Neptunium mononitride as a target material for Pu-238 production

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Deep space exploration requires specialized sources for both thermal and power applications. Radioactive decay heat of plutonium-238 (^{238}Pu) provides these sources in the form of radioisotope thermoelectric generators (RTGs). The ^{238}Pu is produced *via* neutron capture reaction involving neptunium-237 (^{237}Np) target material. Continual optimization of ^{237}Np target materials and evaluation of potential alternative targets for production of ^{238}Pu RTGs are advantageous for meeting ongoing space power system resource requirements. Current production of ^{238}Pu for RTGs for the United States space program utilizes neptunium dioxide (^{237}NpO$_2$) targets; however, the use of neptunium mononitride (^{237}NpN) presents an opportunity to increase the mass of ^{237}Np per target compared to the dioxide form, as well as increase the thermal conductivity of the target. To assess the viability of a ^{237}NpN target material, the material chemistry must be thoroughly evaluated, including synthesis methods and dissolution and reprocessing schemes. This review presents a summary of synthesis pathways for ^{237}NpN based on published literature on actinide mononitrides. Specific literature on ^{237}NpN is limited, necessitating evaluation of other actinide systems to gather parallels. This suggests a need for additional experimental studies on ^{237}NpN. A particular limitation in the existing literature is a lack of information on the differences in material characteristics, such as morphology, particle size, and trace chemical impurities, as a function of synthesis method. These parameters may affect subsequent reactor performance or dissolution of irradiated targets. The evaluation of existing literature is presented with a focus on the efficacy of ^{237}NpN targets for ^{238}Pu production.

KEYWORDS

neptunium-237, plutonium-238, radioisotope thermoelectric generator, isotope production, radioisotope power systems

1 Introduction

Radioisotope thermoelectric generators (RTGs) utilize radiative heat to produce power, which can be used for deep space exploration applications. This serves two purposes, first thermoelectric power and secondly, the heat generated is used to maintain proper operating temperatures for onboard electronic systems. The decay heat of the radioisotope plutonium-238 (^{238}Pu) serves as the most common heat source in the

generator. Some RTGs have used strontium-90 (Sr-90) (Glenn et al., 2012) and more recently the European Space Agency has been investigating americium-241(Am-241) for RTG use (Ambrosi et al., 2019).

Production of ^{238}Pu is achieved through a neutron capture reaction involving neptunium-237 (^{237}Np) target material (Burney and Harbour, 1974). The element neptunium was first produced in 1940 by McMillan and Abelson (Burney and Harbour, 1974; Yoshida et al., 2010) and the isotope ^{237}Np was subsequently discovered in 1942 by Wahl and Seaborg (Burney and Harbour, 1974). ^{237}Np is one of the 22 known isotopes of Np, has a half-life ($\tau_{1/2}$) of 2.144 million years, and is not found in nature. Rather, ^{237}Np is produced through neutron reactions with uranium in a reactor (Yoshida et al., 2010). Readers are directed to more detailed reviews, such as those by Burney and Harbour (1974) and Yoshida et al. (2010) and references therein, for additional information on Np radiochemistry.

Interest in ^{238}Pu production from ^{237}Np for radioisotope power systems (RPSs) was renewed in the early 2000s, spurred by new NASA estimated needs for planned space missions. An evaluation by the National Research Council (NRC) in 2009 identified that projected NASA mission requirements for RPS outpaced the limited stockpile of ^{238}Pu and acknowledged that foreign procurement of ^{238}Pu was not favorable due to national security concerns (NRC, 2009), thus necessitating a reestablishment of domestic supply of ^{238}Pu. The Department of Energy developed plans to meet ^{238}Pu supply goals as early as 2010 (DOE, 2010), with reports of cost estimates shortly following (Howe et al., 2013). The plan for reestablishment of the ^{238}Pu supply was based on known ^{238}Pu production methods, which date back as far as the 1960s (Myrick and Folger, 1964). The general process for ^{238}Pu production involves the following steps, as outlined in the NRC report (NRC, 2009):

1) ^{237}Np target production, including purification of ^{237}Np and target fabrication.
2) Irradiation of ^{237}Np targets to produce ^{238}Pu in research reactors.
3) Post-irradiation processing of target material to extract, separate, and purify ^{238}Pu from ^{237}Np and fission products.
4) Recycling of ^{237}Np for additional target fabrication.

