High Purity Americium-241 for Fuel Cycle R & D Program

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Abstract

Previously the U.S. Department of Energy released Am-241 for various applications such as smoke detectors and Am-Be neutron sources for oil wells. At this date there is a shortage of usable, higher purity Am-241 in metal and oxide form available in the United States. Recently, the limited source of Am-241 has been from Russia with production being contracted to existing customers. The shortage has resulted in the price per gram rising dramatically over the last few years. DOE-NE currently has need for high purity Am-241 metal and oxide to fabricate fuel pellets for reactor testing in the Fuel Cycle R&D program. All the available high purity americium has been gathered from within the DOE system of laboratories. However, this is only a fraction of the projected needs of FCRD over the next 10 years. Therefore, FCR&D has proposed extraction and purification concepts to extract Am-241 from a mixed AmO_2-PuO_2 feedstock stored at the Savannah River Site. The most simple extraction system is based upon high temperature reduction using lanthanum metal with concurrent evaporation and condensation to produce high purity Am metal. Metallic americium has over a four order of magnitude higher vapor pressure than plutonium. Results from small-scale reduction experiments are presented.   These results confirm thermodynamic predictions that at 1000 deg C metallic lanthanum reduces both PuO_2 and AmO_2. Faster kinetics are expected for temperatures up to about 1500 deg C.

Introduction

^{241}Am is an essential isotope for many important household and industrial applications. Its predominantly mono-energetic alpha (5.44 and 5.49 MeV) and gamma (59.6 keV) radiations and convenient half-life of 432.7 years make ^{241}Am a superior source of radiation. It is used as an alpha-particle source in smoke detectors (see Figure 1), as a neutron probe (as Am-Be) for oil-well logging (see Figure 2), as a gamma source for non-destructive analysis of materials, and for quality control in fixed-nuclear-density gauges and nuclear densitometers. The current domestic supply of readily available ^{241}Am has been exhausted, and DOE must decide how to meet near and long-term demands for the material[i]. Therefore, the challenge is the development of a dependable means to provide for the near and long-term needs for usable high purity ^{241}Am

The largest quantity of feedstock for production of ^{241}Am is a mixture of 7-10 wt. % AmO_2 in PuO_2 (Hanford material that was recently shipped to SRS)[ii]. This feedstock material is stored in double-welded 3013 containers that hold approximately 1,000 g of feedstock per container. Taken in total, this feedstock material contains well over 15 Kg of ^{241}Am . This AmO_2-PuO_2 material does not contain gallium, and the feedstock material was originally precipitated from purified nitrate in 1979 using an oxalate precipitation process. Nondestructive analysis (NDA) results indicate that all lots are high-assay material. Measured isotopic-ratio information is available for the Hanford/SRS material, but is classified as official use only (OUO). Some low-level metallic impurities may have been introduced during calcination because metal boats were utilized. All this material is slated for disposition and is awaiting National Environmental Policy

Act (NEPA) documentation at SRS. However, it is currently available to be obtained and "mined" for its americium content.

Figure 1. Smoke detectors (left) employ [241]Am foil (right) as an alpha source.

Figure 2. Oil-well logging device that utilized [241]Am.

Direct Oxide Reduction (DOR) techniques to extract Am metal from available feedstocks have been discussed in detail an INL technical report.[iii] This report includes a literature search that documents previously developed methods of reducing transuranic (TRU) oxides to metal and describes purification techniques. It was concluded that two of the more easily applicable methods for the Hanford/SRS feedstock appear to be metallothermic reduction of oxide with concurrent vaporization/condensation of Am metal and variations of pyro-electrorefining.

Electro-refining using molten salt has been previously used, primarily for refining actinide metals. However, electrolytic reduction has only been recently demonstrated to extract the metals from spent fuel mixed-metal oxides.

Bench-scale electrolytic reduction tests have been recently performed at INL that successfully converted metal-oxide spent nuclear fuel to metal[iv.0] This process is shown in the schematic of Figure 3. The extent of reduction of metal oxides in a fuel basket reached 99.7 % for uranium, 97.8 % for plutonium, >98.8 % for neptunium, and 90.2 % for americium.

