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Americium and Neptunium Purification Processes and Future Directions

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Americium and Neptunium Purification Processes and Future Directions

Nuclear Technology Research and Development

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SUMMARY

Pure americium and neptunium metals are crucial components in the fabrication of transmutation fuels. Unfortunately, neither neptunium nor americium is available in pure metal form. However, a number of oxides, mixed metals, and mixed oxides that include americium and neptunium are available. Methods were to separate and/or reduce the materials available, in order to obtain pure neptunium and americium metals. New techniques were investigated in FY18 to obtain neptunium and americium metals from their oxides. This report details the processes and results.

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AMERICIUM AND NEPTUNIUM PURIFICATION PROCESSES AND FUTURE DIRECTION

1. INTRODUCTION

The disposal of spent nuclear fuel is a challenge currently facing the nuclear power industry due to the hazards associated with long-term storage of the material once it is removed from the reactor. Key to the reduction of these hazards is the reduction or elimination of minor actinides with long half-lives, including neptunium and americium, that are present in spent fuel. Transmutation is one way to potentially resolve this issue. Transmutation aims to incorporate the long-lived actinides into new fuel that can be placed in a fast reactor where the elements of concern will fission into products with shorter half-lives that can be more easily stored in disposal facilities. In order to better understand transmutation and its potential, it is necessary to fabricate small quantities of fuel with minor actinide additives and perform thorough characterization and irradiation testing. In addition, the thermal and physical characterization of pure americium and neptunium metals is incomplete, and the pure metal is needed to perform basic thermal and physical properties measurements. Currently, there is very little pure americium or neptunium metal in existence; therefore, it is necessary to develop methods to isolate these metals from the oxide, mixed metal, and mixed oxide feedstock material that is available. A new approach to isolate both americium and neptunium metals was investigated over the course of FY18. The new method was investigated to go directly from the oxides of both americium and neptunium to the metals using an arc melter to reach very high temperatures under a hydrogen containing cover gas. The idea for this came from reconsolidation efforts in the past that appeared to remove oxide contamination from the surface of americium and plutonium metal when they were arc melted into spheres for protection from further oxidation. It was hypothesized that the extreme temperatures created at the arc would force a separation of the oxygen from the americium or neptunium, and the addition of hydrogen to the cover gas would collect the released oxygen and carry it away as water vapor. The method was tested first on non-radioactive surrogate material, then was applied to both americium oxide and neptunium oxide in the argon atmosphere glovebox with varying percentages of hydrogen in the argon cover gas. In addition to this work, a new starting material was examined for feasibility of separating out the americium. Finally, improvements were made to the stirring mechanism to make the direct oxide reduction technique used to reduce neptunium oxide to neptunium metal more efficient in the future.

2. EXPERIMENTAL

The initial experiments for determining the feasibility of arc melting as a reduction process were conducted in a non-radiological facility using reagent grade zirconium (Alfa Aesar) and zirconia (Alfa Aesar). The zirconium metal material was heated to 650°C for 1.5 hours in an air atmosphere to oxidize it. It was then placed in a copper hearth of an arc melter that was backfilled with safe gas (3% hydrogen, 97% oxygen) for five minutes. A summary of the experiment is presented in Table 1. The material was then arc melted under safe gas. Upon inspection of the material, it appeared to be metallic. Samples were shipped to EAG Laboratories (Liverpool, New York) for oxygen analysis. Reagent grade zirconia was also arc melted under safe gas twice, and the result was a button of what appeared to be metallic material. Optical microscopy images were obtained from cross sections of this sample, and they showed a solid metallic button.

Experiments to test the reduction of neptunium oxide to neptunium metal via this method were designed such that variables including percent hydrogen in the cover gas and atmosphere during cooling could be tested to determine the effect such parameters had on the resulting material. Samples were arc melted under 10%, 25% and 50% hydrogen in argon as a cover gas. They were cooled under the same cover gas used for arc melting or under 100% argon. In addition, some samples were also arc melted under

100% argon and cooled under 100% argon after the initial melts under hydrogen containing cover gas. Cooling or heating under 100% argon refers to cooling or heating under glovebox atmosphere.

