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Application of Prompt Gamma-Ray Analysis to Identify Electrorefining Salt-Bearing Plutonium Oxide at the Plutonium Finishing Plant

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(a) Fluor Hanford, Inc.

Summary

A large fraction of impure plutonium oxide inventory items received in the mid-1980s from the Rocky Flats Plant (RFP) contain sodium chloride and potassium chloride salts from the electrorefining process. Sodium and potassium chloride evaporate at the ≥950°C stabilization temperature mandated for long-term storage under the U.S. Department of Energy plutonium oxide stabilization and storage criteria to plug and corrode process equipment. Because of the equipment damage and associated increased processing time and operator radiation exposure caused by these salts, items found to have these salts qualify for thermal stabilization at 750°C. The present document describes how prompt gamma-ray analysis is being implemented at the Plutonium Finishing Plant (PFP) to screen the items from the RFP for the presence of electrorefining salt.

The prompt gamma ray energies characteristic of sodium, potassium, chlorine, and other low atomic weight elements arise from the interaction the light elements with alpha radiation from plutonium and americium radioactive decay. High-resolution gamma ray spectrometers designed to detect energies up to ~4.5 MeV are used to gather the high-energy prompt gamma spectra.

Observation of the presence of the high-energy gamma peaks representing the natural chlorine-35, sodium-23, and potassium-39 isotopes and the sodium-to-chlorine peak area ratios in the range for plutonium oxide materials known to contain the electrorefining salts give the evidence needed to identify plutonium oxide materials at the PFP that qualify for the lower-temperature processing. Conversely, the absence of these telltale signals in the prompt gamma analysis provides evidence that the materials do not contain the electrorefining salts. Furthermore, based on calibrations using known assayed items, semiquantitative measurement of the quantity of chlorine present in materials containing electrorefining salt also can be performed by using the count rates observed for the chlorine peak, the plutonium quantity present in the measured item, and the plutonium- and chlorine-specific response of the gamma detection system.

The origin and characteristics of the impure plutonium oxide, the process impacts of the electrorefining salts, and the background and technical bases of application of prompt gamma-ray analysis to identify electrorefining salt-bearing plutonium oxide at the PFP are described.

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1.0 Introduction

Prompt gamma-ray analysis (PGA) is being implemented at the Plutonium Finishing Plant (PFP) to identify impure plutonium oxide inventory items received from the Rocky Flats Plant (RFP)[a] that contain salts from the electrorefining (ER) process. The ER salts are primarily sodium chloride and potassium chloride with the possible presence of some magnesium chloride. According to guidance from the U.S. Department of Energy (DOE) based on technical equivalency arguments (Boak et al. 2003), those RFP-origin plutonium oxide items at the PFP containing significant quantities of ER salts may be thermally stabilized at 750°C rather than ≥950°C prior to verification of their residual moisture concentrations and packaging under the DOE standard for long-term storage of plutonium oxide (the "3013 standard") (DOE 2000).

This document describes the technical bases for the application of PGA to identify PFP plutonium oxide inventory items produced at the RFP that contain ER salts. The origins and properties of the ER and other chloride salt-bearing items and the PGA assay equipment are described in Section 2. Our conclusions from the study are presented in Section 3 and cited references in Section 4.

(a) The Rocky Flats Plant (RFP), located about 15 miles northwest of downtown Denver, is now known as the Rocky Flats Environmental Technology Site, or RFETS. The RFETS is a Superfund cleanup site as designated by the U.S. Environmental Protection Agency. From April 1952 until December 1989, the RFP made components for nuclear weapons using radioactive and hazardous materials, including plutonium, uranium, and beryllium and recycled the valuable scrap from the fabrication. Accelerated cleanup began at RFETS in 1995.

2.0 Background

The origin and properties of plutonium scrap containing chloride salts received from the Rocky Flats Plant (RFP) by Hanford's Plutonium Finishing Plant (PFP), processing problems for the salt-bearing scrap, and an overview of the bases of prompt gamma-ray analysis are reviewed in this section.

2.1 Process Origin and Properties of Chloride Salt-Bearing Plutonium Oxide Scrap

Scraps from several RFP chloride salt-mediated pyrochemical processes were sent to Hanford for plutonium recovery in the mid 1980s. Among the scrap was "chlorinated oxides" having RFP item description code (IDC) 067. The scraps arose from electrorefining (ER), molten salt extraction (MSE), and direct oxide reduction (DOR) processes. As described by Boak et al. (2003), the major source of chloride-bearing scrap was the ER process.

Electrorefining was a pyrochemical molten salt process used at the RFP to purify plutonium metal of tramp process and fabrication metals such as iron and gallium. The electrolytic molten salt solvent in the ER process was nominally equimolar in sodium and potassium chloride ($NaCl$ and KCl, respectively). The 740° to 750°C temperature maintained during the electrolysis is above the 641°C melting point of plutonium metal and 658°C melting point of the equimolar $NaCl/KCl$ electrolyte. A small amount of magnesium chloride (usually 3 mol% $MgCl_2$) was added to the $NaCl/KCl$ electrolyte to oxidize plutonium metal and dissolve it as plutonium(III) chloride ($PuCl_3$):

$$3\ MgCl_2 + 2\ Pu \rightarrow 3\ Mg + 2\ PuCl_3$$

Under an applied direct electrical current, the dissolved $PuCl_3$ migrated to the cathode, where it was reduced to plutonium metal. Plutonium, being more readily oxidized than its major impurities, dissolved preferentially as $PuCl_3$ at the controlled potential maintained at the anode. However, americium, which is more readily oxidized than plutonium, also dissolved in the ER salt and was deposited with the product. Plutonium purification thus was accomplished by plutonium leaving the metallic impurities behind at the anode with plutonium migrating to the cathode and electrodepositing as pure metal. Plutonium recoveries during the process were typically ~60 to 70%. The process occurred in crucibles under inert argon cover gas (Cleveland 1970; Boak et al. 2002; Moser and Navratil 1984).

The ER process was operated in tilt-pour furnaces in Building 371 at the RFP. The plutonium not recovered as pure metal constituted the scrap generated either as feed to or byproduct of the ER process. The scrap contained plutonium metal and oxide, and much of it had high levels of associated chloride salt. For example, scrap called "ER scrape-out" arose from periodic cleaning of the crucibles.(a) At the same time, “anode heels” came from the impure residual plutonium metal contaminants left at the anode after the ER process. Other scraps potentially containing ER salts were generated in the RFP Building 371 foundry operations. Such scraps might arise from glovebox floor sweepings and plutonium foundry oxide made by burning dross, turnings, or off-specification metal in adjacent nonaqueous processes.

The RFP produced chloride-bearing scraps from other processes. The molten salt extraction (MSE) process also used equimolar NaCl/KCl but with 30 mol% $MgCl_2$ added. This process was designed to purify plutonium metal by preferentially dissolving americium-241 (^{241}Am), ingrown from ^{241}Pu decay, away from the bulk plutonium metal and into the molten 750°C salt phase (Moser and Navratil 1984).

The direct oxide reduction (DOR) process, which produced chloride-bearing scrap at the RFP, used calcium metal to reduce plutonium oxide directly to the metal at 830° to 835°C:

$$2\ Ca + PuO_2 \rightarrow Pu + 2\ CaO$$

Calcium chloride ($CaCl_2$) was used as the flux in the DOR process to dissolve the product, CaO, which otherwise would have fouled the calcium metal reactant and prevented its interaction with the reactant PuO_2. Yields for DOR above 95% were achieved at the RFP (Moser and Navratil 1984).

Scraps from the foundry processes were rich in plutonium and were collected for plutonium recovery. The scraps were heated in air to convert the plutonium and other accompanying active metals to their respective oxides in anticipation of subsequent dissolution in nitric acid and purification by aqueous processes.

2.2 Plutonium Scrap Shipped from RFP to Hanford, 1984–1986

Scrap plutonium oxide items were shipped from RFP to Hanford’s PFP between 1984 and 1986 for plutonium recovery. The items shipped to Hanford were given item identification numbers of the form ARF-102-84-xxx, where ARF designates the RFP origin, 102 designates the plutonium as oxide, 84 designates the year 1984 (items shipped in 1985 and 1986 have 85 and 86, respectively), and the xxx is a serial number. According to review of process and shipping records (Boak et al. 2003), the ARF-102 items included:

(a) To perform the scrape-out operation, the ER tilt-pour furnace was heated to 1000°C while open to the glovebox atmosphere (N_2 with ~800 to 2000 ppm moisture and 3 to 5% O_2). The molten salt and plutonium metal were scraped from the swiveled and tilted furnace with a long-handled tool. The scrape-out material, IDC 154, then was oxidized at ≥450°C and relabeled as IDC 067. This material was restabilized at least once more at 450°C before it was shipped offsite. Therefore, the scrape-out material was heated at or above 450°C at least three times before shipment to Hanford.

- Chloride salt-bearing scrap generally from the ER process. This scrap constituted 55% of the items and had item description code IDC 067, designated as “chlorinated oxides” or something similar.
- Other scrap items potentially contaminated with ER salt from Building 371. This scrap, from other foundry processes, constituted 41% of the items and was given IDC 061, designated as “non-spec oxide” or something similar.
- Miscellaneous items. This portion made up the remaining 3% of the ARF-102 items. Individual items potentially could be contaminated with ER salt.

Prior to shipment, the materials destined for Hanford were calcined at least once and often twice at ~450°C and the loss on ignition measured to ensure chemical stability. Much of the residual active metal (plutonium, magnesium, or calcium) should have converted to oxide.

However, conversion of the plutonium metal to oxide evidently was not complete because plutonium metal spherules were observed in an ARF-102 item in PFP laboratory tests (Delegard and Bouse 1985a,) though PuO_2 was the only phase identified by X-ray diffractometry (XRD) in this and related characterization of ARF-102 items (Delegard and Bouse 1985b; Materials Identification and Surveillance, MIS, database).[a] Bubbles observed to form in water-wash lab testing of ARF-102 items during process development testing at PFP also give evidence of the presence of an active metal (Jones 2002). The bubbling may be explained as the reaction of plutonium with water to form hydrogen gas (H_2) though magnesium or calcium could have survived the calcination steps by salt coating, impeding their full oxidation. The reaction of plutonium with water to form hydrogen gas is based on observations of H_2 produced by the reaction of plutonium in a thermally nonstabilized ER salt (IDC 411) with room temperature water to form PuOH (Haschke and Phillips 2000; Boak et al. 2002, Appendix B).

Of the 1509 ARF-102 items shipped from RFP to PFP between 1984 and 1986, 570 were processed for plutonium recovery in previous PFP operations. The remaining 939 ARF-102 items were unprocessed and still present in the PFP inventory in early 2003 (Boak et al. 2003).

Though the process origins and numbers of items in the ARF-102 materials shipped from RFP to the PFP are known, as are the net plutonium and gross contents weights for each item, the IDCs, which designate the specific process origins or material characteristics, were not preserved for the individual ARF-102 items. In other words, the potential presence or process type of chloride salt in any individual item, as would be indicated by IDCs 067 or 061, are not known based on material inventory, shipment, item identification, or any other records.

