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Preparation and Characterization of a Master Blend of Plutonium Oxide for the 3013 Large Scale Shelf-Life Surveillance Project

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Executive Summary

A mixture of chlorine-containing, impure plutonium oxides has been produced and has been given the name Master Blend. This large quantity of well-characterized chlorine-containing material is available for use in the Integrated Surveillance and Monitoring Program for shelf-life experiments. It is intended to be representative of materials packaged to meet DOE-STD-3013.[1] The Master Blend contains a mixture of items produced in Los Alamos National Laboratory's (LANL) electro-refining pyrochemical process in the late 1990s. Twenty items were crushed and sieved, calcined to 800ºC for four hours, and blended multiple times. This process resulted in four batches of Master Blend. Calorimetry and density data on material from the four batches indicate homogeneity.

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Introduction

The Department of Energy (DOE) Standard for packaging and storing plutonium-bearing materials, DOE-STD-3013[1], requires a surveillance program to validate that the material can be safely stored up to 50 years. The Integrated Surveillance and Monitoring Program for Materials Packaged to Meet the DOE-STD-3013[2] uses a combination of Field Surveillance, which examines certified 3013 containers in storage, and shelf-life testing where representative and other materials are tested to evaluate potential degradation mechanisms. The Surveillance and Monitoring Program has identified salt-bearing plutonium oxide as a particular concern in terms of container pressurization and corrosion.

A mixture of salt-bearing plutonium oxides has been produced to provide a consistent starting material for LANL large-scale shelf-life experiments. This material, referred to as Master Blend, was formed from the combination of LANL burned anode heels and electro-refining low purity residue items. The intent was to develop a large batch of salt-bearing material so that multiple large-scale experiments could be conducted. The material mixture was prepared similar to how Hanford and Rocky Flats Environmental Technology Site (RFETS) stabilized and packaged pyrochemical salt materials into 3013 containers. This report describes processing conditions and characterization results for the Master Blend. A homogeneous mixture was achieved using a combinatorial method that maximized mixing while adhering to the criticality limits and equipment limitations. Calorimetry and density measurements, which were used to assess the homogeneity of the material, are presented.

Material Selection

The Master Blend contains a mixture of 19 items (PMA#OX and XBS#) produced by the LANL electro-refining pyrochemical process in the late 1990s and one previously stabilized item (PMAXBSC1[3]) from the same sources. PMA-OX items are comprised of pyrochemical oxide residues from recast anode heels, direct oxide buttons, and turnings. Their plutonium content was between 70 and 85 weight percent. XBS items were comprised of pyrochemical oxide electro-refining residues containing $MgCl_2$. Their plutonium content varied from 19 to 24 weight percent. Table 1 is an itemized list of the material that went into the creation of the Master Blend.

Table 1. Master Blend Material

Item ID	Net (g)	SNM	Pu (Wt.%)
PMA6328OX	705.4	556.0	78.82
PMA6331OX	548.4	442.0	80.60
PMA6339OX	328.2	242.0	73.74
PMA6341OX	968.7	810.0	83.62
PMA6355OX	760.9	589.0	77.41
PMA6357OX	866.7	711.0	82.04
PMA7347OX	861.2	701.0	81.40
PMA8451OX	539.8	398.0	73.73

Item ID	Net (g)	SNM	Pu (Wt.%)
PMA8454OX	310.5	256.0	82.45
PMA8456OX	2066.6	1695.0	82.02
PMA8472OX	411.4	303.0	73.65
PMA9441OX	772.8	629.0	81.39
PMA9452OX	381.7	326.0	85.41
PMA9454OX	591.1	449.0	75.96
PMA9465OX	288.8	246.0	85.18
PMA9479AOX1	610.4	508.0	83.22
PMA Total	**11,012.6**	**8,861.0**	**80.04**
XBS9498	1744.9	332.0	19.03
XBS7358	1870.3	452.0	24.17
XBS9486	1727.4	352.0	20.38
XBS Total	**5,342.6**	**1,136.0**	**21.19**
PMAXBSC1	72.0	53.0	73.61

The material shown in Figures 1 through 4 are representative of the PMA feed items. The material in Figure 1 contained a mixture of fine brown oxide and brown chunks. Material in Figure 2 was slightly grayer material containing more flakes along with white flakes of an unknown composition. The material in Figure 3 had a slightly greener tint and contained several brush strands. The material in Figure 4 had a similar appearance to the material shown in Figure 2.

