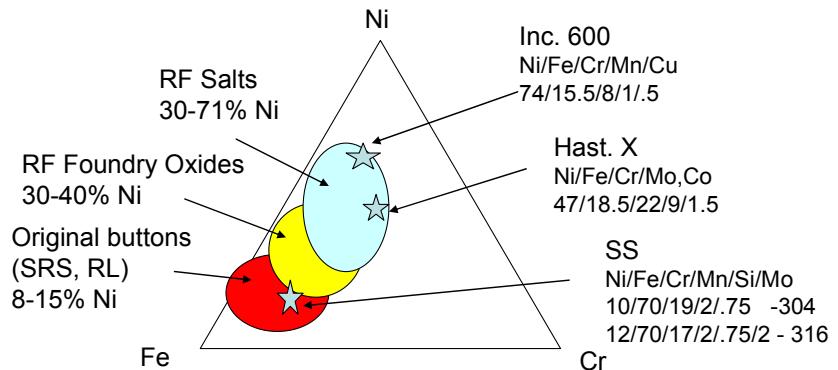
Less mass was found dissolved in solutions than remained in the heels, with chromium the least-soluble element. Although not shown in the plots, an expected relationship was observed between dissolution efficiency and levels of complexants like aluminum.

CORROSION PRODUCT MODEL

The corrosion model assumes that the impurity levels for Fe, Ni, Cr and other elements (Co, Mo, Mn, etc.) can be explained by pickup of these impurities from metal alloys such as stainless steel, Inconel, and Hastelloy used in the production and stabilization processes. The nickel content (as fraction of Ni + Fe + Cr) of the materials initially purified averaged 15.2% at Savannah River Site and 8.8% at Hanford. For comparison, Type 304L stainless steel averages 10.3% and Type 316 stainless steel averages 12.6%. The category of feed materials designated as A (those associated with the aqueous process) should have a composition of Fe, Ni, and Cr that approximates stainless steel. Similarly, category H represents impure aqueous produced residues. Rocky Flats aqueous-produced IDC 080 gave results similar results and the Fe, Ni, and Cr content averaged, respectively, 8.7%, 11.3%, and 80%. The Fe + Ni + Cr content as a percentage of total impurities was typically around 30% for freshly made buttons. Given this correlation and the expected composition as discussed above, one can predict Fe, Ni, or Cr content for a given percentage of total impurity.

As the materials were processed, exposure to equipment with higher nickel content (assumed to be Inconel 600) increased. As the level of processing increased, the nickel content increased and the iron content decreased. This principle is evidenced in the average composition of foundry oxides (category X)⁶ and pyrochemical salts (category C). Foundry oxides averaged 30% nickel (as percent

of Fe + Ni + Cr) before calcination and 40% after calcination. Pyrochemical salts averaged 30% before calcination, 65% after the first calcination, and 70% after the second calcination, shown by increasing nickel content in proportion to exposure to Inconel pans and brushes. The inset figure provides a generalization using a ternary diagram showing the Fe, Ni, and Cr content of process materials. The expected nickel content is bounded at the lower end by stainless steel, in the case of aqueous produced feeds, and at the upper end by exposure to Inconel and Hastelloy materials, as in the case of pyrochemical salts.



Perhaps a more significant source of nickel than the process equipment used during production processing is that Inconel and Hastelloy trays that were used for stabilization of the 3013 materials at high temperatures (950 degrees C). The total corrosion product content based on DE program results shows that the Ni, Fe, and Cr contents is often an order of magnitude higher than would be expected based on process history alone. Although tray weight loss information is available in many cases, principally for Rocky Flats items, oxidation of the trays is a complex process where an increase or decrease in the tray mass for a given run may not be directly correlated to the corrosion product loss to the oxide during stabilization. To account for this fact, the weight loss for each run was estimated from a combination of the individual tray weight loss, the series tray weight loss, empirically measured weight loss for trays having the same level of corrosive impurities, and oxidation-rate data. The presence of chloride greatly increases the corrosion rate and presence of magnesium chloride increases it even more; a Hanford study⁷ reported that the corrosion rate for trays with magnesium chloride present is three times higher than if only chlorine were present. For Rocky Flats items without chloride detected by prompt gamma, the tray weight loss (as a percentage of the plutonium material mass) ranged from 0.2% (where no Mg or Na was detected) to 0.6% where both were detected. For materials with chloride, the losses ranged from 0.3% where Mg was less than 2500 ppm to 0.9% for salts with Mg greater than 2500 ppm. At Rocky Flats, Hanford, and SRS the oxidation tray material was respectively, Inconel 600, Hastelloy X, and Inconel 690. Of these, the latter is much less corroded in a chloride stabilization environment. The tray weight losses using Hastelloy X are lower for runs without chlorides but higher for runs with fluorides. At Hanford, the losses were typically 0.25% where both chloride and fluoride were not detected and ranged to as high as 3% where high levels of fluoride (< 2%) were detected. Higher corrosion rates with magnesium chloride were observed at both Rocky Flats and Hanford.