(a) Plutonium oxychloride (PuOCl) from hydrolysis of $PuCl_3$ also has been identified by XRD at percent levels in thermally nonstabilized inventory items of RFP IDC 411 (ER salt; Boak et al. 2002, footnote of Appendix B-3; also verified in a personal communication with J Boak and EA Conrad). The survival of PuOCl in the chloride-poorer ARF-102 materials is unlikely after the 450°C thermal stabilization steps implemented to prepare the items for shipment to Hanford.

Like all plutonium oxide inventory items present at the PFP and containing greater than 30 wt% plutonium, the ARF-102 items containing >30 wt% Pu must undergo stabilization and packaging operations to fulfill the terms of the 3013 standard for long-term storage of plutonium oxide (DOE 2000). Only 17 of the 939 remaining ARF-102 items were <30 wt% Pu; these items were packaged for shipment to the Waste Isolation Pilot Plant (WIPP) in the spring of 2003. The remaining 922 items therefore required thermal stabilization and packaging to satisfy the 3013 standard.

2.3 Problems in Thermal Processing of Chloride-Bearing Plutonium Oxide Materials

Electrorefining salts have been implicated in processing and moisture measurement difficulties associated with the ≥950°C thermal stabilization of plutonium oxide defined by the 3013 standard. The process problems were illuminated in furnace tests with simulated chloride-bearing plutonium oxide with 1 wt% ER salt loading (Fischer et al. 2002), tests in PFP laboratories with simulated chloride-bearing scrap (Boak et al. 2003, Appendix E), and actual PFP experience in thermal stabilization of ARF-102 items suspected to contain ER salt. Each of these studies showed that the salts that evaporated from process boats at 950°C deposited on cooler downstream off-gas surfaces. The deposits plugged off-gas filters and caused or contributed to localized but severe and process-debilitating equipment corrosion.

The baseline flowsheet developed at the PFP to process the items containing chloride salts called for water washing to dissolve and remove the offending water-soluble chloride salts. The washing step would be followed by the mandated thermal treatment at ≥950°C for a minimum of two hours. Unfortunately, PFP experience showed that the salt removal wash was not sufficient to eliminate the plugging and corrosion associated with the residual salt remaining after the washing step.

Laboratory tests were performed using a simulated ER scrap in which cerium oxide, CeO_2, served as the PuO_2 surrogate. It was found that even with 20 wt% ER salt loading the plugging and corrosion problems observed for similar tests with 1 wt% salt loading at 1000°C could be avoided if processing occurred at 800°C (Schmidt et al. 2003). Thus, the most promising approach to process the ER salt-bearing materials without undue equipment failure was to lower, if possible, the stabilization temperature.

2.4 Technical Assistance Request and Technical Equivalency Document

At the request of the DOE Richland Operations Office (DOE-RL), a team was created to investigate the problems encountered with thermal stabilization of chloride-bearing plutonium oxide at 1000°C and to determine whether technical arguments could be advanced to show that the stabilization goals of the 3013 standard could be met at a temperature lower than 800°C.

This effort was undertaken following the successful demonstration of technical equivalency to the 3013 standard advanced for lower stabilization temperature of ER salt-bearing materials for the RFETS (Boak et al. 2002).

The outcome of the DOE-RL request was a document (Technical Equivalency Document) (Boak et al. 2003) providing the basis to demonstrate the technical equivalency of 750°C thermal stabilization of the ER salt-bearing plutonium oxides to the material stabilization requirements of the 3013 standard. To parallel the previous guidance offered for the RFETS, the possibility for technical equivalency of satisfying the stabilization intent of the 3013 standard at 750°C was entertained only for the ARF-102 materials received from the RFP. In addition, because of the increased risk of encountering constituents requiring the full ≥950°C stabilization in higher impurity items, the lower temperature alternative could be applied only to those items containing >50 wt% plutonium. Finally, the Technical Equivalency Document recommended that prompt gamma analysis (PGA) be applied to identify those items received from the RFP that contain ER salt and that the technical bases of the application of PGA be recorded. Specifically, as stated in the Executive Summary,

> *The technical team recommends the use of Prompt Gamma-Ray Analysis (PGA) to identify chloride-bearing material that may be stabilized at lower temperature. The PGA can be used in conjunction with available assay data to define items that might potentially corrode or plug critical subsystems in the stabilization furnaces.*
>
> *Rapid screening for Na, K, and Cl to identify candidates for lower temperature stabilization will be sufficient to distinguish items that pose a risk to stabilization equipment. This will include material from IDCs related to the ones described in Boak, et al., (2002), but also identifies other IDCs shipped from RFETS that have characteristics sufficiently similar to the RFETS ER oxide to be screened by PGA for lower temperature stabilization. Analysis of the full PGA spectrum after stabilization may be used to identify containers for enhanced monitoring by the Integrated Surveillance Program, which has already identified chloride-bearing Pu oxide as requiring higher levels of surveillance.*
>
> *The technical team recommends that the Integrated Surveillance Program, in cooperation with RFETS and PFP, expedite preparation of a document that lays out the technical basis for PGA and describes the instruments now being used at LANL, Rocky Flats, and Hanford.*

2.5 Prompt Gamma-Ray Phenomenon

The PGA method is based on identification and intensity measurements of gamma rays produced by plutonium and americium alpha particle interaction with nuclei of other elements. In particular, alpha particles (α) emitted by the radioactive decay of plutonium and americium in plutonium oxide materials transmute elements present in the materials, particularly low atomic number elements, by (α,nγ) and (α,pγ) nuclear reactions, releasing a neutron (n) or proton (p), respectively, and associated gamma ray (γ). Inelastic scattering alpha recoil reactions (α,α′γ), without nuclear transmutation, also may occur. All three reactions leave the product nuclei in excited states which, with subsequent decay of the excited states, produce gamma rays with energies characteristic of the excited product isotope. The reactions of alpha particles with the fluorine-19 (^{19}F) nucleus illustrate both (α,nγ) and (α,pγ) nuclear transmutation:

$$\alpha,n\gamma\ \ {}^{19}\mathrm{F} + \alpha \rightarrow {}^{22}\mathrm{Na}^{*} + n;\ {}^{22}\mathrm{Na}^{*} \rightarrow {}^{22}\mathrm{Na} + \gamma\ (1528\ \mathrm{keV})$$

$$\alpha,p\gamma\ \ {}^{19}\mathrm{F} + \alpha \rightarrow {}^{22}\mathrm{Ne}^{*} + p\ ;\ {}^{22}\mathrm{Ne}^{*} \rightarrow {}^{22}\mathrm{Ne} + \gamma\ (1275\ \mathrm{keV})$$

The ^{22}Na* and ^{22}Ne* are sodium-22 and neon-22 in excited states. The ^{22}Na* decays to emit a 1528-keV gamma ray and produce ^{22}Na. The ^{22}Na is itself unstable, with a 2.6-year half-life, decaying by positron emission to form stable ^{22}Ne. The ^{22}Ne* decomposes to give stable ^{22}Ne and a 1275-keV gamma ray.

Measurements of gamma ray energies can be used to identify the impurities in the plutonium oxide matrix. Methods to analyze prompt gamma spectra to identify and quantify impurities in alpha particle-emitting materials have been presented in the technical literature.

2.5.1 Spectra Observed by PGA

Gamma ray spectrometry of prompt gamma-rays from α-particle reactions was applied first to identify light element impurities in $^{238}PuO_2$ (McKibben 1968). The basis for this qualitative analysis was the interpretation of gamma ray spectra, observed up to about 6 MeV, of dry mixtures of $^{238}PuO_2$ with various light element compounds. Compounds of all elements (except the noble gases and oxygen, which is intrinsic to PuO_2) from lithium (Z=3) through potassium (Z=19) were used. No reaction gamma rays were found for carbon, silicon, or sulfur. The remaining elements were found to be increasingly detectable (i.e., sensitivity increased) in the order potassium, chlorine, magnesium, sodium, phosphorus, nitrogen, aluminum~boron ~fluorine, lithium, and beryllium. The spectra McKibben (1968) gathered using a NaI(Tl) detector were of lower resolution than would become available subsequently by using semiconductor detectors.

Martin (1975) obtained spectra up to about 5 MeV of PuO_2 with the same 14 light elements as did McKibben (1968). Martin (1975), sometimes using different compounds (generally pulverized to pass 100-mesh) than McKibben (1968), used a high-resolution Ge(Li) semiconductor detector and used ^{239}Pu oxide (with 133 ppm ^{241}Am; isotopic composition otherwise not stated) instead of the more active ^{238}Pu oxide used by McKibben (1968). In addition to the spectra from the dry-blended materials, Martin obtained spectra of plutonium compounds [PuF_4, Cs_2PuCl_6, $Pu(HCO_2)_3$, and an Al-Pu alloy] from a “molten salt waste” from RFP operations.

Like McKibben, Martin observed no reaction gamma rays for carbon, silicon, and sulfur. Based on the obtained spectra, gamma ray energy assignments were made for the remaining elements and for oxygen (from PuO_2 alone) to produce a catalog of gamma ray energies associated with particular light elements.

Martin's observations regarding the "molten salt waste" (evidently from electrorefining or molten salt extraction) and for a magnesium oxide crucible used in a molten salt process are pertinent to the application of PGA to identify ER salts at the PFP. They are presented in the following paragraphs. The spectrum of the "molten salt waste" is given in Figure 1.

> *The majority of the reaction gamma rays arise from $^{23}Na(\alpha,p\gamma)^{26}Mg$ reactions. The gamma rays at 1524 and 2167 keV are assigned to alpha reactions on ^{39}K and ^{35}Cl, respectively, and the 1779 keV line is assigned to an alpha reaction on ^{25}Mg. The molten salt contains large amounts of sodium chloride and potassium chloride, and a lesser amount of magnesium chloride. In this case, the reaction gamma rays do provide a means of identification and a qualitative estimate of the relative abundance of these light elements.*
>
> *Reaction gamma rays do not always appear as expected. A particular reaction gamma ray's appearance or absence is not necessarily related to the light-element abundance of the total sample. For example, spectra from a magnesium oxide crucible used in a molten salt operation were dominated by sodium reaction gamma rays. In this case, the results would indicate that within the crucible, the plutonium and sodium salts are absorbed into the wall and are in closer contact than the plutonium with the magnesium. Results of this type clearly reveal the intimate contact necessary before reactions occur, also the difficulties one may encounter in trying to predict alpha reactions in inhomogeneous materials.*

Ovechkin and colleagues (1976) developed a method to determine the concentrations of fluorine and nitrogen impurities in plutonium oxide (PuO_2) based on ratios of the gamma peak areas at 1275 keV and 871 keV (for fluorine and nitrogen, respectively) to the peak area at 770 keV for ^{239}Pu decay. The researchers ensured interaction of the alpha particles with fluorine and nitrogen by preparing the pure plutonium compounds Na_2PuF_6, PuF_3, and PuN. The pure plutonium–light element compounds were combined in various ratios with PuO_2, the powders ground together, and the spectra measured. The results were accurate enough to determine fluorine concentrations in the range ~0.2 to 19 wt% and nitrogen concentrations from 0.2 to 3.7 wt% for these narrowly constituted materials. Measurements of unknowns containing fluorine or nitrogen present as other compounds were not reported. Ovechkin (1980) subsequently obtained the specific gamma yields for fluorine in $^{239}PuF_3$ and $^{239}PuF_4$ to improve sensitive and nondestructive fluorine analyses in reprocessing and nuclear fuel production streams.