Plutonium-238 has traditionally been produced from a neptunium dioxide (^{237}NpO$_2$) target material. NpO$_2$ powder is blended with Al metal powder and pressed into a pellet to produce a cermet, which has favorable neutron flux, heat capacity, and crystal density (Myrick and Folger, 1964). During the reestablishment of the ^{238}Pu supply, NpO$_2$/Al cermet was chosen as the preferred target material based on the preestablished capabilities for this process (INL, 2013). NpO$_2$ is also a favorable material for production applications due to its thermodynamic stability (Lemire, 2001; Neck and Kim, 2001)—

which enables long-term storage of the material without concerns of phase alteration—and its high melting point (Manara et al., 2008), which ensures stability in the reactor. The addition of Al is necessary to increase the thermal conductivity of the target and to serve as a binder for the cermet (Wham et al., 2019b). The ^{238}Pu production program in the United States since 2010 has relied on ^{237}Np target production at Oak Ridge National Laboratory (ORNL) and subsequent irradiation of targets at the High Flux Isotope Reactor (HFIR) at ORNL and the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL) (INL, 2013). Though most production-scale NpO$_2$ flowsheets dating back to the 1960s, including Savannah River Site HB-line, have utilized oxalate precipitation of Np followed by calcination to NpO$_2$ (Myrick and Folger, 1964; Porter, 1964; Severynse, 1998; Duffey, 2003a; Duffey, 2003b), ORNL adopted an alternative oxide production process for NpO$_2$ target fabrication. The Modified Direct Denitration (MDD) process was developed as a flowsheet for uranium or mixed-oxide fuel production at ORNL in the 1980s (Haas et al., 1981; Mailen et al., 1982; Notz and Haas, 1989); its advantages included being a continuous process in a rotary kiln and producing a free-flowing powder (Collins, 2015). The MDD process was subsequently adapted for NpO$_2$ production following the restarted need for ^{237}Np targets (Vedder, 2018; Wham et al., 2019b; Depaoli et al., 2019; Collins et al., 2022). Beyond ^{237}Np target fabrication, ORNL also processes targets after irradiation by using dissolution and solvent extraction techniques to chemically separate ^{237}Np, ^{238}Pu, and fission products into individual streams (Wham et al., 2019a; Depaoli et al., 2019).

Although the reestablishment of the ^{238}Pu supply is well underway, and the efficacy of the existing processes are evident, the continued and growing need for ^{238}Pu for deep space missions requires consideration regarding how to increase ^{238}Pu production output. Estimates of production of ^{238}Pu in 2019 were ~400 g/year, with a need of at least 1.5 kg/year (Depaoli et al., 2019). A significant limitation to production is the constraint of reactor space in both HFIR and ATR. These reactors are key components towards overall production goals given that there are not enough reactors domestically with a neutron flux high enough to produce ^{238}Pu. Therefore, the space within these reactors must be optimized for production. This limited neutron economy prevents simply producing more ^{237}Np targets and instead necessitates thought on how to increase the amount of ^{237}Np per target. With this goal in mind, overall reactor operations must still be considered, and the design of potential ^{237}Np targets must account for other targets to avoid compromising other missions. Overall reactor operations and neutron economics within each reactor is outside the scope of this review and would likely fall into consideration during the target design phase. NpO$_2$-only targets (no blending with Al) have been explored at ORNL (Vedder, 2018; Morris et al., 2021) to achieve greater mass of ^{237}Np per target. However, these