High-temperature corrosion studies⁸ indicate that the relative corrosion rates for the three common alloys would be similar to those discussed above. Lai (98) reports the corrosion rates (mg/cm²) for Inconel 601 (similar to Inconel 690), Hastelloy X, and Inconel 600, when exposed to an environment of Ar-20% oxygen-0.25% Cl for 400 hours at 900 degrees C, to be respectively 20.67, 54.41, and 72.08. He reports (175) similar corrosion rates, respectively 2.6, 3.8, and 7.7 mils, for materials exposed to a NaCl bath at 840 degrees C for 100 hours. In an HCl environment, Lai (102) notes that "molybdenum-containing Ni-Cr alloys," e.g., Hastelloy X, performed better than those without

molybdenum, e.g., Inconel 600. Regarding exposure to HF at elevated temperatures, Lai (110, 112) observed: "Nickel is the most resistant among the alloys tested" and "Chromium was found to be detrimental to resistance to corrosion by HF for Ni-Cr alloys." In the case without chloride or fluoride, Lai (24) reports that cyclic oxidation rates at 980 degrees C for 1000 hours for both Inconel 600 and Inconel 625 (similar to Hastelloy X) were very low. Extrapolation from the chart would result in a negligible loss for Inconel 625 and with a weight loss around a 0.1% for Inconel 600. Static oxidation tests at 980 degrees C showed the same low corrosion rate for all three alloys.

Given the methodology for estimating tray corrosion rates, the overall material balance for each sample, and the fact that MIS samples were stabilized in ceramic trays, the contribution of corrosion products from the Inconel and Hastelloy tray loss was found to be proportional to the projected tray weight loss to the 1.2 power. This relationship was confirmed with molybdenum (9% of Hastelloy X) and cobalt (1.5% of Hastelloy X), where levels were highly correlated ($R^2 = 0.78$) with the nickel content for Hanford materials. Further, both Mo and Mn declined with higher nickel levels in Rocky Flats items, as expected because neither element is present in Inconel 600, but may have been used in stainless steel alloys.

Finally, a model was developed that assumes three sources of nickel, from stainless steel and Inconel 600 materials used during production and from the various tray materials used in 3013 stabilization. The following equation was used to estimate the nickel content based on the material category, total impurity level, prompt gamma impurities, and the tray weight loss during oxidation.

- $Z_{Ni} = I * K * (C_{Ni600} * N' + C_{NiSS} * (1 - N')) + (C_{NiTray}) * W^{1.2}$
- Where
 - Z_{Ni} is the expected Ni content as a fraction of the oxide feed mass.
 - I is the non-actinide impurity content as a fraction of the oxide feed mass.
 - $K = (Fe + Cr + Ni) / I$ that is the ratio of corrosion products to total impurity.
 - $N = Ni / (Fe + Cr + Ni)$ that is the ratio of Ni to Fe + Cr + Ni.
 - 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 nickel in various alloys.
 - Analogous equations apply for Fe, Cr, Ni, Mo, Cu, Mn, and Co.

Values used for N and K vary according to the feed category. K varies with the total impurity level and is low for categories A, X, S, and C; medium for categories D and U; and high for category H. N is low for categories A, X, and S (without Cl); medium for categories D and U; and high for categories C and S (with Cl) or for category U items from hydride operations.