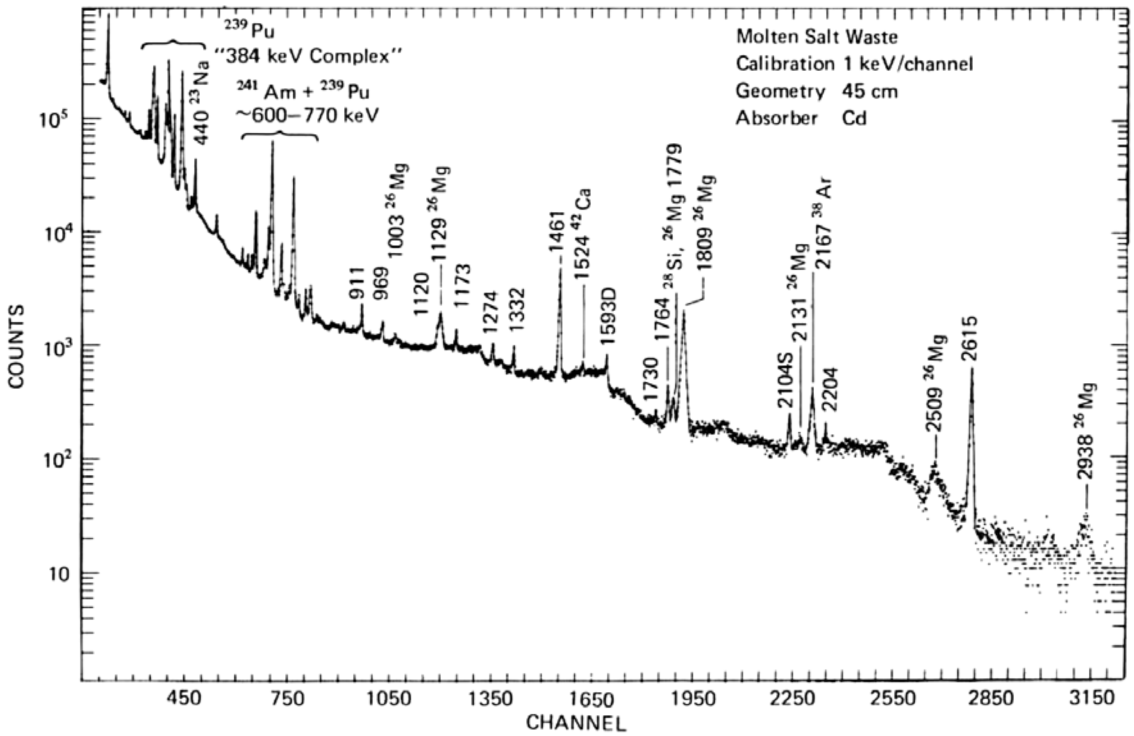


Figure 1. Spectrum of RFP "Molten Salt Waste" Containing Chloride Salts (Martin 1975)

A catalog of alpha-induced prompt gamma ray energies to about 6 MeV was obtained in a survey of 56 elements irradiated with 5-MeV $^4He^+$ particles from a Van de Graaff accelerator (Giles and Peisach 1979). The $^4He^+$ particle is similar to the alpha particle, $^4He^{2+}$, and interacts with the target nucleus in the same way. Giles and Peisach's compilation includes the relative sensitivities for detecting the various elements. In contrast to the findings of McKibben (1968) and Martin (1975), Giles and Peisach (1979) found prompt gamma rays from silicon. In agreement with the previous studies, they found no signal for carbon or sulfur. They also found no signals for calcium or gallium. For a given $^4He^+$ particle flux, the elements detected most easily are lithium, boron, nitrogen, fluorine, sodium, aluminum, phosphorus, vanadium, manganese, and rhodium. Beryllium was not measured in their studies.

Measurement of the concentrations of light element (boron, carbon, nitrogen, oxygen, and fluorine) impurities in relatively pure ^{238}Pu, ^{239}Pu, ^{241}Am, and mixed U-Pu reactor fuel was investigated by analysis of intrinsic prompt gamma ray intensities as calculated from first principles (Shumakov et al. 1994). The analyses were used to predict detection limits and count rates for these elements at trace or low levels. The predictions for nitrogen were verified by measurements of ^{239}Pu and a U-Pu alloy and found to agree within 20%. A prompt gamma signal at 6130 keV arising from the reaction $^{13}C(\alpha,n\gamma)$ also was calculated. The estimated yield for carbon's 6130 keV gamma ray is about 2800 times lower than that of fluorine's 1275 keV gamma ray. However, the existence and intensity of the purported 6130-keV carbon prompt gamma ray was not verified experimentally.

The published studies show that the prompt gamma method can identify beryllium, fluorine, sodium, magnesium, chlorine, and potassium. All of these elements are present, or potentially present, in plutonium oxide materials from RFP pyrochemical processes. Other elements possibly present in RFP materials, including aluminum, silicon, and nitrogen, produce characteristic gamma rays and also may be identified. However, a few notable exceptions such as calcium, sulfur, and gallium produce no significant gamma yield and cannot be identified. The predicted existence of the carbon prompt gamma ray has not been confirmed, based on the limited survey of the technical literature. Quantitative analysis of impurity concentrations by PGA also is demonstrated under certain conditions, most importantly if intimate contact of the plutonium and americium alpha emitters with the target impurity elements is achieved.

2.5.2 Effects of Mixing in PGA

Intimate mixing is best achieved by forming a compound of plutonium or americium with the light element of concern. However, for the ARF-102 materials, the only plutonium compounds identified are PuO_2 and possibly some plutonium metal. In such a case, intimate mixing by compound is only ensured for plutonium with oxygen.

Intimate mixing of light elements with plutonium oxide is necessary because the range of the 5.2-MeV alpha particle emitted by ^{239}Pu and ^{240}Pu is about 70 μm in plutonium oxide (Ensslin 1991). This is well illustrated by the excerpt from Martin (1975) because the salt-saturated magnesium oxide crucible material that showed prompt gamma signals for sodium, with which the plutonium was thoroughly mixed, dominate the spectrum with relatively little signal from magnesium. The alpha particles could only impinge on the magnesium oxide at the crucible surface whereas the frozen sodium salt coated the plutonium oxide particles to intercept most of the alpha radiation.

Using Monte Carlo techniques, Foster and colleagues (2002) calculated the probability of 5-MeV alpha particle escape from PuO_2 as a function of PuO_2 particle diameter. The calculations showed that all alpha particles escaped the PuO_2 particle if its diameter was less than 10 μm. The escape probability decreased at higher diameters such that about 75% of the alpha particles escaped at 20 μm, ~60% at 30 μm, ~30% at 50 μm, and ~15% at 100 μm. Based on the PuO_2 particle size distribution presented by Foster et al. (2002) with a mass-based maximum at 50 to

70 μm, an integrated escape fraction of 0.32 is estimated (i.e., about 32% of the alpha particles would leave their source PuO_2 particle).(a)

The probabilities of $^{19}F(\alpha,n)$ reaction as a function of PuO_2 particle diameter and fluorine concentration in intimate mixtures of PuO_2 and CaF_2 also were calculated by Foster et al. (2002). The calculations showed the expected result that for 5 μm and 10 μm PuO_2 particles, the (α,n) reaction probability increasing nearly linearly at low (0 to 10 wt%) fluorine concentrations. Some curvature downward with increasing fluorine concentration was seen because as fluorine concentration increased the complementary PuO_2 concentration decreased, providing lower alpha irradiation. However, the probability of (α,n) reaction with larger PuO_2 particles (25, 50, and 100 μm) flattened markedly as fluorine concentration increased above 1 wt%.

The effects of intimate mixing were demonstrated by measurement of gamma spectra of PuO_2 powder blended with particulate CaF_2 and a 1:1 mole ratio NaCl:KCl blend similar to that constituted for ER and MSE processes (Foster et al. 2002). The fluoride in the CaF_2 and the chloride in the NaCl/KCl blend each composed 5 wt% of the powder mixture. The characteristic 1274, 1528, and 2081 keV emissions from the ^{19}F reactions could be discerned after the powders had been mechanically blended (Figure 2). At the same time, the 1809 keV peak characteristic of the $^{23}Na(\alpha,p\gamma)$ reaction and the 2168 keV peak of the $^{35}Cl(\alpha,p\gamma)$ reaction were observable but weak. Similar spectra were obtained after the mixtures had been heated to 600°C for two hours.

(a) The PuO_2 particle size distribution in Foster et al. (2002) is high but may accurately represent the PuO_2 derived in thermal processing of ER scrape-out. Plutonium oxide particles prepared by "extended air oxidation of electro-refined plutonium metal at 25°C" have 3.1% particles less than 1 μm and 96.9% less than 5 μm—the particles themselves are agglomerates of 0.01 μm crystallites (Stakebake and Dringman 1968). With these particle size distributions, nearly all alpha particles would leave their source PuO_2 particles and be available to irradiate adjacent compounds or materials. However, plutonium oxide particles derived by burning Pu metal in air or pure oxygen at 500°C are considerably coarser, with 98% or more of the mass particles greater than 30 μm. Slow reaction rates favor smaller particles (Haschke et al. 1998).

Studies show that about 10 mass% of ER residue salt is plutonium metal shot (Haschke and Phillips 2000; Boak et al. 2002, Appendix B). In this work, 10-g samples of thermally nonstabilized ER salt residue were dispersed in 50 mL of water and the gas evolution amounts and rates measured for the reaction:

$$2\,Pu + 2\,H_2O \rightarrow 2\,PuOH + H_2$$

Based on knowledge of the corrosion rates of plutonium metal in 2 M chloride solution (arising from the associated ER salts) and the smoothly decreasing gas generation rate curve observed with time and supported by molten metal surface tension arguments, the plutonium metal was postulated to be present as 1.2 ± 0.5-m-diameter spheres composing 10 ±5 wt% of the ER residue. According to the alpha escape fraction curves presented by Foster et al. (2002) and given the higher particle density of plutonium metal, the alpha particle escape fraction from the 1.2-mm-diameter shot would be negligible. Though total plutonium concentrations in the nonstabilized ER residue studied by Haschke and Phillips (2000) were not reported, Pu metal shot in the thermally stabilized >50 wt% plutonium PFP ARF-102 items could constitute no more than 20% of the total plutonium, likely much less. Thus little diminution in the prompt gamma signal is expected from what is likely to be very little Pu metal shot.