Obviously, the apparatus could be used to reduce "pure" actinide oxides (e.g., AmO_2 or NpO_2) into their respective metals. Experiments could be conducted that would improve the yield of the pure metals (e.g., americium). In theory, this process could separate Am metal from Pu metal during the reduction of mixed PuO_2 plus AmO_2, or, possibly, could increase the Am content in Pu metal product during the reduction of mixed PuO_2 plus AmO_2. However, it is not thought that these upgrades can be practically accomplished because the cathode voltages for Am and Pu extraction are too close to the same values. This is a definite disadvantage because then there would need to be an additional evaporation step to separate the Am metal from the Pu/Am alloy that would be produced from using the Hanford feedstock.
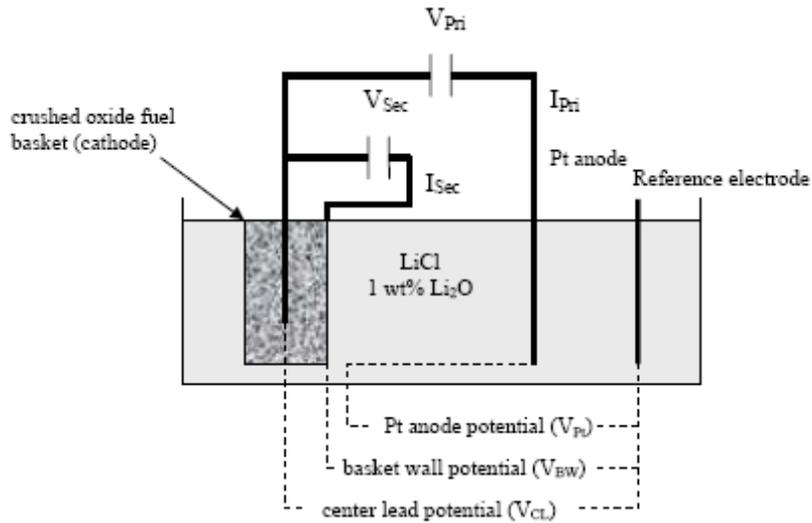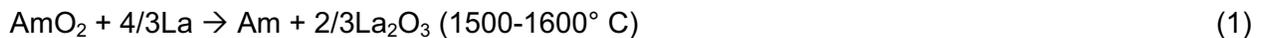
Figure 3. Schematic of INL electrolytic reduction cell – Courtesy of S.D. Herrmann.

A preferred historical metallothermic method of preparing americium metal from AmO_2 is illustrated by Equation 1, Reduction of AmO_2 with lanthanum metal:

$AmO_2 + 4/3La \rightarrow Am + 2/3La_2O_3$ (1500-1600° C) (1)

It is a logical extension to use La to attempt to reduce a mixture of AmO_2 and PuO_2 to metals, as shown in Figure 4. Since there exists a significant difference in vapor pressure[v] between Am and Pu (Am vapor pressure approx. 3 orders of magnitude higher), Am can be separated from Pu by evaporation. A pelletized mixture of the actinide oxides and of reducing metal (La) can be heated in vacuum at a temperature allowing a rapid evaporation of the Am metal, leaving behind the oxide Pu metal and the excess of the reducing metal. Since the reduction and evaporation/condensation is concurrent, the process can be considered to be "one step". A second simple step is added to convert the Am metal to AmO_2. Some important advantages of the DOR method are listed in Table 1.