RESULTS

Assuming a log-log relationship, the equations of Table 5 predict the impurity levels. Laboratory results correlate strongly ($R^2 \geq 0.80$) with the estimated Ni, Fe, and Cr levels resulted for all material categories and for every sample source. Figure 3 shows this correlation for nickel, while Figure 4 shows similar results for iron and chromium.

$$\begin{aligned}
 \text{Ni} &= 707,248 Z_{\text{Ni}}^{1.0277} & R^2 &= 0.87 \\
 \text{Fe} &= 403,642 Z_{\text{Fe}}^{0.9265} & R^2 &= 0.84 \\
 \text{Cr} &= 676,825 Z_{\text{Cr}}^{1.0049} & R^2 &= 0.80 \\
 \text{FeCrNi} &= 584094 Z_{\text{FeNiCr}}^{0.9642} & R^2 &= 0.88
 \end{aligned}$$

Table 5. Prediction Equations for Ni, Fe, and Cr

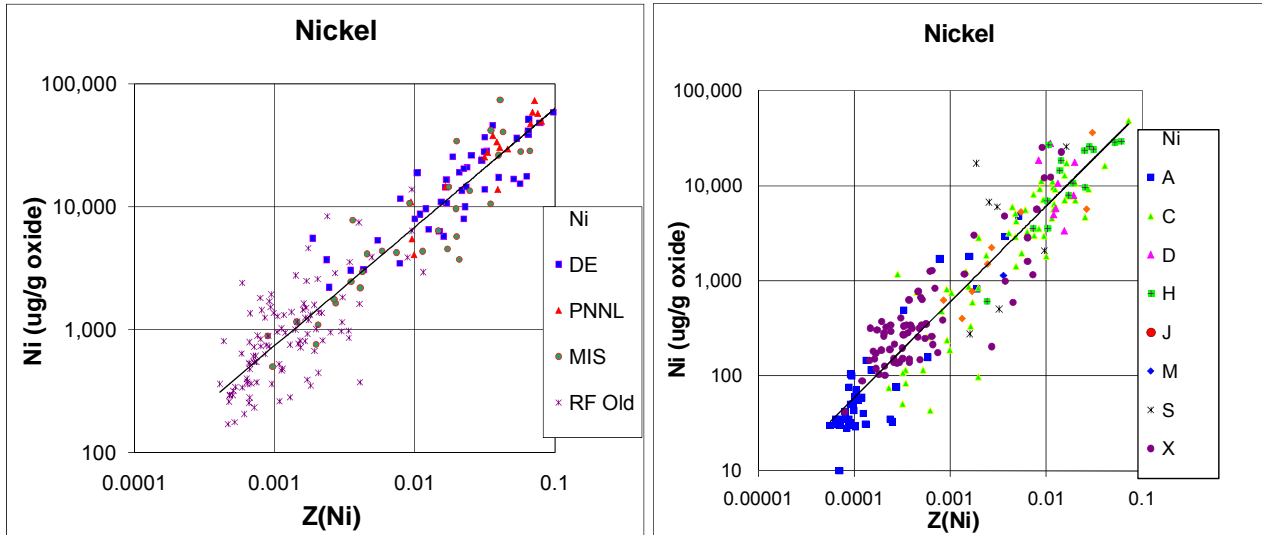


Figure 3. Nickel Level (Samples) Versus Predicted Z(Ni) by Source and Category

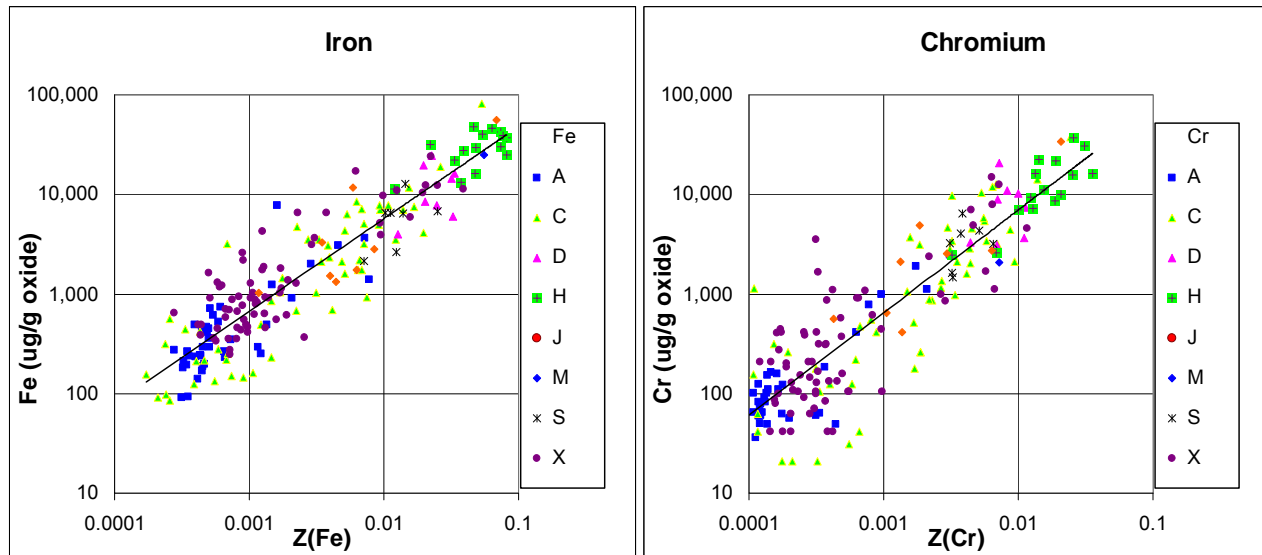


Figure 4. Iron and Chromium Levels (Samples) Versus Predicted Z(Fe & Cr) by Category

Figures 5 and 6 show estimated impurity levels for Ni, Cr, and Fe versus total impurity levels. Values are the mid-point of the projected value based on equations derived from fitting actual sample