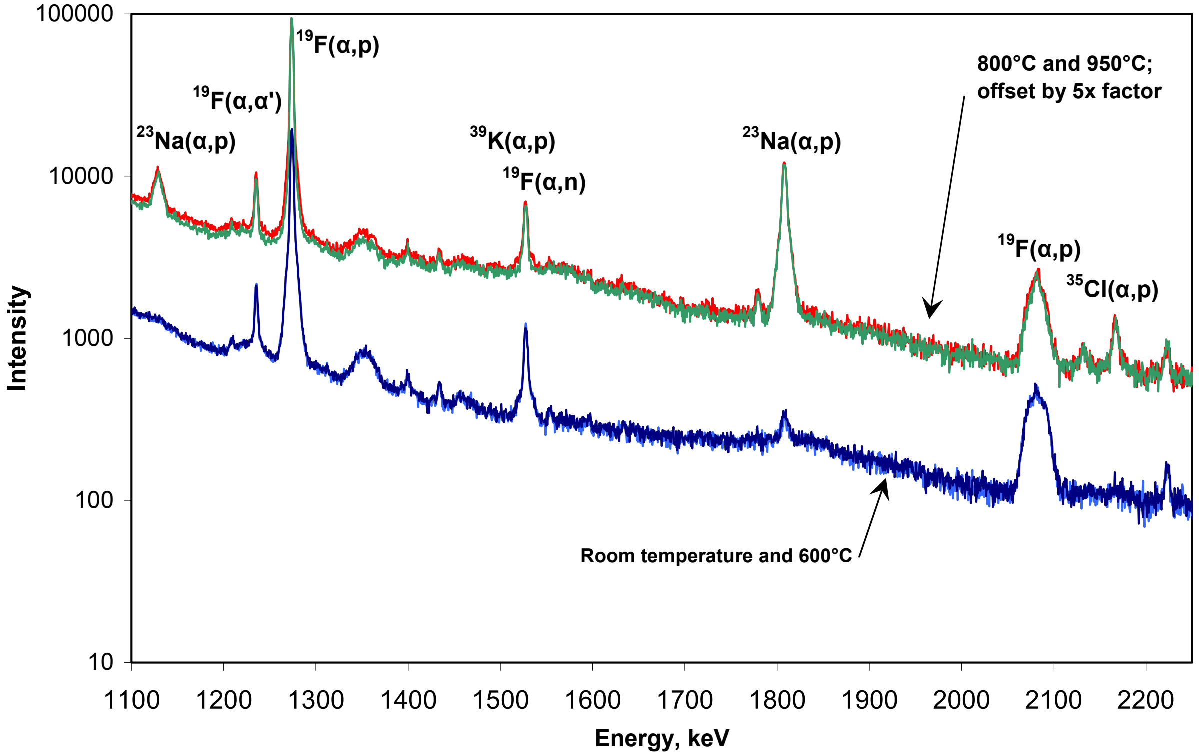


Figure 2. Prompt Gamma Spectra of PuO_2 Blended with NaCl/KCl and CaF_2 (Foster et al. 2002). The lower two traces are at room temperature and after 600°C heating; upper two are after 800°C and 950°C heating.

However, when the mixtures were heated to 800°C, above the melting point of the NaCl/KCl eutectic, the 1809 and 2168 keV peaks characteristic of sodium and chlorine, respectively, strengthened about an order of magnitude. At the same time, little change occurred in the fluorine peak. Other sodium peaks appeared at about 1130, 1779, and 2131 keV. The peak for $^{39}K(\alpha,p\gamma)$ expected at 1524 keV is not discernable due to the strong adjacent 1528 keV peak for $^{19}F(\alpha,p\gamma)$. Further heating to 950°C did not change the spectrum from that observed in the 800°C product.

The data show that melting increased the contact of the NaCl/KCl salt with the PuO_2 and thus increased the gamma count rate for sodium and chlorine. At the same time, the fluorine count rate did not increase with heating because the melting point for CaF_2 (1423°C) was not exceeded. Note that the NaCl/KCl electrolyte mixture must be molten in ER and MSE processing. Thus intimate mixing of NaCl/KCl with the plutonium and americium alpha emitters is reasonably ensured for PuO_2 materials containing ER salt.

Foster et al. (2002) also attempted to correlate the chlorine (2168 keV) and fluorine (1275 keV) count rates for items in the Materials Identification and Surveillance (MIS) inventory with their chemically analyzed chlorine and fluorine concentrations. The count rates were normalized to the specific alpha activities of the analyzed items based on the gamma count rates observed for ^{239}Pu (414 keV) and ^{241}Am (662 keV). General trends of increasing chlorine and fluorine signal with increasing concentration were observed for 12 and 9 items, respectively. However, strict correlation of the prompt gamma signal to the concentration of chloride was not observed (Foster et al. 2002):

> *While there is a relatively large deviation in the chlorine signal from that expected in several cases, as much as a factor of 5 or more, none of the oxides for which the chemical analysis showed chlorine concentrations of greater than 1 wt.% failed to show any chlorine signature from the prompt-gamma analysis. This gives us good confidence that we can at least identify containers that contain elevated levels of chlorine and fluorine, even if quantification is not possible.*

2.6 Prompt Gamma-Ray Analysis Screening

Prompt gamma-ray analysis was designated in the Technical Equivalency Document to identify the ARF-102 items that contain ER salts. The screening logic given in Figure 3 shows the sequence of yes/no determinations made based on PGA of the ARF-102 items containing

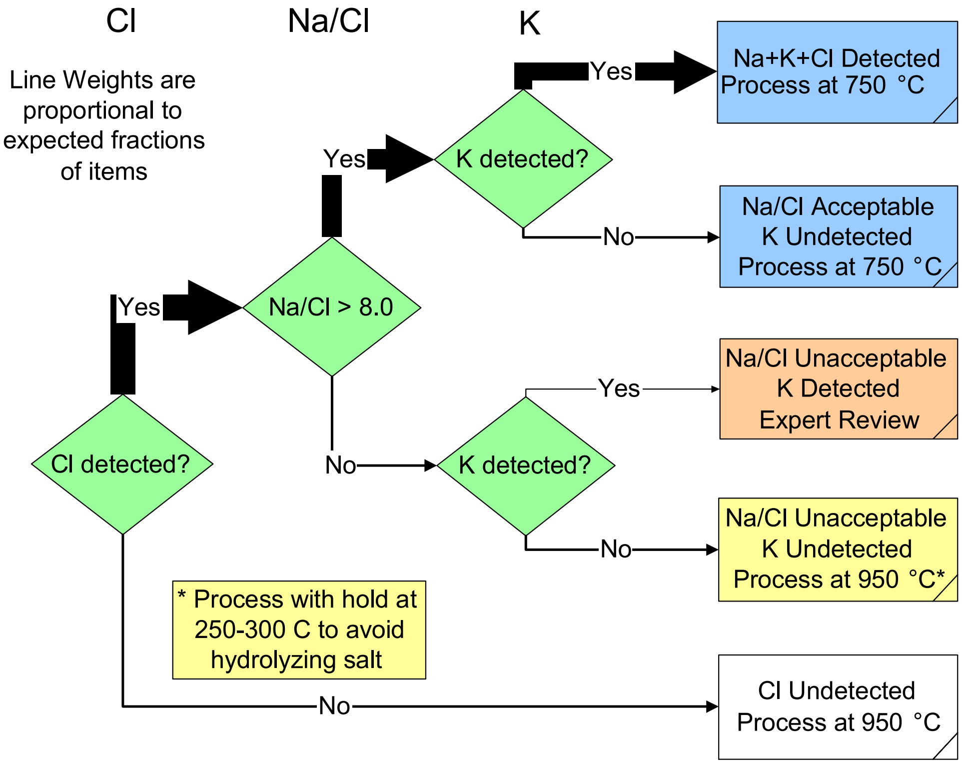


Figure 3. Prompt Gamma-Ray Analysis Screening Logic to Identify Candidate Materials for Lower Temperature Stabilization (Boak et al. 2003). Note that the lower Na/Cl threshold is 8.0 rather than 8.2, as stated in Boak et al. (2003).

>50 wt% to identify their thermal stabilization processing paths to fulfill the 3013 standard. The first step is to determine whether chlorine is present. Based on measurements of items with known chlorine concentrations, semiquantitative analysis of chlorine concentration can be made by PGA. Next, the PGA spectrum is evaluated to see whether the peak due to sodium is more than 8 times larger than the peak due to chlorine. Sodium/chlorine prompt gamma peak area ratios above 8 have been found for materials containing ER salts in RFETS inventory items. Finally, the PGA spectrum is examined to determine whether the peak due to potassium, arising from the presence of KCl in the ER salt, can be detected. The bases of these screening steps are described in this section. The gamma spectrometers used to obtain the prompt gamma spectra also are described.

2.6.1 PGA Systems at the PFP

As part of the Integrated Surveillance Program (ISP), the PFP has brought online four prompt gamma energy analysis (GEA) systems to characterize the stabilized plutonium oxide being packaged for long-term storage in 3013 containers. These systems also are being used to measure ARF-102 items prior to their thermal stabilization to meet the 3013 standard as well as to identify, by the logic diagram in Figure 3, the items that may undergo lower temperature stabilization and those that must undergo the full ≥950°C stabilization.

Each GEA system has an EG&G ORTEC 45% efficiency, coaxial, high-purity germanium detector. Three of the systems' detectors are placed to take a horizontal view of the item being measured. One detector views the sample from below. To decrease the detector dead time, a 1-inch thick Pb (lead) filter is interposed between the sample and detector to minimize x-rays from plutonium (mostly multiplets around 100 keV) and americium-241 (~60 keV). Some attenuation of 331 to 450 and 600 to 770 keV energy peaks from plutonium and ^{241}Am also occurs. The distance from the sample to the detector is adjusted to bring the dead time within a suitable range for measurement. A Pentium-class PC-based, EG&G ORTEC nuclear spectroscopy system is used for data acquisition and spectral analysis. Multichannel channel analyzer (MCA) emulation is provided by ORTEC's *Maestro*®*-32*.

Two software programs are used to interpret the gamma energy spectra. Both peak analysis software routines can operate on the same spectral dataset produced in the ORTEC .chn format. The first program, PGA Version 3.0, was developed by Los Alamos National Laboratory (LANL) personnel and identifies the presence of prompt gamma rays from ~100 through 5000 keV by taking the second derivative of the spectra. The program then measures the background-corrected areas of each analytical peak.

Based on the measured spectrum, a custom data file is created to analyze each data set for the prompt gamma rays from 12 selected elements. These elements and the locations of their most important prompt gamma peaks are listed in Table 1. The primary peaks are usually the largest or most sensitive for a given element. However, potentially useful peaks may occur in regions of

Table 1. Primary and Secondary Peaks Used in the PGA Version 3.0 Software

Element/ Number of Peaks	Primary Peak/ Intensity	Secondary Peaks/ Intensities		
Aluminum 21 peaks	2235.5 100	1263 36.4(a)	3498 11.4	2476 6.9
Beryllium/C 3 peaks	4439.2 100	3928.2 50	3417.2 25	
Chlorine 6 peaks	2167.6 100	1146 11.6		
Chromium 3 peaks	783.3 100	564 97.6		
Copper 4 peaks	1115.5 5.8	962 24	670 100	
Fluorine 20 peaks	1274.6 18.8	891 5.2	1236 1.4	2081 1.4
Iron 7 peaks	846.8 84.3			
Magnesium 11 peaks	1014.5 55.2	1273 100	2028 10.7	2839 8.3
Potassium 3 peaks	1524.2 100			
Silicon 8 peaks	2233.8 29.9	1266 7.6	1213 5.6	1779 4.3
Sodium 19 peaks	1808.7 100	1130 51.5	2132 2.3	2938 2.1
Tantalum 3 peaks	301.4 3.3			

(a) Shaded fields indicate secondary peaks used to resolve ambiguous qualitative element assignments.

the spectrum dominated by plutonium or americium peaks. For example, the most intense peak for copper occurs at 670 keV and can be obscured in the 600 to 770 keV ^{239}Pu-^{241}Am multiplet. Light elements also can produce peaks that interfere with the intense peaks of other light elements. For example, the neighboring strongest peaks for aluminum (2235.5 keV) and silicon (2233.8 keV) can interfere with one another, and the primary peak for fluorine (1274.6 keV) and the secondary peak for magnesium (1273 keV) interfere. In such cases, secondary peaks are used to confirm the presence of an element but only if the primary peak exists. The secondary peaks used to resolve these ambiguities are shaded in Table 1. Further study of the spectra using other secondary peaks may be necessary to achieve conclusive assignments.