Samples were analyzed using a technique to selectively dissolve the oxide material and the metal material. This method used ethyl acetate, magnesium oxide (for pH control) and bromine to selectively dissolve the metal. Then the residual oxide was dissolved in acid. The metal and oxide fractions were analyzed separately. The results shown in Table 2 are part of a preliminary analysis report after the fractions were analyzed via inductively coupled plasma-mass spectrometry (ICP-MS). Results from optical emission spectrometry (ICP-OES) are forthcoming.

An abbreviated version of the same arc melting experiment was performed using americium oxide starting material. The material was arc melted under 10%, 25% and 50% hydrogen in argon as a cover gas. Detailed descriptions of each sample treatment can be found in Table 3 of the results section. Samples from this set of runs have not yet been submitted for analysis and likely will not be analyzed in the same manner.

In addition to investigations of the new technique, distillation was attempted using a starting material of 20% americium and 80% plutonium. The same distillation set-up used in previous years was used for this process. Approximately 2.5g of the starting material was placed in the bottom of a tantalum crucible which was then placed inside the americium distillation furnace. The material was heated to 1170°C and agitated every 5 minutes for 30 minutes. The set-up was then allowed to cool, and the tantalum crucible was removed and measured using a gamma detector to pinpoint the location of the americium. The crucible was sectioned, and the material was retrieved using the modified lathe as was done in previous runs.

In order to improve the efficiency of the previously proven direct oxide reduction, stirring mechanisms and speeds were tested to determine the best combination for material mixing. A number of different stirrer designs were 3D printed or fabricated from stainless steel and tested. Designs including an auger, the existing design with blades rotated at different angles, and blades that were parallel to the stirring shaft and a beater type design. All of these designs were tested on a bench top using transparent crucibles with two immiscible liquids and sand in the bottom to mimic the mixture in the reduction crucible. The benchtop motor was also tested a different rotation per minute to determine the necessary speed to obtain adequate mixing.

3. RESULTS

Table 1 shows the summary of the zirconium oxidation and reduction results. The first sample was the starting material, reagent grade zirconium. The second sample was the reagent grade zirconium that was heated for 1.5 hours at 650°C in air. The third sample was subjected to the same heat treatment followed by arc melting. The final sample was the reagent grade zirconium arc melted without first heat treating to oxidize it.

Table 1. Summary of zirconium results.

Sample Treatment	Concentration of oxygen (ppm wt.%)
Reagent grade zirconium (feedstock)	0.15
650°C for 1.5 hours	0.26
650°C for 1.5 hours then arc melted	0.15
Feedstock after arc melting	0.17

Figure 1 shows an optical microscopy image at 25X magnification of the product from arc melting zirconia under safe gas. The majority of the sample appears metallic.

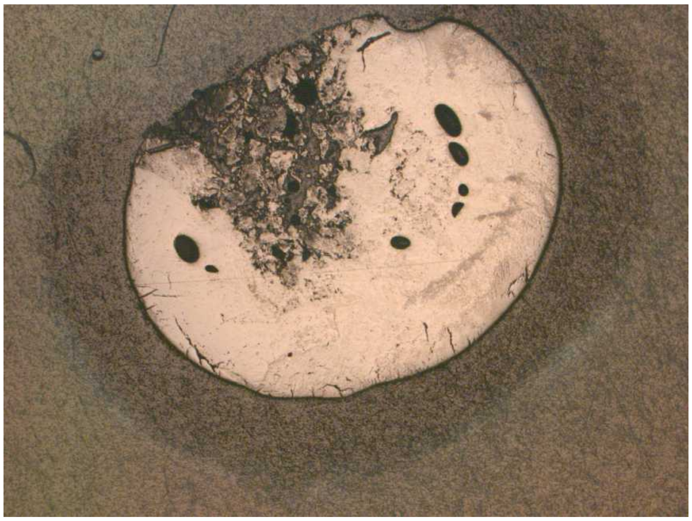
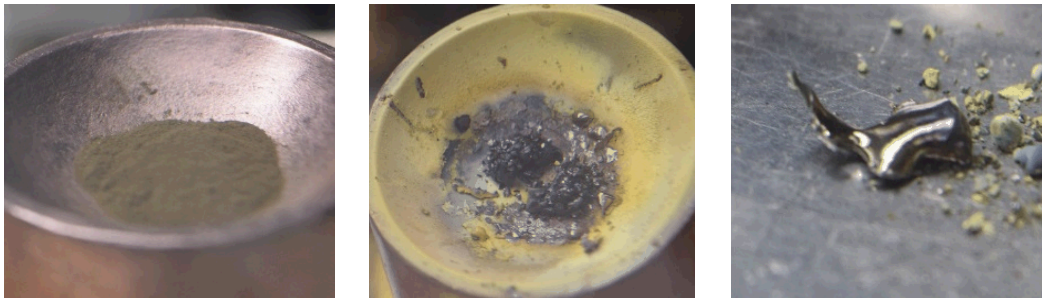