results to scalar variables, proportional to known material properties such as the total impurity level, the material category, and prompt gamma results. Each point represents a value that could be a factor of 2 higher or lower based on the associated root mean square error. Figure 5 shows the pro-

jected nickel levels for all feeds currently tagged as potential MOX feeds, including feeds that require homogenization or repackaging to meet weight limits, as well as for items not currently MOX-tagged. Figure 6 shows the iron and chromium projections for MOX-tagged items. Without adjustment for the uncertainty of the estimates, it is visually apparent for Ni, Fe, and Cr in the MOX-tagged items that the projected values are slightly below the 75% and 98% limits of Table 1. However, it is also apparent that the limits could be exceeded when accounting for uncertainty. Further, the items that pose the highest risk for nickel are different from those that pose the highest risk for iron exceeding the specification.

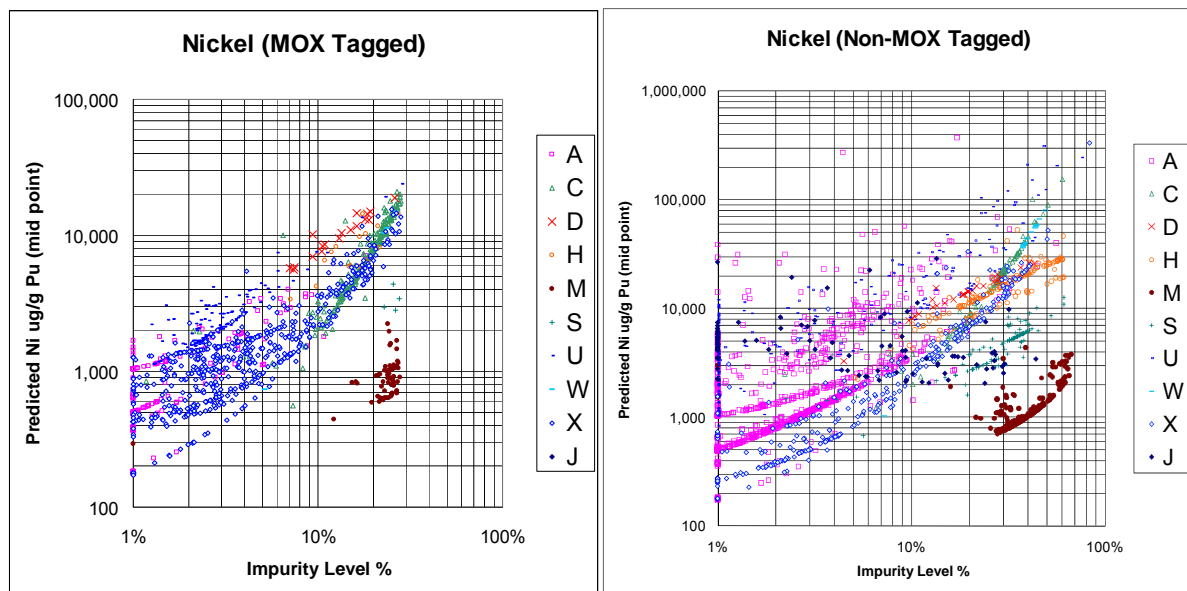


Figure 5. Predicted Ni level for MOX & non-MOX-tagged 3013s versus total impurities