Figure 1. PMA 63280OX Feed Material

Figure 2. PMA 6355OX Feed Material

Figure 3. PMA 8472OX Feed Material

Figure 4. PMA 8450OX Feed Material

The material shown in Figures 5 and 6 are representative of the XBS feed material. The material shown in Figure 5 contained no powder and had chunks ranging in size from pebble sized to two inches across, and was gray in color. The material seen in Figure 6 was tan to slightly greenish in color. The material contained some powder though the majority of the material was contained in a single, large cylindrical mass. The condition of the two cans also differed significantly. The slip top lid container seen in Figure 5 was like new while the can seen in Figure 6 was heavily tarnished and possibly corroded. The interiors of the container and lid are shown in Figures 7 and 8, respectively. The upper interior of the container and the interior of the lid had a more tarnished or possibly corroded appearance than did the bottom interior of the container.

Figure 5. XBS 7358 Feed Material

Figure 6. XBS 9486 Feed Material

Figure 7. XBS 9486 Can Interior

Figure 8. XBS 9486 Lid Interior

Material Preparation

Feed material used in the Master Blend was grouped into three categories: PMA, XBS, and P (material left over from the creation of item PMAXBSC1). Feed materials from the XBS and P groups were combined, rod-milled, and V-blended prior to combining them with PMA feed material.

PMA feed material was sieved, and chunks accounted for 2771.3g, or 25 weight percent of the approximately 11,013g of material. These chunks were rod-milled for two hours and forty-five minutes. The reduced chunks were then recombined with the fines and V-blended for one hour.

Each XBS item was rod-milled in its entirety. The fines were then separated and the chunks from each item were combined for additional rod-milling. Table 2 summarizes rod-milling times for each item and reports the percent of material remaining as chunks after rod-milling. The remaining chunks were discarded and not used in the Master Blend.

Table 2. Rod-Milling of XBS Items

Item ID	Milling Time (hrs)	Initial Weight	Final Weight Fines	Final Weight Chunks	Wt.% Chunks Remaining
XBS7358	2.5	1870.2	1676.9	183.4	9.8
XBS9498	3.0	1744.5	1517.4	157.6	9.0
XBS9486	4.0	1727.0	1463.4	151.5	8.8
XBSCHU	Not Reported	25.8	19.0	2.2	8.5

Three batches of K_2MgCl_4 were prepared for use in the Master Blend to spike the material with a hygroscopic salt compound likely to be present in the material after heating. Each batch contained approximately 16.6660 g (0.175 mols) of $MgCl_2$ and approximately 26.1000 g (0.350 mols) of KCl. After hand shaking in a glass vial, the mixture was transferred to a ceramic crucible, placed in a furnace and heated to 825^{o}C. After a soak time of one hour, the material was cooled inside the furnace. The weight loss upon heating and the amount of salt transferred to PF-4 for each batch is shown in Table 3.

Table 3. Weight Losses of K_2MgCl_4 **upon Heating and Amount Transferred to PF-4**

Batch	Wt Loss Upon Heating (g)	Batch Size Transferred (g)
A	0.2286	40.5089
B	0.2220	41.4262
C	0.2331	40.6413

Figure 9 is a photograph of the K_2MgCl_4 material prepared for batch A, after it was removed from the furnace. The blackish color is most likely attributable to furnace ash. After the material was removed from the furnace, it was broken out of the ceramic crucible leaving crucible residue in the material and material residue in the crucible. The material was then ground into a fine powder using a mortar and pestle. The powder was transferred to a plastic container, then sealed into a conflat container for transfer to PF-4.

Figure 9. Batch A after Heating

Calcination

After being split into three batches, the material was calcined in a Hastelloy X calcination vessel at 800°C for four hours. Calcination parameters for the three batches are summarized in Table 4.

Table 4. Calcination Temperature, Ramp Rate, and Time

Item ID	Calcination Temperature (°C)	Calcination Time (hours)
Batch A	800	4.0
Batch B	800	4.0
Batch C	800	4.0

Material weights, vessel weights, and bed depths for the three batches are summarized in Table 5.