Figure 1. Optical microscope image of a cross section of zirconia that was arc melted twice under safe gas.

Figure 2 shows the change undergone by the neptunium oxide starting material during the arc melting process. It was noted early on in the experiments that allowing the material to cool under the hydrogen containing cover gas resulted in the formation of, first, a metallic like piece that then decomposed to a black powder between 200°C and 150°C. This was thought to be a hydride reaction and was found to be reversible by reheating the material either under hydrogen containing cover gas or under argon.



A. Neptunium oxide starting material

B. Material arc melted and cooled under hydrogen containing cover gas.

C. Material after re-melting under hydrogen containing cover gas and cooling under argon.

Figure 2. The progression of neptunium oxide as it was arc melted under hydrogen containing cover gas and cooled.

Table 2 summarizes the experimental parameters and the preliminary analysis results from the tests to reduce neptunium oxide to neptunium metal via arc melting under hydrogen containing cover gas. Chemical analysis results are given as the percentage of neptunium in the solutions after the metal specific and oxide specific dissolutions.

Table 2. Summary of experimental parameters, sample masses and percentage of neptunium in the metal versus the oxide phase for neptunium oxide reductions.

Hydrogen Cover Gas Percentage	Treatment	Sample Weight (g)	% Np in metal	% Np in oxide
10	*Arc melt for 34 seconds to 250 amps. *Cool under argon	0.289	0.08	99.92
10	*Arc melt for 16 seconds to 160 amps *Cool under argon *Flip sample over and heat for 26 seconds to 125 amps *Heat for 19 seconds to 160 amps *Cool under argon *Heat under argon 30 seconds to 150 amps *Cool under argon	0.122	0.24	99.76
10 50	*Arc melt for 27 seconds to 140 amps *Cool under argon *Arc melt for 17 seconds to 240 amps *Increse cover gas to 50% hydrogen *Arc melt for 20 seconds to 190 amps *Cool under cover gas	0.168	0.11	99.89
10	*Arc melt for 22 seconds to 155 amps *Cool under argon *Arc melt 23 seconds to 175 amps *Cool under argon *Arc melt 17 seconds to 160 amps *Cool under argon	0.202	0.17	99.83
10	*Arc melt for 16 seconds to 230 amps *Cool under cover gas *Arc melt for 14 seconds to 165 amps *Cool under cover gas *Arc melt for 16 seconds to 160 amps *Cool under argon	0.297	0.62	99.38
10	*Arc melt for 21 seconds to 115 amps *Cool under argon *Arc melt for 22 seconds to 122 amps *Cool under cover gas *Arc melt under argon for 26 seconds to 130 amps *Cool under argon	0.284	0.48	99.52
25	*Arc melt for 20 seconds to 118 amps *Cool under argon *Arc melt for 21 seconds to 120 amps *Cool under argon *Arc melt for 22 sedonds to 140 amps *Cool under argon	0.083	0.49	99.51
25	*Arc melt for 23 seconds to 115 amps *Cool under cover gas *Arc melt for 23 seconds to 118 amps *Cool under cover gas *Arc melt for 21 seconds to 135 amps *Cool under argon	0.135	0.52	99.48
25	*Arc melt for 22 seconds to 145 amps *Cool under argon *Arc melt for 24 seconds to 240 amps *Cool under argon *Arc melt for 22 seconds to 260 amps *Cool under cover gas *Arc melt under argon for 23 seconds to 216 amps *Cool under argon	0.132	1.18	98.82
50	*Arc melt for 25 seconds to 213 amps *Cool under argon *Arc melt for 23 seconds to 216 amps *Cool under argon *Arc mel for 25 seconds to 226 amps *Cool under argon	0.14	0.17	99.83
50	*Arc melt for 15 seconds to 230 amps *Cool under cover gas *Arc melt for 22 seconds to 216 amps *Cool under cover gas *Arc melt for 22 seconds to 190 amps *Cool under argon	0.299	0.22	97.88
50	*Arc melt for 23 seconds to 160 amps *Cool uner cover gas *Arc melt for 21 seconds to 210 amps *Cool under cover gas *Arc melt under argon for 28 seconds to 255 amps *Cool uner argon	0.23	0.10	99.90