The primary potassium peak at 1524.2 keV and the fluorine peak near 1528 keV present a special case because the fluorine peak is prominent and can easily overwhelm the weak potassium peak. This is evident in Figure 2 for mixtures having 5 wt% fluorine and ~2.8 wt%

potassium. The potassium peak at 1524.2 keV is not detectible in the low-energy tail of the 1528 keV fluorine peak. Because potassium is a constituent in ER salt and fluoride is present in many process materials from the RFP, the overlap of the potassium and fluorine peaks will be considered in more detail later in this report.

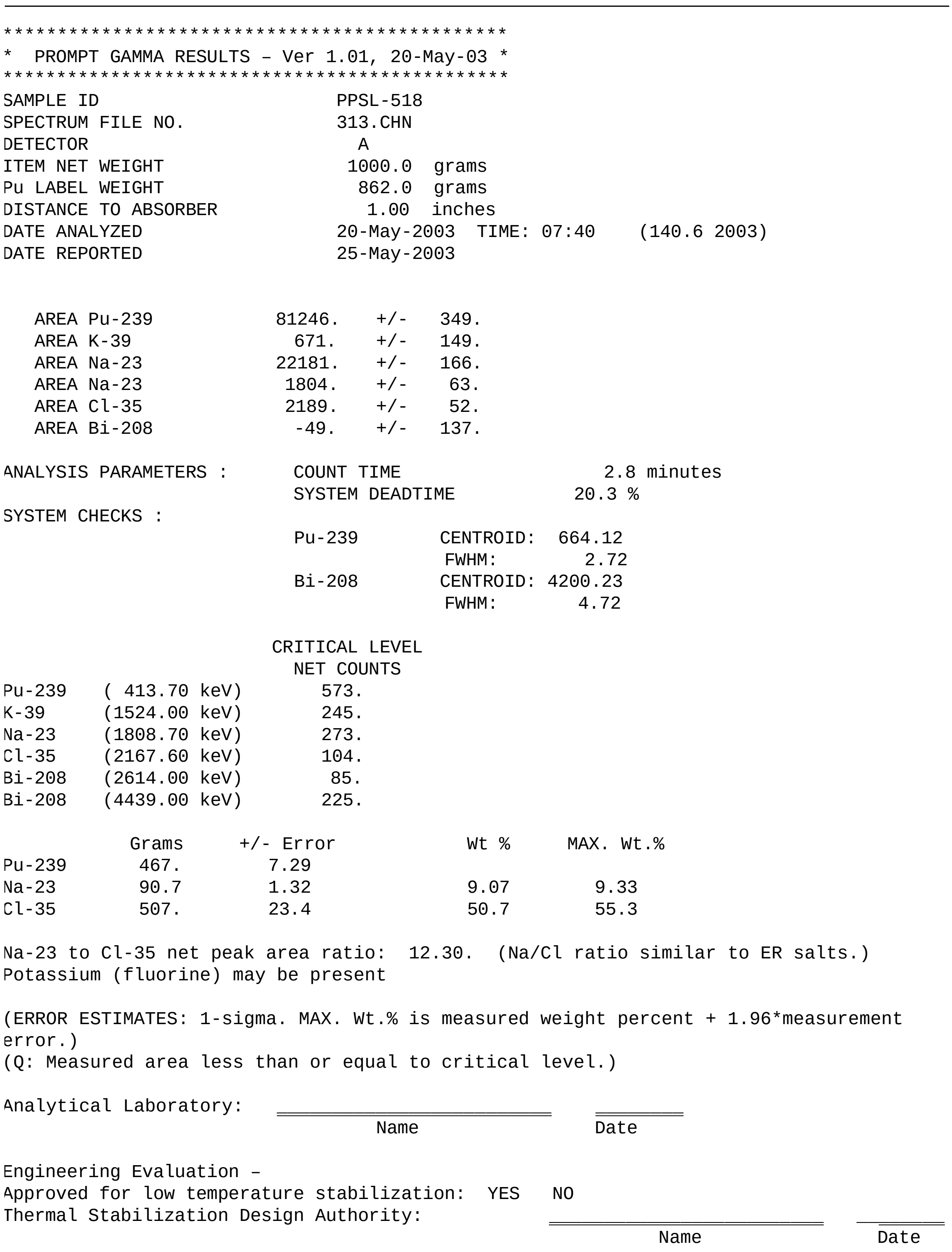
Reports from the LANL PGA Version 3.0 software useful for PFP operations are not generated automatically and require interpretation of the more complicated peak patterns using the knowledge and judgment of a trained scientist or specialist. To accelerate processing of material and minimize the necessity for expert data interpretation, PFP created and implemented software to give more directed results for plant operations purposes, with the option for expert review using PGA Version 3.0 software reserved as needed.

PFP personnel developed the program PROMPT (Version 1.01) to address their specific needs in prompt gamma-ray energy analysis. The PFP's initial objective in PGA was to estimate chlorine quantities in ARF-102 inventory items and identify, for washing, those items that might contain more than about 1 wt% chlorine. Lab tests with CeO_2 and $NaCl/KCl/MgCl_2$ (CeO_2 used as a PuO_2 surrogate) showed that materials with this concentration of chloride were sufficiently hygroscopic to merit water washing to remove the soluble chloride salts. The purpose of the prompt gamma screening subsequently was to identify those ARF-102 items having the lowest chloride quantities for 1000°C thermal stabilization processing.

The complete PROMPT program, an expansion of PFP's initial prompt gamma chlorine estimation program, was created to satisfy the need to interpret the PGA spectral data in terms of the PGA screening logic shown in Figure 3. In addition to identifying (and estimating the quantities of) chlorine, the PROMPT program determines the relative background-corrected areas of the 1809-keV sodium and 2168-keV chlorine peaks and identifies the presence of potassium at its 1524 keV peak.

Like the PGA Version 3.0 software from LANL, the PROMPT software uses the prominent ^{239}Pu peak at 413.7 keV and the ^{208}Bi peak at 2614 keV for energy calibration. To attain good assurance of the chlorine quantity estimates without unduly extending counting times, the PROMPT software collects spectral data until the 1-sigma counting error in the background-corrected area accruing to the 2168-keV chlorine peak is less than 3.5% of the total chlorine peak area. For most ARF-102 items, with the highly efficient detectors, the goal precision is reached in less than 10 minutes of counting time. The software is set to gather spectra to attain the goal precision in the chlorine prompt gamma signal, or three hours, whichever comes first. The program produces a report at the end of the counting time.

The report output is sufficient for the process oversight scientist/engineer to identify whether or not the item is candidate for lower temperature stabilization based on the screening criteria. A sample report is shown in Figure 4. The system calibration and sample analysis routines are formalized in PFP operating procedures.



```
**********************************************
*  PROMPT GAMMA RESULTS – Ver 1.01, 20-May-03 *
**********************************************
SAMPLE ID                     PPSL-518
SPECTRUM FILE NO.             313.CHN
DETECTOR                        A
ITEM NET WEIGHT                1000.0  grams
Pu LABEL WEIGHT                 862.0  grams
DISTANCE TO ABSORBER             1.00  inches
DATE ANALYZED                 20-May-2003  TIME: 07:40    (140.6 2003)
DATE REPORTED                 25-May-2003


   AREA Pu-239           81246.   +/-   349.
   AREA K-39               671.   +/-   149.
   AREA Na-23            22181.   +/-   166.
   AREA Na-23             1804.   +/-    63.
   AREA Cl-35             2189.   +/-    52.
   AREA Bi-208             -49.   +/-   137.

ANALYSIS PARAMETERS :      COUNT TIME                   2.8 minutes
                           SYSTEM DEADTIME           20.3 %
SYSTEM CHECKS :
                           Pu-239       CENTROID:  664.12
                                         FWHM:        2.72
                           Bi-208       CENTROID: 4200.23
                                         FWHM:       4.72

                         CRITICAL LEVEL
                           NET COUNTS
Pu-239   ( 413.70 keV)       573.
K-39     (1524.00 keV)       245.
Na-23    (1808.70 keV)       273.
Cl-35    (2167.60 keV)       104.
Bi-208   (2614.00 keV)        85.
Bi-208   (4439.00 keV)       225.

            Grams     +/- Error            Wt %     MAX. Wt.%
Pu-239       467.        7.29
Na-23        90.7        1.32              9.07        9.33
Cl-35        507.        23.4              50.7        55.3

Na-23 to Cl-35 net peak area ratio:  12.30.  (Na/Cl ratio similar to ER salts.)
Potassium (fluorine) may be present

(ERROR ESTIMATES: 1-sigma. MAX. Wt.% is measured weight percent + 1.96*measurement
error.)
(Q: Measured area less than or equal to critical level.)

Analytical Laboratory:   __________________________   ________
                                  Name                  Date

Engineering Evaluation –
Approved for low temperature stabilization:  YES   NO
Thermal Stabilization Design Authority:        __________________________   ________
                                                        Name                 Date
```

Figure 4. Item Analysis Report for PFP's Prompt Software

2.6.2 Chlorine Measurement Using PGA

Qualitative identification of the presence of chlorine in the ARF-102 plutonium oxide materials at the PFP is based on observation of the 2168 keV chlorine peak in the spectrum. The quantification of chlorine is based on the counting rate measured for the item at the 2168 keV peak. The counting rates are corrected for background counting rates in the region of interest in the chlorine peak and distance of the item from the detector. To determine the chlorine quantity in the item, the count rate is divided by the known plutonium mass in the item and divided by the particular chlorine- and plutonium-specific count rate calibration factor for the detector.

The calibration factors at the PFP were determined by prompt gamma measurements of two selected ARF-102 items having known contained chlorine and plutonium quantities. One of the selected ARF-102 items (PPSL-518) is reserved for periodic checks of system performance. The plutonium quantities for each reference item are taken from their book values determined by nondestructive plutonium assay techniques, which combine gamma spectrometric isotopic analysis and calorimetry.

The chlorine concentration in the PPSL-518 calibration item was determined by water leaching of samples of item ARF-102-86-387 and analysis of the leachates by chloride ion selective electrode. The remainder of item ARF-102-86-387 was packaged as PPSL-518 and re-assayed for plutonium content. The chlorine concentration for the item ARF-102-85-185-5 was obtained through work reported for item ARF-102-85-186-5 (Cooper 1991). The chloride concentration for this item was determined using the Volhard titration method by precipitating the chloride with a known quantity of excess silver ion (Ag^+), separating the supernatant solution, and titrating the excess Ag^+ with thiocyanate using ferric ion (Fe^{3+}) as indicator.