targets have not been employed yet in production flowsheets. Another method to achieve greater mass of ^{237}Np per target would be to change the target material. One such material of consideration could be neptunium mononitride (NpN). Actinide mononitrides (AnN) have been studied as potential reactor fuel forms (Arai et al., 1993b; Ogawa and Handa, 1995; Albiol and Arai, 2001; Minato et al., 2003; Arai, 2012; Ekberg et al., 2018) with applications ranging from minor actinide transmutation to accident-tolerant Generation IV reactor fuels, suggesting the suitability of NpN as a reactor target. This review details the existing literature on the materials chemistry of NpN, including synthesis pathways, characterization, and dissolution methods, with emphasis on the efficacy of ^{237}NpN as a potential area of development in Np targetry for radioisotope power systems. The focus of the review centers around fundamental chemistry reported in literature. Application of NpN chemistry, including target design and reactor performance, are outside the scope of this review and would require significant experimental and computational efforts.

2 Neptunium mononitride materials chemistry

2.1 Selected properties of neptunium mononitride

The first report of NpN in the literature is the structure published by Zachariasen, (1949), though the first published report on synthesis and preparation is from Sheft and Fried (Sheft and Fried, 1953). Sheft and Fried reported that the solid did not react with water but did dissolve in hydrochloric acid (HCl) and nitric acid (HNO$_3$) (Sheft and Fried, 1953). Zachariasen found NpN to have a cubic, NaCl-type (F$m3\bar{m}$) structure with a unit cell measurement of 4.887 ± 0.002 (Zachariasen, 1949), whereas a more recent publication by Silva et al. reports a unit cell measure of 4.889 ± 0.001 (Silva et al., 2012). First-principles calculations confirm the unit cell of Zachariasen (Murugan et al., 2016).

Some important properties of actinide mononitrides for potential use in a reactor target—besides higher percentage mass of actinide versus the oxide—include thermal conductivity, melting temperature and solubility in various acids (Arai, 2012; Ekberg et al., 2018). Compared to oxide fuels, melting temperatures of actinide mononitrides are similar (Arai, 2012). The melting temperature of NpN is found to be 2830 K (Olson and Mulford, 1962), which compares well to the 3070 K temperature reported for NpO$_2$ (Manara et al., 2008). There is a consensus in the literature that the thermal conductivity of actinide mononitrides is higher than that of oxides: the mixed U/Pu mononitride thermal conductivity has been reported as 4–6 times higher, depending on temperature (Arai, 2012). Reports of the thermal conductivity of pure NpN

are limited in the literature. Ogawa and Handa report that NpN thermal conductivity varies by temperature from 15 to 17 W/m•K (Ogawa and Handa, 1995). Devraj reports that NpN thermal conductivity varies by crystallographic orientation, with values calculated at "room temperature" varying from 1.25 to 2.75 W/m•K (Devraj et al., 2016). More commonly, thermal conductivity of mixed mononitrides, which include Np, are reported. The thermal conductivity of U/Np and Pu/Np mononitride solid solutions at 600–1600 K are reported by Arai, ranging from 10 to 25 W/m•K, depending on composition of the solid solution and the temperature (Arai et al., 1998). Thermal conductivity of Np/Am solid solutions are also reported, and values range from 6 to 14 W/m•K in a temperature range of 500–1000 K (Uno et al., 2020). The variation in these data and the limited reports on pure NpN suggest a need for additional measurements to characterize the thermal conductivity of NpN. Additional data may be required as well to meet proper quality assurance (QA) needs for potential target materials due to the material being used in a reactor. For example, at HFIR, the quality assurance program is based on 10 CFR 830, Subpart A requirements as well as practices from ASME/NQA-1 (ORNL).

2.2 Neptunium mononitride synthesis

Although there are limited synthetic routes reported in the literature, the three main reaction pathways that have been reported for the synthesis of actinide mononitrides are carbothermic reduction, nitridation, and ammonolysis. Therefore, other actinide mononitrides including thorium (Th), uranium (U), plutonium (Pu), and mixed actinide mononitrides are discussed to provide additional context. Given the similar chemical properties across the actinide series, chemical reaction pathways for synthesis may be used as a comparison but are not a replacement for element-specific data.