Table 5. Batch Weights and Bed Depth Pre- and Post-Calcination

Parameter	Batch A	Batch B	Batch C
Pre-calcination Vessel Wt (g)	2665.5	2605.0	2629.5
Pre-calcination Gross Wt (g)	8163.3	8117.2	8118.5
Pre-calcination Net Wt (g)	5497.8	5512.2	5489.0
Pre-calcination Bed Depth (in)	2	1.75 - 2	2.5
Post-calcination Vessel Wt (g)	2606.7	2645.4	2701.9
Post-calcination Gross Wt (g)	8019.6	7935.8	8106.0
Post-calcination Net Wt (g)	5354.1	5330.8	5476.5
Post-calcination Bed Depth (in)	2.5	1.5 - 2	2.5
Gross Weight Change (g)	-143.7	-181.4	-12.5
Vessel Weight Change (g)	-58.8	38.7	72.4
Material Weight Change (g)	-84.9	See Text	See Text

The Batch A vessel and material after calcination are shown in Figures 10 and 11.

Figure 10. Batch A Material and Vessel after Calcination

Figure 11. Batch A Material and Vessel after Calcination

The calcination vessel showed signs of heavy oxidation during calcination. Several large flakes seen in the first photograph fell off the vessel before it could be weighed. The Master Blend material differed in color between the two photographs. It is likely that the color seen in the second picture is more indicative of the true color because the first picture was taken through plastic shielding. After weighing the vessel, the material was removed using a hammer and screwdriver. The material was extremely hard and required two hours of work to completely remove from the vessel. Figures 12 and 13 show the material after it was removed.

Figure 12. Batch A Chunks Removed from Vessel

Figure 13. Batch A Stratified Layers in Post-calcination Material

The chunk on top of Figure 12 is the width of the vessel. The chunks in Figure 13 show indications of stratification within the material. There are several regions that appear brightly metallic in color, suggesting a different chemical composition.

Figure 14 shows the calcination vessel after all material had been removed, with the exception of a small amount in the vessel’s upper right hand corner.

Figure 14. Batch A Calcination Vessel after Material Removal

The post-calcination vessel weight was obtained at this point in the process. The vessel shows damage consistent with corrosion, possibly caused by the chloride in the material.

The Batch B vessel and material after calcination are shown in Figure 15. The photograph seen in Figure 15 was obtained through the same plastic shielding as the photograph seen in Figure 10 for Batch A.

Figure 15. Post-calcination Batch B Vessel and Material Sitting on Furnace Door

The material shown in Figure 15 is much darker and appears to have fine dislodged vessel material around its edge. Vessel oxidation and flaking for Batch B was much less than that seen in Batch A. Material was removed from the vessel in the manner previously mentioned, and is shown in Figure 16.

Figure 16. Post-calcination Batch B Material

Calcination vessel material can be seen adhering to a chunk of material on the left of Figure 16. The calcination vessel had a net weight gain of 38.7g. Two possible causes are readily apparent for this gain. First, the vessel was seasoned in the first calcination run and does not appear to have lost as much of its structure. Second, as is seen in Figure 17, material both fixed and loose is still seen in the vessel when it was weighed.

Figure 17. Batch B Calcination Vessel after Material Removal

The increased gross weight loss in Batch B, 181.4g, compared to 143.7g from Batch A indicates the material lost more weight than the material in Batch A, especially since less gross weight loss is attributable to calcination boat flaking. The best estimate of product material loss is the 181.4g of gross weight loss, considering the relatively small amount of visible vessel loss when compared to that seen in Batch A.

Pre-calcination material for Batch C had a tan coloration (Figure 18). This photograph was taken through the glovebox window with no plastic shielding in place.

Figure 18. Batch C Pre-calcination

The vessel and material after calcination is shown in Figure 19.

Figure 19. Batch C Post-calcination

The photograph in Figure 19 was taken through a window with no plastic shielding. The material in this photograph is very similar in color to that seen in Batch A and does not appear as dark as that in Batch B, though the picture for Batch B was obtained through the plastic shielding. Vessel flaking for Batch C was nonexistent. Material was removed from the vessel in the manner previously mentioned and a photograph of the material after removal was not obtained. The calcination vessel had a net weight gain of 72.4g. Two possible causes are again readily apparent for this gain. First, the vessel was seasoned in the first and second calcination runs and does not appear to have lost any appreciable amount of its structure. Second, as is seen in Figure 20, fixed material is again visible on the inside walls of the vessel. The gross weight loss in Batch C of 12.5g is significantly less than that observed in Batch A and Batch B of 143.7g and 181.4g, respectively.