The background-subtracted specific count rates [i.e., the count rate per gram of chlorine and per gram of plutonium or counts/(second·g Cl·g Pu)] for the $^{35}Cl(\alpha,p)$ reaction at 2168 keV were determined for each calibration standard in a fixed geometry for each of the four detector systems. The specific count rates for the standards at the fixed geometries for each system are calculated to become the calibration constants. Specific count rate data for the four systems are summarized in Table 2.

The two items selected for standards (PPSL-518 and ARF-102-85-185-5) are rich in chlorine (9.7 and 20 wt% Cl, respectively) and range over the plutonium concentrations (69.1 and 26.1 wt%, respectively) observed for most of the ARF-102 items. Despite the differing compositions, the specific count rates for the two standards are similar (within about 20%). The similarity supports the underlying thesis that the ARF-102 materials produced during pyrochemical operations at the RFP had comparable physical properties, were processed similarly, and, by virtue of the high temperature processing that melted the NaCl/KCl, were intimately blended such that the count rates for the 2168 keV ^{35}Cl peak are proportional to both the plutonium and chlorine quantities.

Table 2. PGA Calibration for Chlorine Quantity Determination in ARF-102 Items

Detector(a)	Standard(b)	2168-keV ^{35}Cl Count Rate, counts/sec	Average Specific Count Rates, counts/(sec · g Pu · g Cl)	
			Item	Overall
A	ARF-102-86-387	8.75	8.33×10^{-5}	$1.14 (\pm 0.10) \times 10^{-4}$
	PPSL-518	10.88, 10.82, 10.59, 10.07, 9.89, 11.41, 10.89, 10.74, 9.86	$1.15 (\pm 0.06) \times 10^{-4}$	
	ARF-102-85-185-5	3.22, 3.54, 3.68, 3.40, 3.22	$1.19 (\pm 0.07) \times 10^{-4}$	
B	PPSL-518	11.52, 11.38, 11.92, 9.79, 12.18, 10.97, 11.43, 10.39, 11.94, 11.64	$1.24 (\pm 0.08) \times 10^{-4}$	$1.22 (\pm 0.08) \times 10^{-4}$
	ARF-102-85-185-5	3.23, 3.54, 3.67, 3.39, 3.22	$1.18 (\pm 0.07) \times 10^{-4}$	
C	PPSL-518	10.73, 11.38, 11.54, 12.79, 11.24, 12.97, 11.87, 12.88, 10.47	$1.28 (\pm 0.10) \times 10^{-4}$	$1.28 (\pm 0.10) \times 10^{-4}$
	ARF-102-85-185-5	None	–	
D	PPSL-518	7.29, 8.01, 7.78, 8.09, 7.59, 6.90, 6.74, 7.34, 7.35, 6.49	$8.03 (\pm 0.58) \times 10^{-5}$	$9.77 (\pm 2.37) \times 10^{-5}$
	ARF-102-85-185-5	3.69, 3.71, 3.59, 3.67, 3.65	$1.27 (\pm 0.16) \times 10^{-4}$	

(a) Detectors A, B, and C view the item from the side; Detector D views the item from below.
(b) Item PPSL-518 was made from ARF-102-86-387; item ARF-102-85-185-5 has been discarded to WIPP.

The following example illustrates how the Prompt Version 1.0 software calculates the chlorine quantity and concentration in a measured item. Suppose a 1050-gram (net weight) item, known by nondestructive assay to contain 800 grams of plutonium, is counted for 38.3 minutes (2298 seconds) using detector A and that the 2168 keV peak contained 4132 net (background-subtracted) counts. The count rate would be 4132 counts / 2298 seconds or 1.798 counts/sec. According to Table 2, the detector A calibration factor is 1.14×10^{-4} counts/(sec·g Pu·g Cl). By the calculation given below, the item would contain 19.7 grams of chlorine:

$$\frac{1.798 \text{ counts}}{\text{sec}} \times \frac{\text{g Pu} \cdot \text{g Cl}}{1.14 \times 10^{-4} \text{ counts}} \times \frac{1}{800 \text{ g Pu}} = 19.7 \text{ g Cl}$$

and the chloride concentration in the item would be 1.88 wt% (100% × 19.7 g Cl/1050 g net wt). At this concentration, under prior PFP guidelines for processing ARF-102 materials, the item would have qualified for water washing because it contains more than 1 wt% chlorine.

2.6.3 Analysis of the Sodium-to-Chlorine Peak Area Ratio Using PGA

The second step to identify the presence of ER salt in ARF-102 items according to the screening logic given in Figure 3 is determining the intensities of the ^{23}Na(α,pγ) at peak 1808 keV and the ^{35}Cl(α,pγ) peak at 2167 keV, calculating the ratio of the intensities, and comparing those ratios with those observed for certifiably ER salt-bearing plutonium oxide materials. The validity of this measurement of peak area ratios is based on the following assumptions:

- The chemical ratios of sodium chloride to potassium chloride were closely maintained in RFP pyrochemical (ER and MSE) operations.[a]
- The mole ratio of sodium to chlorine is not significantly altered during processing or subsequent thermal stabilization.
- The sodium and chlorine mix to the same degree of intimacy with the plutonium/ americium oxide (i.e., there is no preferential segregation of sodium or chlorine away from the alpha particle-emitting materials).

To test these assumptions, prompt gamma-ray spectra were taken at RFETS of 20 items known to be from IDC 067 (chlorinated oxides) and IDC 086 (ER scrape-out oxide). In most cases, two of the feed items were combined to produce the 10 3013 items listed, respectively, below their constituent feed items in Table 3. The spectra were interpreted at the RFETS using the LANL PGA software and the integrated peak areas for sodium and chlorine determined. The spectral files also were sent to the PFP and analyzed using the PROMPT software. The ratios of the sodium-to-chlorine peak areas were calculated for both sets of peak area data. Though the peak areas determined by PFP's PROMPT software are somewhat greater than those found by the PGA software, the Na/Cl peak area ratios are comparable. The integrated 1808 (Na) and 2167 (Cl) keV peak areas show good correlation such that the average net background-subtracted Na peak is about 12 times as high as the net Cl peak for either software program. However, the standard deviation (σ) is greater for the feed items evaluated by the PFP's PROMPT program than for the LANL PGA software. The difference likely lies in methods used for background subtraction.

Subsequently, PGA spectra from 34 product 3013 containers, gathered using RFETS spectrometers, were analyzed using the PGA Version 3.0 software. The materials being stabilized for packaging into the 3013 product containers were IDC 067 and 086 items. Seven of the 34 items were 3013 products shown in Table 3. The Na/Cl ratios (Table 4) range from 9.8 to 15.0 with average of 12.0 ± 1.1 at one standard deviation (Narlesky 2003a). The average is similar but the range tighter than shown in Table 3 for 3013 containers measured at RFETS by the PGA Version 3.0 software.

(a) The analyzed Na/(Na+K) mole ratio in some IDC 086 ER scrape-out items reportedly varied from ~0.47-0.64 (Guadagnoli and Esquibel 1986, as reported in Boak et al. 2002) versus 0.5 expected for an equimolar NaCl-KCl mixture. The apparent enrichment of the salt-bearing scrap in NaCl is consistent with the higher vapor pressure of KCl compared with NaCl.

Table 3. PGA Peak Areas for RFETS IDC 067 and IDC 086 ER Items

IDC-3013	Item Number Feed – 3013	Peak Area, counts				Na/Cl Peak Area Ratio	
		RFETS (PGA)		PFP (PROMPT)			
		Cl	Na	Cl	Na	RFETS	PFP
067	C01796	808	12819	863	13435	15.87	15.57
086	C00470	1249	16278	1507	17042	13.03	11.31
3013	H000804	1296	18287	1561	21815	14.11	13.98
086	C00688	1439	17641	1758	20112	12.26	11.44
086	C00821	1453	13691	1739	15690	9.42	9.02
3013	R610285	1814	19266	1788	22538	10.62	12.61
067	CLLANL063	756	10108	823	11785	13.37	14.32
086	C01313	2424	25847	2286	25730	10.66	11.26
3013	R610269	1038	11824	1375	13574	11.39	9.87
086	C00290	1814	20758	2117	23822	11.44	11.25
086	C00299	1203	16711	1502	18595	13.89	12.38
3013	R610324	1344	14714	1352	17912	10.95	13.25
086	C000129	1400	15911	1873	17914	11.37	9.56
086	C01154(a)	1880	18958	1924	21432	10.08	11.14
3013	H000549	1344	14714	1352	17912	10.95	13.25
067	C00356	812	12385	730	13009	15.25	17.82
067	C00655	558	5581	764	6713	10.00	8.79
3013	R610326	917	11298	845	13723	12.32	16.24
067	CLLANL026	1184	14194	(b)	(b)	11.99	–
067	CLLANL067	712	10939	770	12879	15.36	16.73
3013	R610439	1760	20439	1884	24092	11.61	12.79
067	CLLANL060(c)	–	–	–	–	–	–
086	C00876	997	10354	1038	12010	10.39	11.57
3013	R610391	1288	16162	1295	19367	12.55	14.96
086	C00877	1215	12672	1372	14777	10.43	10.77
086	C01141	1514	14595	1345	16579	9.64	12.33
086	C01154(a)	1880	18958	1924	21432	10.08	11.14
3013	H000798	1760	19852	1877	23914	11.28	12.74
067	C00106	49	755	66	854	15.41	12.94
067	CLLANL062	ND(d)	1134	(b)	(b)	–	–
3013	R610417	ND	925	(b)	(b)	–	–
Feed Items			Average			11.75	11.97
			Standard Deviation, σ			1.09	2.35
3013 Product Items			Average			12.10	13.30
			Standard Deviation, σ			2.19	1.76

(a) This item split between H000549 and H000798.
(b) Spectrum not obtained.
(c) Data file blank.
(d) ND – not detected.

Table 4. PGA Peak Areas for RFETS 3013 Products Containing IDC 067 and IDC 086 ER Items

Item Number	Peak Area, counts		Na/Cl Peak Area Ratio
	Cl	Na	
R610911	1319	12900	9.78
R611033	1453	14914	10.26
R610406	533	5579	10.47
R610868	888	9654	10.87
R610977	1535	16834	10.97
R610427(a,b)	1221	13436	11.00
R610269(a)	960	10580	11.02
R610747	1357	14980	11.04
R610324(a)	1192	13187	11.06
H000798(a)	1589	17618	11.09
R610673	689	7691	11.16
R610607	628	7083	11.28
R610853	382	4323	11.32
R610639	955	11103	11.63
R610775	1225	14353	11.72
R610285(a)	1224	14622	11.95
R610388	1332	16196	12.16
R610356(c)	821	10056	12.25
R610586	727	8925	12.28
R611066	1306	16039	12.28
H000804(a)	1329	16385	12.33
R610845	1474	18221	12.36
R610391	1154	14461	12.53
R610755	702	8826	12.57
R610931	1350	17065	12.64
R611078	837	10626	12.70
R610697	1299	16529	12.72
R610439(a)	1405	18262	13.00
R610875	1149	15040	13.09
R610898	1398	18368	13.14
R610655	662	8735	13.19
R610869	1147	15224	13.27
R610405	965	13214	13.69
R610761	700	10516	15.02
		Average	12.00
		Standard Deviation	1.10

(a) Item listed in Table 3.
(b) Was H000439.
(c) Was R610326.