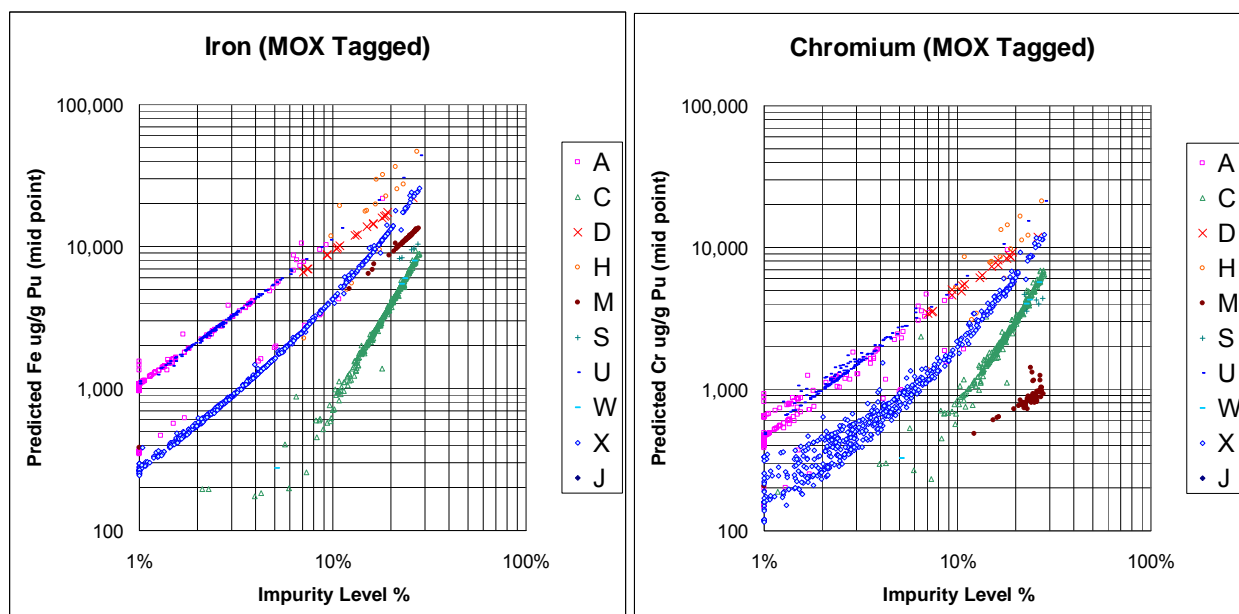


Figure 6. Predicted Fe & Cr Levels for MOX-tagged 3013s Versus Total Impurities

REFERENCES

- ¹ J. S. Allender, E. N. Moore, and S. H. Davies, "Characterization of Surplus Plutonium for Disposition Options," *Proceedings of the Institute of Nuclear Materials Management*, 49th Annual Meeting, July 2008.
- ² U.S. Department of Energy, "Integrated Surveillance Program in Support of Long-Term storage of Plutonium-Bearing Materials," Revision 1, LA-UR-00-3246, March 2001.
- ³ J. E. Narlesky, L. A. Foster, E. J. Kelly, and R. E. Murray, IV "A Calibration to Predict the Concentrations of Impurities in Plutonium Oxide by Prompt Gamma Analysis: Revision 1," LA-14411, December 2009.
- ⁴ T. B. Edwards, "A Statistically-Based Decision Support System for Assessing the Compliance to Impurity Criteria of Containers Destined for Processing at the MOX Facility," SRNL-SCS-2005-00056, December 27, 2005.
- ⁵ J. M. Tingey and S. A. Jones, Pacific Northwest National Laboratory, "Chemical and Radiochemical Composition of Thermally Stabilized Plutonium Oxide from the Plutonium Finishing Plant Considered as Alternate Feedstock for the Mixed Oxide Fuel Fabrication Facility," PNNL-15241, July 2005.
- ⁶ Alice Murray, "Characterization of RFETS Plutonium Metal and Oxide," WSRC-TR-00056. See also J. L. Long, et al. "Direct Oxide Reduction Demonstration Small-Scale Studies, RFP-4128, December 9, 1991.
- ⁷ J. Boak, Los Alamos National Laboratory, E. A. Conrad, Kaiser-Hill Rocky Flats, C. H. Delegard, Pacific Northwest National Laboratory, A. M. Murray, Savannah River Technology Center, G. D. Roberson, U.S. Department of Energy, and T. J. Venetz, Fluor Hanford, "Recommendations on Stabilization of Plutonium Material Shipped to Hanford from Rocky Flats," LA-UR-03-2469, May 28, 2003.
- ⁸ George Y. Lai, *High Temperature Corrosion of Engineering Alloys* (Materials Park, Oh: ASTM International, 2007), 24, 98, 102, 110, 112, 173.