Figure 20. Batch C Calcination Vessel after Material Removal

1st Post-Calcination Processing and Mixing

After calcination the material was processed as seen in Diagram 1.

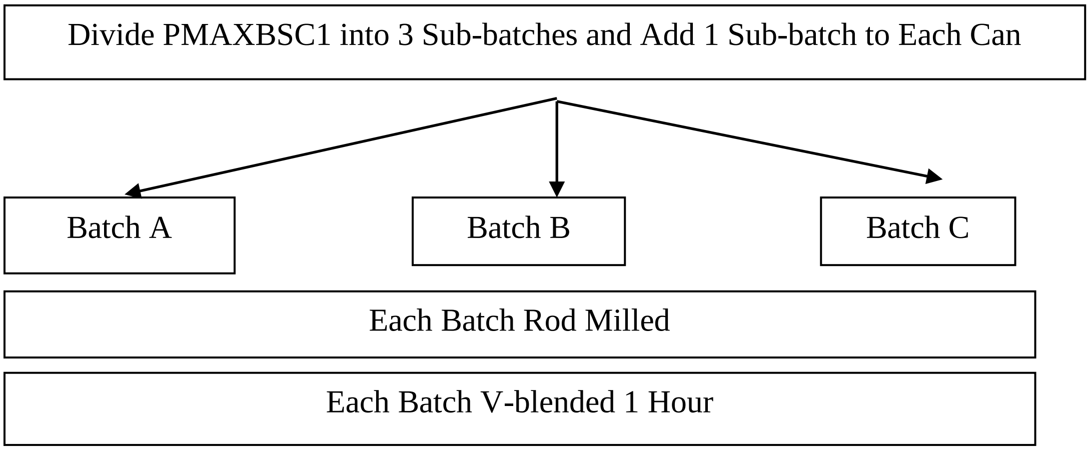

Diagram 1. Post-calcination PMAXBSC1 Addition, Rod Mill, and V-blend

After each batch was removed from the calcination vessel, an equal proportion of material left over from the preparation of PMAXBS was added to the Master Blend material. This material was prepared and calcined as part of the preparation of S&M Large-Scale Surveillance item PMAXBS in August 2003. The Master Blend material was then rod-milled. The batches were then V-blended for one hour. After V-blending, each can was split into three equal batches as seen in Diagram 2.