Table 1. Advantages of Direct Oxide Reduction Method to Produce Am

+ Very high purity Am produced (due to evaporation/condensation)
+ No gallium in feedstock
+ A large amount of feedstock available
+ No production of aqueous waste
+ Less total waste produced than in other methods
+ Very high Am-241 content in feedstock (should lead to lower production costs)
+ Less processing steps than other methods (should lead to lower production costs)

PuO_2/AmO_2 Reduction via Direct Oxide Reduction (DOR) Method

90 PuO_2/10 AmO_2 powder from Hanford

La metal – high purity

High Vacuum
RF Heating
Ta & Ceramic
Hardware

TANTALUM LID
CYLINDRICAL WATER-COOLED COLLAR
WATER CHANNEL
55-mm-o.d. QUARTZ TUBE
25 mm-o.d. X 175-mm-DEEP TANTALUM CRUCIBLE
INDUCTION FIELD COIL
PERFORATED TANTALUM BAFFLE
TANTALUM REFLECTOR

GAMMA ACTIVITY (mv)
0   100   200   300

DISTANCE FROM CRUCIBLE BOTTOM (mm)
150
100
50
0

0   500   1000   1500
TEMPERATURE (°C)

Residuals:
• Pu metal
• La_xO_y
• Am (trace)
• Ceramic Crucible

PuO_2/AmO_2 +
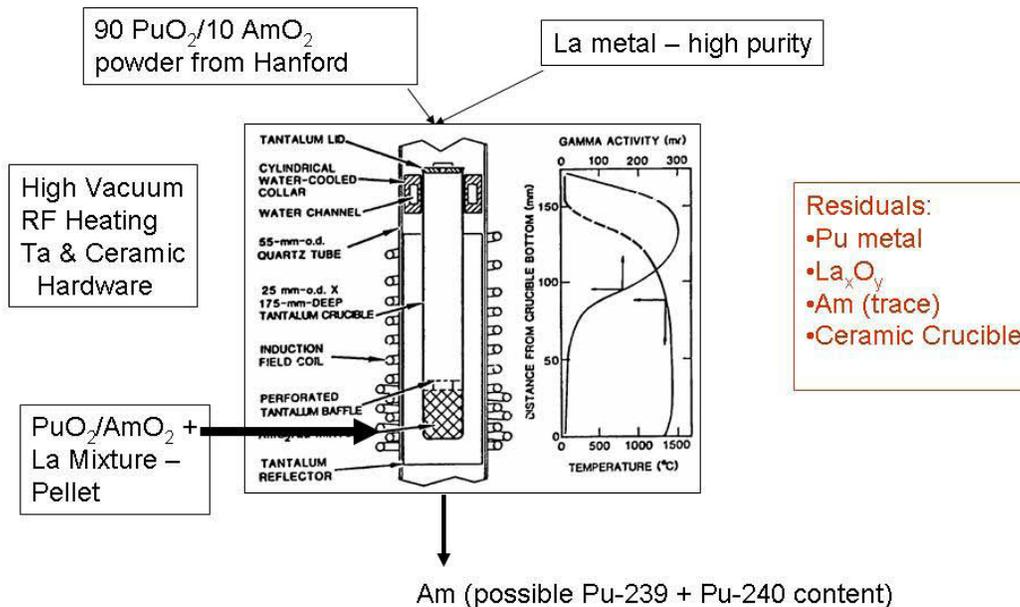La Mixture –
Pellet

Am (possible Pu-239 + Pu-240 content)

Figure 4. A combined DOR/evaporation/condensation method proposed for Hanford feedstock (now stored at SRS) to produce Am metal. The figure also shows internal temperature distribution and γ radiation profile.

Experiment

Literature reports document work at LANL and the Institute for Transuranium Elements which demonstrate that AmO_2 can be reduced to Am metal using La metal and that the Am can be vaporized and condensed on a "cold finger." However, no information was found in the open literature on the reduction of PuO_2 with La metal.

Thermodynamic calculations of the Gibbs energy (ΔG) and enthalpy (ΔH) for reduction of the individual oxides at 1000°C were performed using HSC software[vi]. Manganese oxide is often used as a nonradioactive surrogate for americium oxide. Results are shown in Table 2. All three reactions were found to be are exothermic at 1000°C.

Despite favorable Gibbs energies of the reactions at equilibrium, even at room temperature, the rate of oxide reduction can be limited by the slow diffusion processes in the condensed phases[vii]. To alleviate the problem, it was decided to use excess La, press a pellet using the reactants, and heat it (the pellet) to the melting temperature of lanthanum. Since kinetics of the reaction may also depend on the condition of the oxide feedstock and La metal (particles surface area and any oxidation of La metal present) it was preferable to grind the reactant powders to fine particles.