2.2.1 Carbothermic reduction

The most published synthetic route for actinide mononitrides, including NpN, is carbothermic reduction. NpN (Suzuki et al., 1994; Ogawa and Handa, 1995), PuN (Yahata and Ouchi, 1975; Muromura, 1982; Ogawa et al., 1997; Takano et al., 2001), UN (Matthews et al., 1988; Hunt et al., 2014), ThN (Parkison et al., 2016), and mixed mononitrides (Greenhalgh and Weber, 1968; Arai et al., 1993b; Minato et al., 2003) are all reported *via* carbothermic reduction. The general reaction for carbothermic reduction is as follows:

$$NpO_2(s) + 2C(s) + \frac{1}{2}N_2(g) \rightarrow NpN(s) + 2CO(g). \quad (1)$$
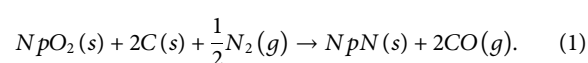
Powdered forms of the dioxide and graphitic carbon are mixed, pressed, and then heated under a nitrogen gas stream;

exact ratios and reaction constraints vary between studies. The reaction requires heating at temperatures above 1600 K (Pautasoo et al., 1988). Although this method has significant advantages—namely, simple reactants and a lack of hazardous chemicals and by-products—concerns exist about chemical impurities, primarily oxygen and carbon, in the final product. Small oxygen impurities (<1% by weight) in uranium nitride fuels resulted in a 9–13% decrease in thermal conductivity of the material, depending on temperature (Arai et al., 1993a). Similarly, carbon impurities have been shown to decrease thermal conductivity of nitride fuels (Solntceva et al., 2016). Therefore, synthesis methods seek to minimize or eliminate both carbon and oxygen chemical impurities in the actinide nitride phase. The ratio of carbon to actinide dioxide varies between reports, with agreement that excess C is necessary to avoid oxygen contamination in the product (Arai, 2012). As the oxide reacts with the carbon and nitrogen, a mixed carbonitride is first formed at lower temperatures before converting fully to the mononitride at higher temperatures (Pautasoo et al., 1988). To remove residual carbon associated with this carbonitride phase, advanced methods were developed and typically involve addition of a hydrogen gas stream for final product purification. The importance and efficiency of a secondary carbon removal step with nitrogen/hydrogen gas stream was elucidated through evolved gas analysis of the reactions, which revealed that hydrogen cyanide (HCN) is released as an intermediary and subsequently reacts with the remaining carbon to remove final impurities (Bardelle and Warin, 1992). Kinetically, the reaction is rapid; however, longer reaction times result in lower chemical impurities in the product (Pautasoo et al., 1988). Whereas the mechanics and kinetics of the carbothermic reduction reaction are well established, details on the particle size, morphology, and microstructure are largely absent from the literature. Particularly, the two reports of NpN synthesis (Suzuki et al., 1994; Ogawa and Handa, 1995) present only x-ray diffraction analysis of the synthesized phase.

2.2.2 Nitridation

Nitridation is the least commonly reported method for mononitride production. Only one early report on NpN (Olson and Mulford, 1962) and one on PuN (Brown et al., 1955) are available. The general reaction scheme is as follows:

$$Np(s) + \frac{1}{2}N_2(g) \rightarrow NpN(s). \qquad (2)$$
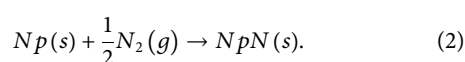
As is clear from the above reaction, this method is favorable as there are limited concerns about chemical impurities in the final product due to the very simple reaction mechanism. However, handling of Np or other actinide metals that are pyrophoric, presents significant challenges. Particularly, scaling of this reaction would present substantial safety concerns. The safety challenges associated with this reaction are likely a main

reason this method has not been further studied. Instead of Np metal, Np hydride (NpH_3) could also be used, though Np metal is still required to produce NpH_3.