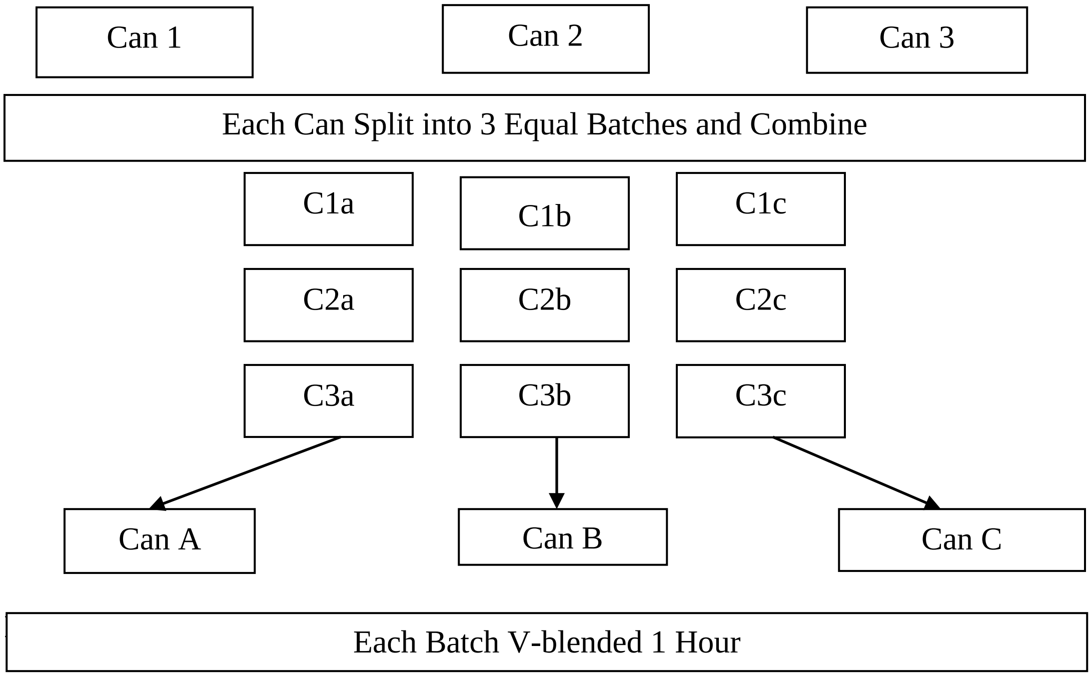

Diagram 2. Post-calcination Split and Combine

These batches were then combined as indicated and formed three new items referred to as Can A, Can B, and Can C. These new items were then V-blended for one hour. After V-blending each can, a sample was obtained for bulk and tap density measurements. The cans were sent to nondestructive assay (NDA) for calorimetry.

2nd Post-Calcination Mixing

A second mixing was performed to ensure homogeneity across the cans. As shown in Diagram 3, each can was split into four batches and combined with batches split from the other two cans to create MBCAN 1, MBCAN 2, MBCAN 3, and MBCAN4.

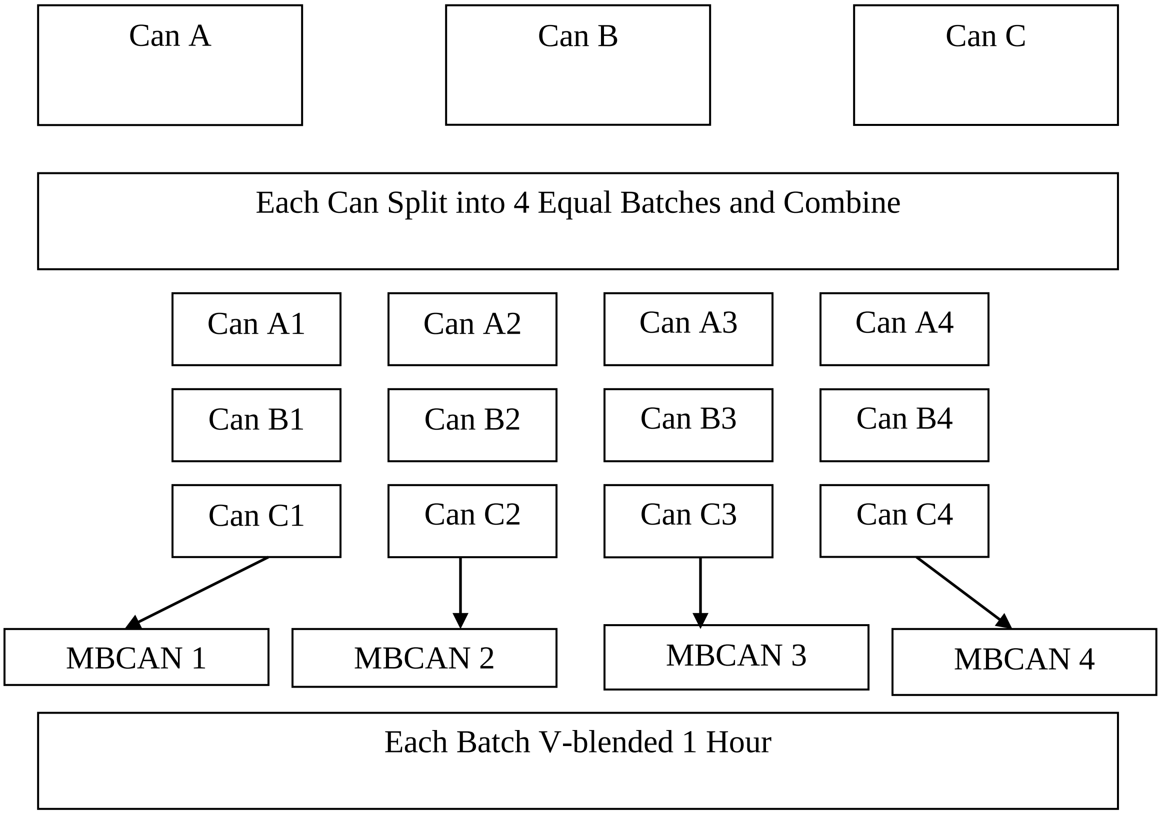

Diagram 3. 2nd Post-calcination Split and Combine

Each item was then V-blended for one hour. After V-blending each can, a sample for density measurements was obtained. The cans were then sent to NDA for calorimetry measurement.