Table 2. Results of the thermodynamic calculations at 1000°C[vii].

| Reaction	$\Delta G_{1000°C}$, kcal	$\Delta H_{1000°C}$, kcal
$3PuO_2 + 4La = 2La_2O_3 + 3Pu$	-103.668	-107.657
$3MnO + 2La = La_2O_3 + 3Mn$	-133.952	-153.049
$3AmO_2 + 4La = 2La_2O_3 + 3Am$	-183.390	-202.238

To verify the thermodynamic calculations that PuO_2 can be reduced by La metal and also that a mixture of AmO_2 plus PuO_2 can also be reduced by La metal, small scale experiments were conducted in a shielded glovebox at INL. Each experiment was performed simultaneously in two different crucibles to confirm compatibility with crucible materials, i.e. in a tantalum crucible and in an yttria crucible. In addition, each reaction is being conducted in: a) in argon atmosphere and b) in rough vacuum atmosphere.

1. Reduction of PuO_2 with La metal at 1000°C:

$$3PuO_2 + 4La = 2La_2O_3 + 3Pu \qquad (2)$$
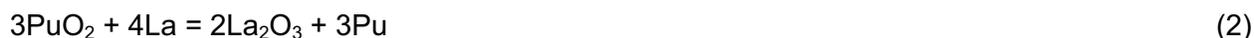
The purpose of experiment 1 was to demonstrate that PuO_2 can be reduced to Pu metal with La at 1000°C in rough vacuum and in the argon atmosphere of the glovebox.

2. Reduction of the mixture of PuO_2 and 10 wt% AmO_2 with La metal at 1000°C:

$$3(PuAm)O_2* + 4La = 2La_2O_3 + 3PuAm \qquad (4)$$
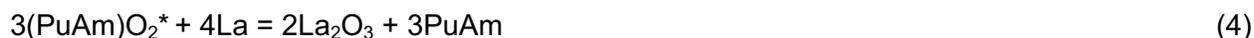
* a mixture of 90 wt.% PuO_2 and 10 wt.% AmO_2

The purpose of experiment 2 was to demonstrate that a mixture of PuO_2 and AmO_2 can be reduced to Pu and Am metals in a "rough" vacuum and also an argon atmosphere.

Figure 5 contains a view of the special tantalum and yttria crucibles (and their lids) prior to loading of the pressed pellets. The lids were "loose" fitting. Figure 6 shows a pellet after heating to 1000°C (with 3 hour hold time). Typically, there was some evidence of reaction in the heated pellets (hardening of the pellet, roughening of the surface, or a slight change in pellet color). There was no evidence of slumping or gross change of shape to the pellets or of reaction with the tantalum or yttria crucibles.
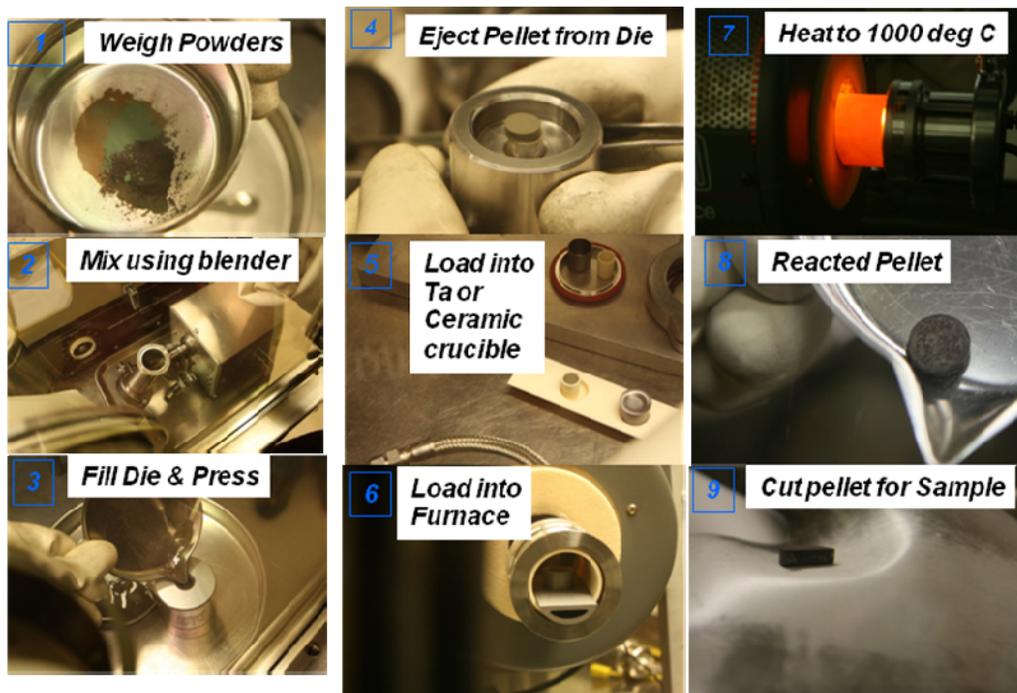
Figure 5. Historic INL experimental sequence for small DOR Experiments (Am related): no concurrent distillation.