An abbreviated version of the experiments performed using neptunium oxide as a starting material were performed using americium oxide as a starting material. Figure 3 shows before and after pictures of the material.

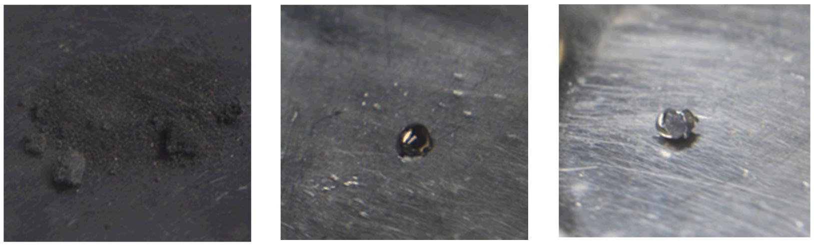

(a) (b) (c)

Figure 3. a. americium oxide prior to arc melting b. top view of pellet after arc melting under 25% hydrogen cover gas c. bottom view of pellet after arc melting under 25% hydrogen cover gas.

Table 3 summarizes the experimental parameters used for the americium oxide reduction trials. The product from these runs has yet to be analyzed. Based on the results from the neptunium analysis it is most likely that these samples will not be analyzed chemical, but instead will be examined via scattered electron microscopy (SEM) and X-ray diffraction (XRD).

Table 3. Experimental parameters and product mass from americium oxide reduction via arc melting runs.

Hydrogen Cover Gas Percentage	Treatment	Sample Weight (g)
10	* Arc melt for 27 seconds to 98 amps * Cool under argon * Arc melt for 23 seconds to 138 amps * Cool under argon	0.180
25	* Arc melt for 26 seconds to 290 amps * Cool under argon * Arc melt for 27 seconds to 110 amps * Cool under argon * Arc melt for 25 seconds to 190 amps * Cool under argon	0.272
50	* Arc melt for 23 seconds to 200 amps * Cool under argon * Arc melt for 22 seconds to 124 amps * Cool under cover gas	0.163

Attempts to obtain americium metal from the mixture of 20% americium and 80% plutonium were not successful. A very small quantity of material was retrieved (0.15g) and analysis showed the material to be highly contaminated with tantalum from the crucible walls.

Testing of the stirrer design and stirring speed used for the direct oxide reduction determined that the speed had more effect on the mixing of reagents than the physical design of the stirrer. Figure 4 shows the different stirrer designs tested, some of which were fabricated of stainless steel and some of which were 3D printed. It also shows the bench top set up with the transparent crucible. From these tests, it was determined that it would be beneficial to change the stirring motor on the Hot Uniaxial Press furnace used for the direct oxide reduction runs to one capable of higher rotations per minute. This was done, and now approximately 100 rotations per minute are achievable.

(a) (b) (c)

Figure 4. a. The stirrer designs tested b. the test set-up prior to mixing c. the test set-up after mixing.