Material Characterization

Results of calorimetry and density measurements performed on the material after the first post-calcination mixing are presented in Table 6.

Table 6. Calorimetry and Density Measurement Results after 1st Post-calcination Mixing

	Pu	mW/g Pu	Net	Wt% Pu	mW/g Net	Bulk Density (g/cm^3)	Tap Density (g/cm^3)
Can A	3396.45	2.3436	5352.9	63.45	1.487	3.1	3.9
Can B	3342.51	2.3547	5262.1	63.52	1.496	2.9	3.9
Can C	3387.84	2.3580	5351.4	63.31	1.493	3.0	3.9
Average		2.3521		63.42	1.492	3.0	3.9

Calorimetry and density data indicate homogeneity existed across the cans after the1st mixing.

Data from calorimetry and density measurements performed after the second post calcination mixing are presented below in Table 7. The data indicate that homogeneity exists across the cans. Information on electro-refining oxide produced at RFETS and packaged into 3013 containers published elsewhere is available for comparison.[4]

Table 7. Calorimetry and Density Measurement Results after 2nd Post-Calcination Mixing

	Pu	mW/gPu	Net	Wt. % Pu	mW/g Net Wt.	Bulk Density (g/cm^3)	Tap Density (g/cm^3)
MBCAN1	2499.08	2.3676	3967.4	62.99	1.491	2.9	4.2
MBCAN2	2524.43	2.3579	3981	63.41	1.495	3.1	4.2
MBCAN3	2515.84	2.3618	3975.7	63.28	1.495	3.3	4.2
MBCAN4	2524.93	2.3455	3988.4	63.31	1.485	3.1	4.2
Average		2.3582		63.25	1.492	3.1	4.2

Isotopics data is presented in Table 8.

Table 8. Isotopic Results after Second Post-Calcination Mixing

	Date	mass % Pu^{238}	mass % Pu^{239}	mass % Pu^{240}	mass % Pu^{241}.	mass % Pu^{242}	µg/gPu Am^{241}
MBCAN1	11/01/2006	0.01159	96.66183	6.18591	0.11567	0.02500	465.0
MBCAN2	7/11/2006	0.01137	94.09431	5.75270	0.11662	0.02500	585.2
MBCAN3	7/26/2006	0.01277	93.99109	5.85234	0.11879	0.02500	502.3
MBCAN4	7/11/2006	0.01123	94.21971	5.62619	0.11787	0.02500	540.6
Average		0.01174	94.74174	5.85429	0.11724	0.02500	523.3

Analytical chemistry was performed on material from grab samples taken from the four cans after the 2nd post-calcination mixing. Table 9 summarizes the weight percent of key elements as well as any impurity present in 0.05 wt% or greater.

Table 9. Major elemental impurities

Element	Wt %		Element	Wt %
K	6.9		Fe*	0.40
Na	3.8		Ni*	0.25
Mg	0.59		Cr*	0.07
Ca	0.02		Ta	0.08
Chloride	15 ± 2.5%		Si	0.05
Fluoride	0.16 ± 0.06			

* Elevated values of Fe, Ni and Cr are probably from the Hastelloy boat used in calcination.

Conclusion

Approximately 16 kg of Master Blend plutonium oxide containing chloride salt impurities has been produced. The blend was produced so that a large quantity of oxide material would be available for Surveillance and Monitoring Program shelf-life experiments. The Master Blend contains a mixture of items produced by the LANL electro-refining pyrochemical process in the late 1990s. These crushed and sieved items were calcined to 800ºC for four hours and blended multiple times. Calorimetry and density measurements were compared between the various cans of Master Blend material and indicated homogeneity. The average Pu composition of the final material was 63.2% with an average wattage of 1.492 mW/g Net Wt, bulk density of 3.1 g/cm^3 and tap density of 4.2 g/cm^3.

Acknowledgements

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