Figure 6. Pellet containing La-metal plus oxides after exposure to high temperature.

Results

The most convenient method to determine the degree of reaction within the pellets was X-ray diffraction (XRD). XRD data was sent to Prof. Thomas Hartmann of the University of Nevada at Las Vegas, who performed Rietveld refinement and analyses of the data.

The XRD pattern of the reduction of PuO_2 using La as the reducing agent revealed PuO (41 wt.-%,, La_2O_3 (55 wt.-%), and about 4 wt.-% delta Plutonium. Results of the analysis shown in Figure 7 confirmed that, at 1000°C, the La powder caused formation of Pu metal. It is unclear if the PuO results from the incomplete reduction of PuO_2 or if the reduction to Pu was complete and then PuO formed from the subsequent re-oxidation of Pu metal. Information found in the literature shows that PuO is typically seen as a film on Pu metal. In this case, the results would support the supposition of re-oxidation.

In a second sample, as shown in Figure 8 the following phases were identified as a result of the XRD analysis of the products from the reduction of AmO_2-PuO_2 with lanthanum: La_2O_3 (65 wt.-%), PuO (10 wt.-%), delta Pu (14 wt.-%) and, eventually, beta La (6 ± 1 wt.-%). As minor phases, alpha La and beta La_2O_3 might be present, while Am_2O_3 and beta Pu_2O_3 were not identified. It is possible that Am metal was not identified in XRD analysis due to its full or partial evaporation from the sample. To verify this, the AmO_2-PuO_2 pellet was analyzed using gamma spectrometry. The reported result was 6.5E4 microCuries of [241]Am per gram of sample, which is equivalent to 0.01895 g [241]Am per gram of sample. This indicates that roughly 40% of the original Am content remained in the pellet and 60% had evaporated.
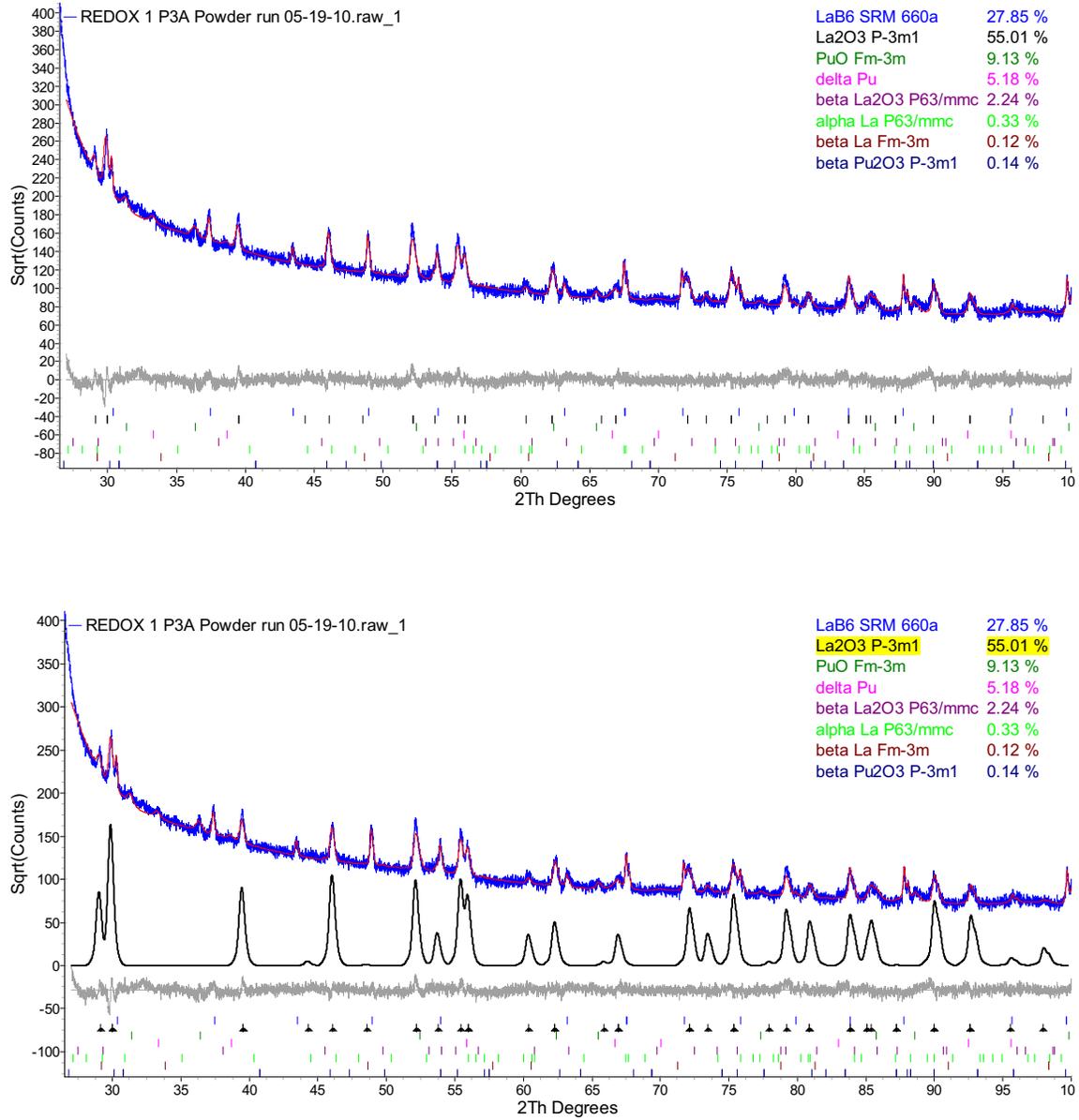
REDOX 1 P3A Powder Run 05-20-10

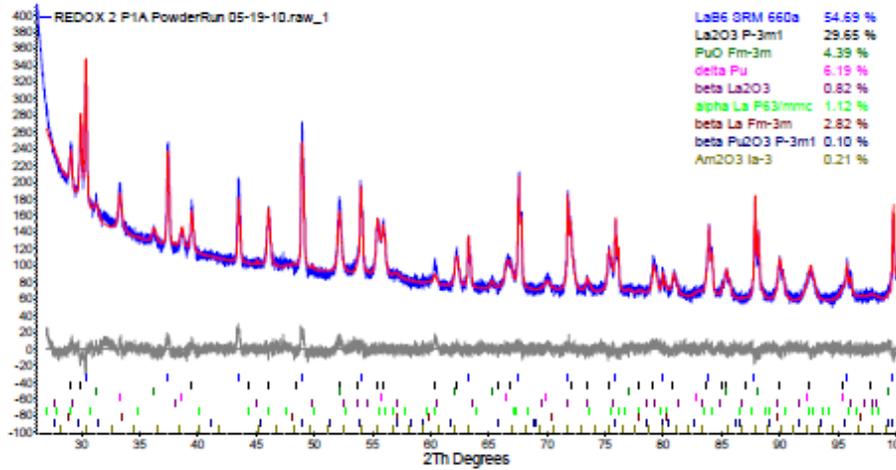Figure 7. Refined Analysis of XRD pattern for reaction of PuO_2 plus La powder.