To be an effective screening tool, the Na/Cl peak areas and peak area ratios for items containing NaCl/KCl pyrochemical salt should differ distinctly from those observed for items known to be uncontaminated with NaCl/KCl salt. To this end, the database for the plutonium materials represented for storage under the 3013 Standard under the MIS program was reviewed to find items measured by PGA and compare the findings with process knowledge (RFP IDC), chemical analysis (for Cl, Na, and K), and phase characterization (as determined by XRD) of the same items. The chemical and XRD analyses of the MIS inventory items given in the MIS database were performed at LANL. In most cases, chemical analyses of the items were available in their as-received condition and after thermal testing at 950°C.

The prompt gamma spectra presented in the MIS database also were gathered at LANL and analyzed using manual peak integration. Some of the spectra subsequently were reviewed using the PGA Version 3 software (Narlesky 2003a). The integrated Na peaks obtained by the PGA Version 3 software generally were lower than those obtained manually, and some of the Cl peaks found manually were not observed to be statistically significant above background by the PGA software. The results of the chemical, physical, and prompt-gamma spectra database review are compared in Table 5.

The RFP IDCs 067 and 086 (represented by items HL025 and T0695, respectively) are from pyrochemical processing and should include NaCl/KCl salts. IDC 046 is derived from 067 (Boak et al. 2002) and therefore also should include NaCl/KCl. The chemical analyses confirm these expectations and show 1 to 10% levels of Cl, Na, and K, while the PGAs of these items show strong Na and Cl signals with Na/Cl peak area ratios around 15 (based on MIS data) for the IDC 067 and 086 items and 31 for the IDC 046 item. The XRD of the IDC 046 item suggests the presence of NaCl.

The RFP IDC 061 is non-specification plutonium oxide and may contain pyrochemical salt impurities. However, only trace Cl, Na, or K were found for the two representatives of this IDC, consistent with the absence of PGA signals for Na and Cl.

Three IDC Y61 items are presented in Table 5. This IDC arose from mixed Pu/EU (enriched uranium) oxide with over 10,000 ppm (1%) EU. These items should contain little salt according to process knowledge. Only low salt concentrations were found by chemical analyses of C1407 and L9194 and the PGA results confirm this expectation by finding weak Na signals and no detectible Cl. However, chemical analyses found item O3038 to have percent-level Cl, Na, and K with NaCl and KCl detected by XRD. The PGA results are consistent with the chemical analyses and find strong Na and Cl signals (with 7.3 peak area ratio). The chemical and PGA evidence indicate that the IDC for this item may be incorrect.

Item H2282 is the sole IDC 062 item. This IDC is nominally a high purity dissolution heel and should contain little salt. However, the chemical analyses found about 1 wt% total salt and the PGA detected small but measurable Na and Cl signals with a 9.7 Na/Cl peak area ratio.

Table 5. Chemical, Physical, and PGA Properties of MIS Materials

Item Number	IDC	Description				PGA Peak Area, counts, MIS/Ver. 3		Na/Cl Peak Area Ratio
		Comp, wt%, as-rec'd/950°C			XRD			
		Cl	Na	K		Na	Cl	
RFETS								
B1579 (ORF52-5501579)	061	0.06/0.07	<0.01/<0.01	0.03/0.03	NA(a)	ND(b)	ND	–
C1407 (ORF52-5501407)	Y61	0.30/0.16	<0.01/<0.01	0.03/0.03	NA	474/–	ND	–
H2282 (ORF59-07032282A)	062	0.17/0.72	0.03/0.25	0.01/0.12	NA	848/2565	87/ND	9.7/–
HL025 (ORF59-CLLANL025)	067	10.0/5.90	1.96/1.01	5.12/2.90	NA	24512/10586	1686/861	14.5/12.3
J2201 (ORF59-07242201A)	289	1.28/0.50	0.05/0.28	1.06/0.70	NA	5779/NA	ND/NA	–
L9194 ORF52-669194)	Y61	0.81/0.02	0.01/0.19	0.01/0.13	NA	272/NA	ND/NA	–
O3038 (ORF52-053038)	Y61	9.0/4.45	1.1/1.1	1.0/1.4	PuO_2 NaCl KCl	11688/8379	1607/7684	7.3/5.4
S1856 (ORF52-07161856)	081	0.9/0.02	0.65/0.04	0.04/0.04	PuO_2	1438/NA	ND/NA	–
T0695 (ORF52-C00695)	086	9.00/5.50	7.43/1.77	3.47/1.75	NA	28339/22458	1872/1727	15.1/13.0
V0024 (ORF59-C00024A)	046	5.68/ 0.53-11	2.19/1.06	2.62/1.72	PuO_2 NaCl(?)	8161/5763	262/ND	31.1/–
W1490 (ORF52-MT1490)	653	0.008/ 0.017	0.036/0.06	0.023/0.02	NA	176/NA	ND/NA	–
X2165 (ORF59-072422165A)	289	0.04/0.009	1.0/0.14	<0.004/0.13	NA	1388/NA	ND/NA	–
Can 92	061	0.25/0.09	<0.007/0.01	0.02/0.18	PuO_2	ND/NA	ND/NA	–
Hanford								
ARF-102-85-223	?	11.2/5.50	4.78/1.47	6.62/1.87	NA	40836/30346	2534/2261	16.1/13.4
ARF-102-85-295A	?	>20/7.70	3.65/2.36	5.44/2.33	PuO_2 NaCl KCl	11486/8913	722/601	15.9/14.8
ARF-102-85-355	?	2.90/0.74	0.10/0.03	0.08/0.01	NA	16157/15087	1643	9.8/10.5
ARF-102-85-365	?	1.13/3.80	4.43/1.63	5.77/0.22	PuO_2 NaCl KCl	22307/17383	1148/1075	19.4/16.2
PSU-84-06-05	?	0.007/0.001	0.069/0.067	<0.01/<0.01		140/NA	ND/NA	–
LANL								
MISNE2	?	~86 wt% Pu				405/NA	ND/NA	–
MISNE4	?	0.091	0.73	1.12	NA	24775/19367	2235/1997	11.1/9.7

(a) NA – not analyzed.
(b) ND – not detected.

The two IDC 289 items are nominally low-purity plutonium oxide dissolution heels with low soluble salt concentrations expected. The chemical analyses for both items show ~1 to 2 wt% Na/KCl, with PGA finding Na but no detectible Cl. The IDC 653 is a mixed plutonium/ neptunium oxide with the possible presence of pyrochemical salt. Both the chemical analyses and PGA show little salt present in the single IDC 653 item. IDC 081 is a bomb-reduction glovebox sweeping that should have little salt. The chemical analysis shows around 1 wt% salt; the PGA detects Na but no Cl.

Four ARF-102 items from Hanford are described in Table 5. All four items show multi-wt% Cl concentrations, and three of the items show corresponding multi-wt% Na and K concentrations (the fourth item has low Na and K and a poor material balance). Two of the four were examined by XRD, and both showed NaCl and KCl to be present. The PGAs for all four items have strong Na and Cl peaks with Na/Cl ratios ranging from 9.8 to 19.4, consistent with the chemical analyses. Item PSU-84-06-05 has low salt concentration with no Cl and small Na signals by PGA.

Of the two LANL items, item MISNE4 evidently contains pyrochemical salt by chemical analysis (though the Cl concentration is low) and gives strong Na and Cl PGA peaks with 11:1 Na/Cl ratio. The second LANL item is essentially pure plutonium oxide with a small PGA signal for Na and no Cl signal.

The findings in Table 5 indicate that the IDCs can be inexact predictors of the salt contents of the RFETS items. However, the chemical analyses and PGA results for all materials show good correspondence, with percent or greater pyrochemical salt levels being readily detected by PGA using the LANL gamma spectrometer. In addition, though the Na/Cl ratio values for the high salt items have wider scatter, they are generally consistent with the ratio (~12) observed for the known ER materials (Tables 3 and 4).

The ^{35}Cl and ^{23}Na peak area results of RFETS prompt gamma-ray spectra of the IDC 067 and 086 feed and product 3013 items analyzed by PFP's PROMPT program are plotted in Figure 5. The ^{23}Na/^{35}Cl peak area ratios are 12.6, on average, for these items; the line in Figure 5 corresponds to this average ratio. Also plotted in Figure 5 are the ^{35}Cl and ^{23}Na peak areas obtained by using the PROMPT software to interpret the prompt gamma spectra obtained from Foster and colleagues (2002) tests of PuO_2 blended with equimolar NaCl/KCl and CaF_2 heated past NaCl/KCl melting to 800° or 950°C. Results from duplicate LANL prompt gamma measurements of MIS item ARF-85-102-295, interpreted by the PROMPT software, also are given in Figure 5. The ^{35}Cl and ^{23}Na peak areas observed for 34 RFETS 3013 container items prepared from stabilized IDC 067 and 086 materials (obtained using the PGA Version 3.0 software; data from Table 4) likewise are plotted in Figure 5.

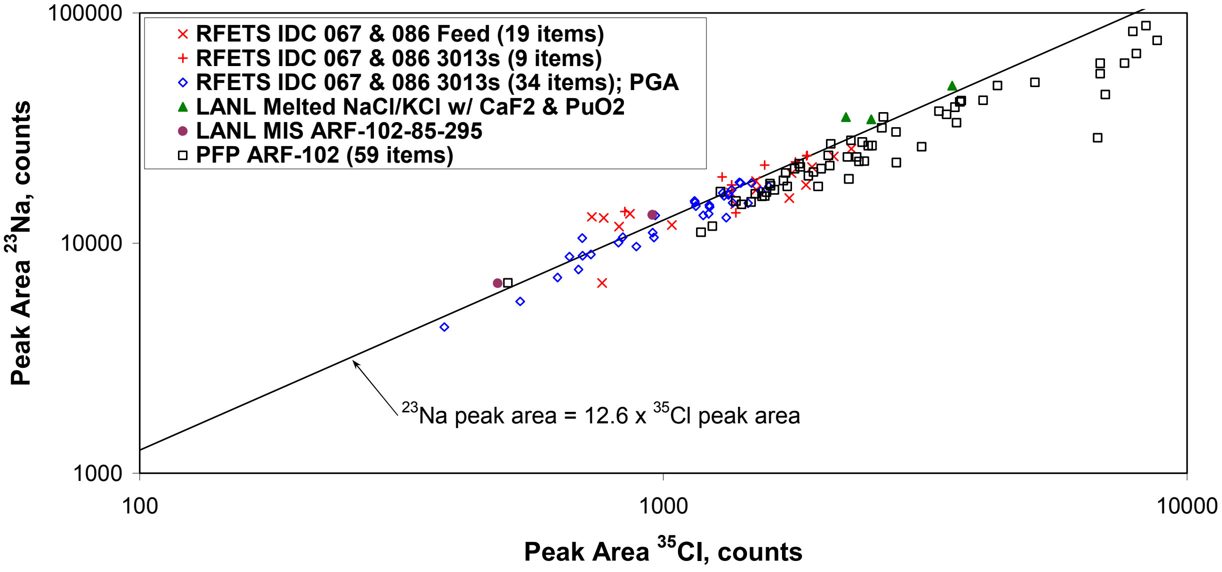


Figure 5. Peak Areas for ^{23}Na at 1808 keV as a Function of ^{35}Cl Peak Area at 2167 keV. All spectra were interpreted using PROMPT except the 34 RFETS IDC 067 and 086 3013 container items, which were interpreted using PGA Version 3.0 (three ARF-102 item data points lie slightly off the plot near the upper right corner, and one IDC 067 and 086 feed lies off the low end of the plot).