2.2.3 Ammonolysis

A final alternative to produce actinide mononitrides is ammonolysis of actinide hydrides or fluorides. The first report of NpN from Sheft and Fried produced NpN *via* ammonolysis of the hydride (Sheft and Fried, 1953):

$$NpH_3(s) + NH_3(g) \rightarrow NpN(s) + 3H_2(g). \qquad (3)$$
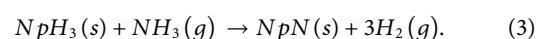
A series of reports by Silva and others suggest that actinide (Np or U) nitrides can also be synthesized by ammonolysis of tetrafluorides (Silva et al., 2008; Silva, 2009; Silva et al., 2009; Silva et al., 2012):

$$NpF_4(s) + 2NH_3(g) \rightarrow NpN_2 + 4HF(g) + H_2(g). \qquad (4)$$
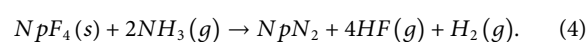
Then, higher nitrides decompose to the mononitride at high temperatures (>1000 °C) and in inert atmospheres (Silva et al., 2009):

$$2NpN_2(s) \rightarrow 2NpN(s) + \frac{1}{2}N_2(g). \qquad (5)$$
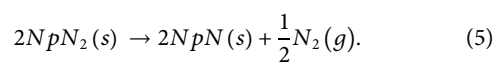
This reaction pathway is not discussed outside the above reports and represents a non-traditional method for synthesis, particularly compared to carbothermic reduction. Chemical safety concerns with the handling of ammonia gas, as well as production of actinide tetrafluorides, may make this method difficult at production scale. Nevertheless, these reports provide some of the only advanced solid-state characterization of actinide mononitrides, including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The reports shed light onto the complex microstructures and variable particle size of UN, as well as UO_2 surface or grain boundary impurities after an ammonolysis synthesis reaction (Silva et al., 2008).

2.3 Neptunium mononitride dissolution

To separate [238]Pu from [237]Np and produce a pure [238]Pu stream, irradiated [237]Np targets must be easily dissolved with [237]Np recycle, making the dissolution mechanism of NpN a key piece of information. Like synthesis methods, reports on NpN dissolution and reprocessing are limited in the literature, whereas more information is available on other actinide systems. Much of the information on actinide mononitride dissolution and processing is related to the development of accident-tolerant fuels.

2.3.1 Aqueous

Neptunium mononitride may dissolve in a variety of aqueous systems including water, nitric acid (HNO_3) and

peroxide. Early considerations for actinide mononitrides as advanced fuel forms required the evaluation of mononitrides in water. UN was found to corrode in water at ambient temperatures, converting to UO_2 and off-gassing ammonia (Sunder and Miller, 1998). Although water can alter and dissolve the surface of UN, this is not a method for complete dissolution. UN fuels have also been evaluated for tolerance to steam at temperatures up to 1200 °C as part of testing for Gen IV reactors (Jolkkonen et al., 2017; Sooby et al., 2022). Findings indicated pellet corrosion and evolution of ammonia and hydrogen gases. The fate of NpN in steam would require further study prior to use in reactor settings. Similarly, mixtures of high molarity LiOH and peroxide were reported to dissolve UN; however, dissolution was incomplete (Hickam et al., 2019). Complete dissolution of actinide mononitrides is successfully achieved in nitric acid. However, there are conflicting reports in the literature as to whether an addition of hydrofluoric (HF) acid is necessary. According to some reports, 8 M HNO_3 at 50–60 °C (Kulyukhin et al., 2014) or 10 M HNO_3 at 22 °C over 8 h (Fedorov et al., 2021) was sufficient for full dissolution. Others suggest 10–14 M HNO_3-0.05 M HF(Aneheim and Hedberg, 2016) or 8 M HNO_3-0.02M HF at 65 °C for 12 h (Campbell and Judge, 2021). Across all systems with or without HF, NO_x gas is a known effluent from the dissolution reaction. The addition of HF to the dissolution produced an intermediate UF_4 solid, which was subsequently dissolved (Campbell and Judge, 2021). A potential intermediate precipitation of PuO_2 during HNO_3-only dissolution was also suggested (Fedorov et al., 2021). Overall, the published literature on actinide mononitride dissolution exclusively covers U and Pu. Although the chemistry of the actinide series exhibits similarity, the lack of studies on NpN dissolution indicates a critical gap in the literature and necessitates the study of dissolution of NpN in aqueous systems, along with reaction kinetics. For an aqueous dissolution, traditional solvent extraction techniques would subsequently be employed for separation of ^{238}Pu/^{237}Np.