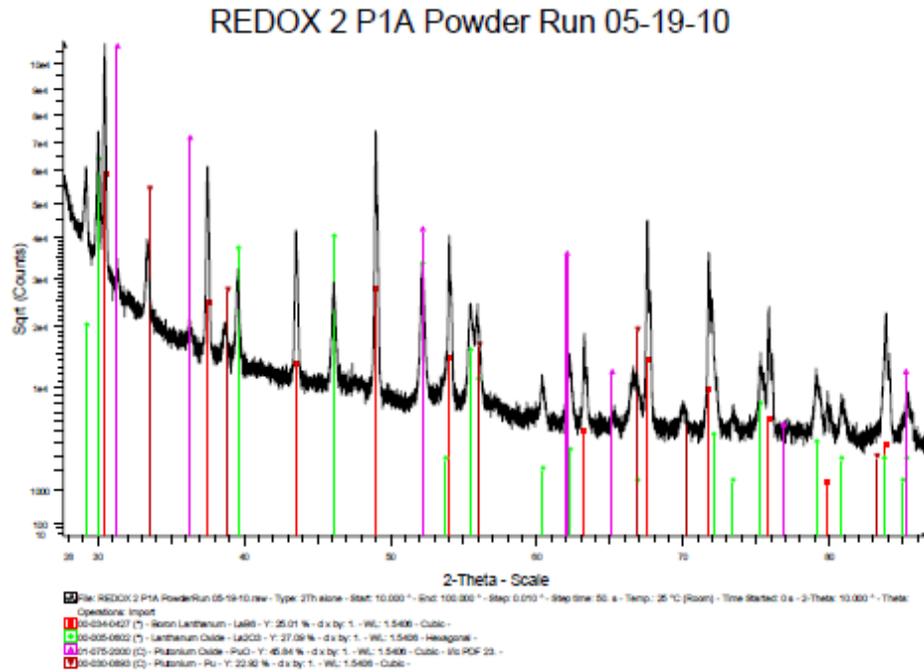Figure 8. Analysis of XRD data for Redox 2 P1A ($3(PuAm)O_2 + 4La = 2La_2O_3 + 3PuAm$)

Conclusion

Using information from the literature and previous results obtained at INL, it is extremely probable that La metal can be successfully used to reduce 7-10%AmO_2 /PuO_2 with the concurrent evaporation of Am at temperatures as low as 1000 C. We propose to build a very small-scale reaction vessel to definitively prove that 10%AmO_2/PuO_2 feedstock from SRS/Hanford can be concurrently reduced by La (in the approximate temperature range of 1000 – 1500 ^{o}C) and the Am distilled and collected on a "cold finger".

[i] National Strategic Plan for Nuclear Materials – Final Draft, U.S. D.O.E, FY 2011.

[ii] A series of electronic communications from Theodore "Ted" J. Venetz (Hanford) to Roger Haga (INL) during 2007.

[iii] INL/EXT-07-13254, Rev. 0, "GNEP Fuel Feedstock Characterization and Supply," Paul Lessing, September 2007.

[iv] Herrmann, S. D., et al., 2006, "Electrolytic Reduction of Spent Nuclear Oxide Fuel as Part of an Integral Process to Separate and Recover Actinides from Fission Products," *Separation Science Technology*, *41 (10*): pp. 1965-1983.

[v] Spirlet, J. C., and W. Muller, 1973, "The Preparation and Purification of Americium Metal by Evaporation," in *Handbook on the Physics and Chemistry of the Actinides*, pp. 31, 35.

[vi] HSC software: http://www.hsc-chemistry.net/

[vii] J.C. Spirlet and W. Muller, "The Preparation and Purification of Americium Metal by Evaporation", *Journal of the Less-Common Metals,* 31 (1973) 35-46.