4. DISCUSSION

In the past, americium metal was isolated from a mixed metal starting material consisting of approximately 90% americium and 10% neptunium. The difference in vapor pressures of the two metals was used to perform a distillation separation and approximately 12g of americium metal was successfully obtained using this process, which was detailed in a 2018 publication [1]. Unfortunately, this specific starting material was exhausted at the end of FY17; therefore, a new mixed metal starting material containing approximately 20% americium and 80% plutonium was used for distillation at the beginning of FY18. Early distillation experiments using the method previously applied to the americium/neptunium mix showed that the material could not be efficiently collected using the existing set-up. This was mostly due to size limitations. The small volume crucible could not accommodate enough starting material to obtain significant amounts of americium, since the starting material contained only 20% americium. For example, if a starting material charge of 3g was used, then only 0.6g of that was americium to begin with. The small crucible diameter was also less than ideal as it provided little surface area for the vaporization of the americium from the small quantity of starting material. The material that did vaporize deposited in a thin layer such that the retrieval of the americium without tantalum contamination from the crucible walls proved to be impossible. Thus, the small amount of metal obtained was a mixture of americium and tantalum that came from the walls of the crucible during the retrieval process. In order to make this method feasible for retrieval of americium from the 80/20 mixture it would be necessary to redesign the furnace and crucible. Increasing the crucible diameter would increase the surface area for volatilization to occur and would make the process more efficient. It would also allow for larger quantities of material to be used which would theoretically increase the process yield. Increasing the crucible diameter would require a larger furnace that would have to be evaluated prior to insertion in a glovebox in a nuclear facility. The collection technique would also need to be addressed to ensure pure material, without tantalum, was retrievable. Neptunium metal was produced in previous years via a direct oxide reduction using calcium metal as a reducing agent and calcium chloride salt [2]. A number of improvements were made to the stirring mechanism used for direct oxide reduction in FY18. These improvements include a new stirrer design, new crucible dimensions, and a new stirrer motor that will allow for twice as many rotations per minute as the previous motor. These improvements will make the reduction of neptunium oxide via the calcium/calcium chloride more efficient in the future. One large issue that arose for both the neptunium and americium metal produced via the respective processes was storage. The metallic forms of both americium and neptunium were found to oxidize readily, even sealed in an airtight container and kept in an argon atmosphere glovebox. It was deemed desirable to find a method of producing the material at the time of fuel fabrication rather than producing it and storing it for later use. Since the americium distillation method was going to need a major redesign effort, a different approach was taken that, if successful, would result in the ability to readily produce both metals from their oxides on an as needed basis. It had been demonstrated in the past that arc melting could be used to consolidate or clean up oxide from small chunks of metal that were oxidizing in the glovebox. The method appeared to remove the surface oxidation from the material leaving behind shiny metal. Therefore, it was decided to attempt to use arc melting as a method to reduce neptunium and americium oxides to their respective metals. The addition of hydrogen to the cover gas during arc melting was made to remove the liberated oxygen as water. Results from arc melting zirconia under hydrogen containing cover gas indicated that this method was feasible, and so it was applied to americium oxide and neptunium oxide. Both the americium and the neptunium oxides appeared to reduce to shiny metallic material during the process. It was only after the material was submitted for chemical analysis that it was found to be mostly oxide or, at least, a material that has similar dissolution properties to the oxide. It is important to note that the selective dissolution method applied to these samples has been previously used to selectively dissolve and analyze uranium and uranium oxide fractions, but it has never been used for neptunium or other transuranics. It is obvious from visual observation that the material undergoes a significant change during the process (Figure 2 and Figure 3), so the analysis results were a bit surprising. The metallic appearance of the resulting material seemed quite promising. It would be beneficial in the future to understand the type of the transition the material is undergoing in the process. Future work would analyze the material using microscopy and x-ray diffraction. It will be necessary to further analyze these samples using such techniques in order to understand what is happening if the oxide is not being reduced to metal, but is instead undergoing a different transition. If this technique could be further refined and demonstrated to be successful, it would provide a method to produce transuranic metals at the time they are needed, thereby eliminating the storage requirement and the difficulty of protecting the material from oxidation over long periods. It would also be much faster than current methods of direct oxide reduction for neptunium isolation or distillation for americium isolation.

5. REFERENCES

1. Squires, L.N. King, J.A. Fielding, R.S. Lessing, P. **Isolation of high purity americium metal via distillation** J. Nuc. Mat., 500 (2018), pp. 26-32. https://doi.org/10.1016/j.jnucmat.2017.12.010.
2. Squires, L.N. Lessing, P**. Direct chemical reduction of neptunium oxide to neptunium metal using calcium and calcium chloride** J. Nuc. Mat., 471 (2016), pp. 65-68. https://doi.org/10.1016/j.jnucmat.2016.01.007.