2.3.2 Pyrochemical

Pyroprocessing presents an alternative method for dissolution of nitride fuels, with the advantage of coupling reprocessing options into dissolution methods. In general, the nitrides dissolve into a molten salt so that the actinide metal can be recovered as a solid. Fission products would not follow the actinide metals in this process. NpN reportedly dissolved into LiCl-KCl eutectic melts (Shirai et al., 2000; De Córdoba et al., 2007), as are other actinide mononitrides such as UN (Hayashi et al., 2002) and PuN (Shirai et al., 2005). The reaction of the

mononitride in the eutectic melt releases N_2(g) as an effluent and recovers the actinide metal as a solid. The UN, NpN, and PuN have slightly different redox potentials (Shirai et al., 2000), suggesting the possibility of separate recovery of each metal. This could be advantageous for separation of ^{238}Pu and ^{237}Np from irradiated targets.

3 Discussion

Currently, the ^{238}Pu for RTGs used in NASA space exploration missions is sourced from irradiated $^{237}NpO_2$ targets. The need of ^{238}Pu for RTGs on an annual basis is still higher than current supply output, and domestic reactor limitations complicate scaling of the current production flowsheet. To achieve higher percent ^{237}Np per target, alternative target materials such as NpN may need to be explored. This review sought to compile and summarize existing literature on NpN as a base evaluation toward target development. Three main synthesis pathways are reported in literature, including nitridation, carbothermic reduction, and ammonolysis, though much of the detailed information on these pathways is from other actinides, not Np. The dissolution and reprocessing schemes that have been presented, which could be utilized for post-irradiation processing of targets, are predominantly reported schemes for other actinides.

Materials chemistry of NpN and other actinide mononitrides has been studied for more than seven decades, yet data on NpN still remain limited. Synthesis pathways, including nitridation, carbothermic reduction, and ammonolysis, are well documented. However, materials characterization, including advanced techniques such as SEM, TEM, x-ray photoelectron spectroscopy, and x-ray absorption spectroscopy, have not been applied to these systems, likely due to the age of many of the studies compared to the recent development of these analytical techniques and the safety challenges related to analyzing radioactive materials. Elucidation of morphology, particle size, nanostructure, and trace chemical impurities as a function of synthesis method for mononitrides can inform subsequent reactor performance and dissolution of irradiated targets. Overall, there exists a need for directed Np-only studies on mononitrides and application of the most advanced solid-state characterization techniques available for a more thorough understanding of NpN materials chemistry. Without a strong foundation of basic science, further development toward reactor targets cannot proceed. Beyond fundamental materials chemistry, development toward a reactor target would require

significant engineering and science efforts. Such efforts would include selection of a synthesis route, testing synthetic chemistry with analogue elements and Np, design of process equipment, development of dissolution and reprocessing chemical flowsheets, irradiation testing and safety evaluations for reactors, and ultimately, process scaling to achieve production goals. Given the growing need for [238]Pu supply to support deep space exploration, continued evaluation of alternative production flowsheets is strategic for domestic isotope production efforts.

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Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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