These measurements, obtained from materials known to originate from electrorefining processes or to contain ER salts, are seen to have similar relative ^{23}Na and ^{35}Cl peak areas and lie near the line representing the 12.6 ratio. The ^{23}Na and ^{35}Cl peak areas observed for 59 PFP measurements of ARF-102 items, interpreted using the PROMPT software, are also shown in Figure 5. Most of the ARF-102 data lie near the line representing the 12.6 ^{23}Na/^{35}Cl peak area ratio, thus supporting their likely origin from ER processing.

Results from the same items shown in Figure 5 are replotted in Figure 6 to show the ^{23}Na/^{35}Cl peak area ratio as a function of the ^{35}Cl peak area. The Na/Cl peak area ratios for the RFETS IDC 067 and 086 feed and product (3013) items, evaluated using the PROMPT software, are 12.6 ± 4.6 (at 2σ). The ±2σ tolerances (i.e., ratio range 8.0 – 17.2) are larger than observed for the feed and product 3013 RFETS items analyzed by the PGA Version 3.0 software (Tables 3 and 4) but accurately reflect the range observed by the PROMPT software to be used in the PFP operations to sort for presence of ER salt in ARF-102 items. These limits encompass all but one of the source data and include all the data measured for the PuO_2/NaCl/KCl/CaF_2 LANL melted blends (Foster et al. 2002), the duplicate LANL measurements of MIS item ARF-85-102-295, and the 34 RFETS 3013s from IDC 067 and 086 feed (as analyzed using the PGA Version 3.0 software).

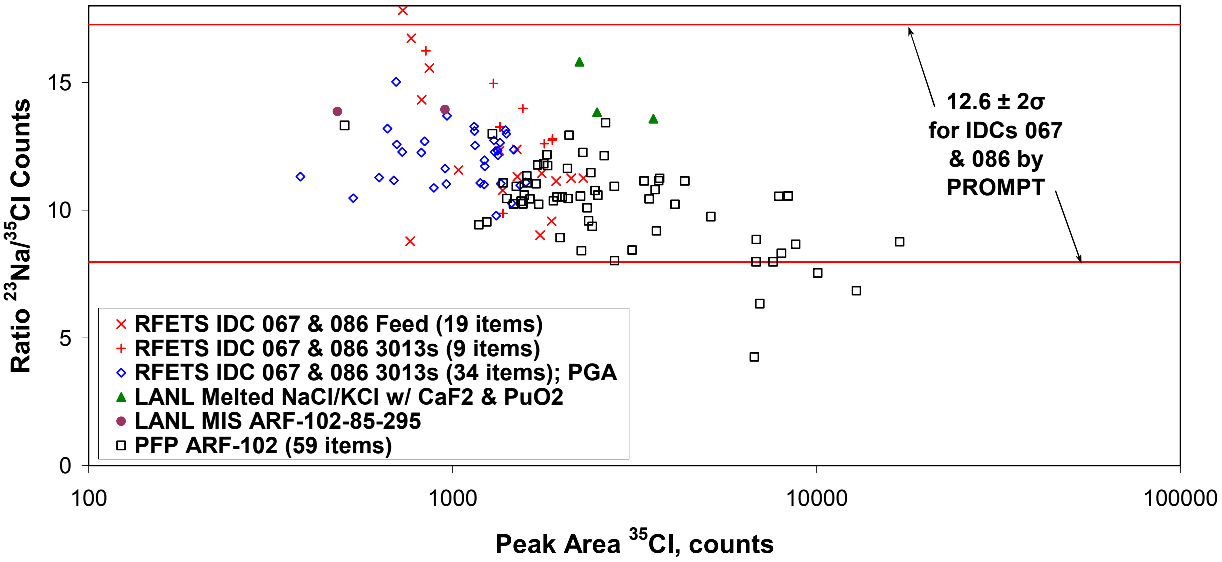


Figure 6. Ratio of Peak Areas for ^{23}Na at 1808 keV to ^{35}Cl at 2167 keV as a Function of ^{35}Cl Peak Area. All spectra were interpreted using PROMPT except the 34 RFETS IDC 067 and 086 3013 container items, which were interpreted using PGA Version 3.0.

Measurements at PFP of the ^{23}Na and ^{35}Cl prompt gamma peak area ratios for 59 ARF-102 items, several in duplicate, also are plotted in Figure 6. Though the individual peak areas generally are larger (probably because of the greater sensitivity of the PFP detector system), the relative areas of the ^{23}Na and ^{35}Cl integrated peaks are similar to those observed for the RFETS ER salt items. All but a few of the ARF-102 ^{23}Na/^{35}Cl peak ratios lie between the ±2σ limits of the average ^{23}Na/^{35}Cl peak area ratio observed for the RFETS items known to originate from ER processing and again support the ER processing origin of most of the ARF-102 items. Though the ^{23}Na signal is prominent in all of the ARF-102 items measured by prompt gamma, the observation of ^{23}Na/^{35}Cl peaks ratios lower than 8 might be evidence of additional chloride from DOR salt ($CaCl_2$) with a significant ER component or might reflect some residual unconverted MgC_{l2}.

Some of the ARF-102 items that plot below the lower limit for Na/Cl ratio still have a significant sodium signal. This may be due to differences in detector efficiencies for the RFETS and PFP instruments. Detection of potassium in the items containing low ^{23}Na/^{35}Cl peak area ratios but with an appreciable sodium peak likely indicates that the dominant chlorides were still NaCl/KCl.

2.6.4 Analysis of the Potassium Peak

The third means to screen items for the presence of ER salt in ARF-102 items is to search for the presence of potassium (Figure 3), which is indicated by its peak at 1524 keV. To detect potassium in a NaCl/KCl mixture reliably, the counting times mandated by the PROMPT counting routine is set to attain <3.5% error in the background-corrected ^{35}Cl peak at 2167 keV or three hours, whichever comes first. This sensitivity for chlorine would yield an error for the potassium peak of <7% for items containing the nominal equimolar NaCl/KCl ER salt.

The <7% counting error estimate arises given the ~2-fold lower sensitivity for potassium (Table 6) and the fact that ER salt (equimolar NaCl/KCl) contains about twice as much chlorine as potassium on a mole basis. However, the potassium peak could be obscured if enough fluorine (peak at 1528 keV) is present. Thus, if assessment of the potassium peak is required to judge the presence of ER salts, expert evaluation of the spectrum may be needed.

A prompt gamma spectrum of PFP's ARF-102-85-185-5 standard is given in Figure 7. The inset in the spectrum magnifies the interval near 1528 keV to illustrate the overlap of the potassium (^{39}K) and fluorine (^{19}F) peaks. In practice, however, few of the ARF-102 items examined to date at the PFP have shown significant interference of the 1524 keV potassium peak by the 1528 keV fluorine peak.

Table 6. Estimated PGA Detection Limits for 60-Minute Counts at LANL (Narlesky 2003b)

Element	Peak(s) Required for Detection, keV	Estimated Detection Limit, wt%	Estimates Based on MIS Item
Al	2236, 1263	0.3	MISNE4
Be	4439.2	0.03	O53038
Cl	2168	0.75	07032282A
F	1275, 891	0.1	072422165A
K	1524	1.4	O53038
Mg	1273, 1014	0.05	669194
Na	1808	0.04	MT1490

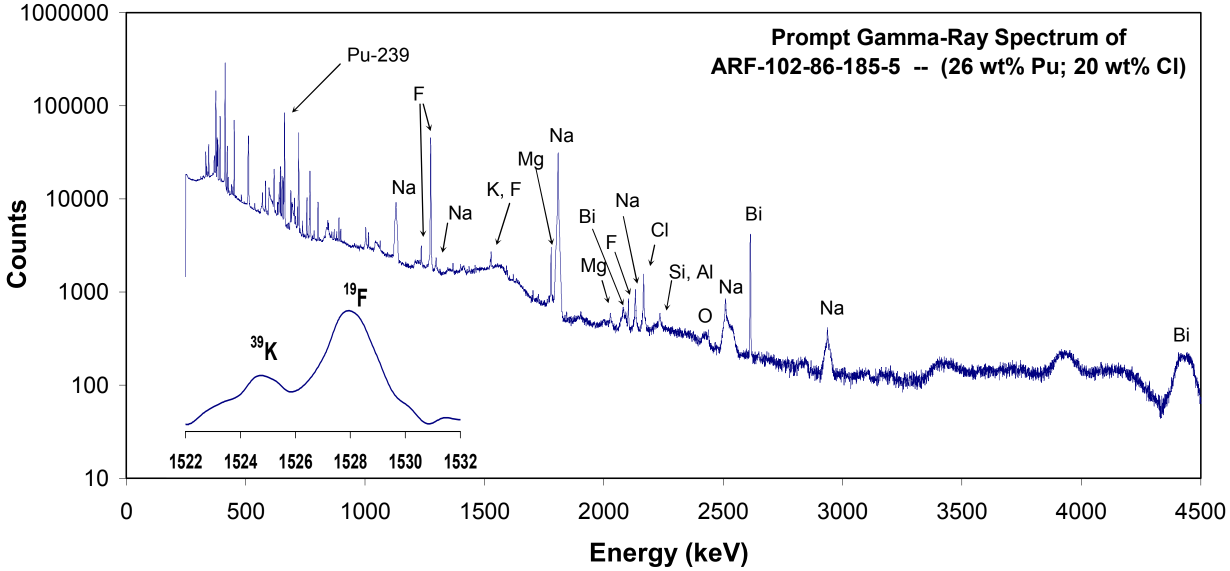


Figure 7. PGA Spectrum of Chlorine Standard ARF-102-86-185-5. Inset expands the 1522 to 1532 keV interval to show overlap of the ^{19}F and ^{39}K peaks.

3.0 Conclusions

Prompt gamma measurements made at RFETS of materials certifiably originating from ER processes clearly show the 2167 keV ^{35}Cl peak and relative constancy of the 1808 keV ^{23}Na and 2167 keV ^{35}Cl peak area ratios. Chemical and prompt gamma analyses of items in the MIS inventory confirm these conclusions and also show that items without the ER salts lack the characteristic prompt gamma signatures. Therefore, identification of ^{35}Cl signal in an ARF-102 item, evaluation of the item's ^{23}Na/^{35}Cl peak area ratio, and comparison of the measured ratio with those observed for RFETS ER material provide a simple means for PFP operations to identify items containing ER salt. Further assessment of the prompt gamma spectrum to find evidence of potassium (peak at 1524 keV) also can be performed but with possible compromise if significant fluorine is present. In practice, little interference of fluorine on the potassium peak for ARF-102 items has been observed.

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