

Short communication

Direct chemical reduction of neptunium oxide to neptunium metal using calcium and calcium chloride



Leah N. Squires*, Paul Lessing

Idaho National Laboratory 2525 Fremont Avenue, Idaho Falls, ID 83415, USA

ARTICLE INFO

Article history:

Received 1 October 2015

Received in revised form

5 January 2016

Accepted 12 January 2016

Available online 13 January 2016

ABSTRACT

A process of direct reduction of neptunium oxide to neptunium metal using calcium metal as the reducing agent is discussed. After reduction of the oxide to metal, the metal is separated by density from the other components of the reaction mixture and can be easily removed upon cooling. The direct reduction technique consistently produces high purity (98%–99% pure) neptunium metal.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A key to reducing the long term health and safety hazards presented by the storage of spent nuclear fuel is reduction or elimination of the minor actinides in the fuel such as neptunium, americium and curium. One method currently under investigation for the elimination of these elements is transmutation; whereby, the minor actinides are incorporated into new fuel which is placed in a fast reactor where the minor actinides of interest fission to shorter lived products. In order to develop the process of transmutation it is necessary to first fabricate small quantities of fuel with minor actinide additives and perform thorough characterization and irradiation testing on it.

Neptunium metal is a key component in the fabrication of transmutation fuels and, currently, there is very little neptunium metal available. The majority of the neptunium that is available is in the oxide form and much of it is of questionable purity. It is imperative to the future of transmutation development that high purity neptunium metal is obtained to be incorporated as an additive to approximate spent fuel. In order to produce the needed material from that which is available, a relatively high throughput process of reducing neptunium oxide to neptunium metal was developed. A number of literature references describe methods of reducing plutonium or uranium oxide to metal using calcium [1–4] or lithium [3,5,6] as the reducing agent. A process of reducing americium oxide to americium metal using lithium [7] was also developed; however, no previous work has applied these processes

to neptunium. Thus, a method was developed to directly reduce neptunium oxide to neptunium metal using calcium as a reducing agent. A number of experiments were performed to optimize the process. In this process the reagents are heated, stirred and separated by density. This density separation results in a relatively easily retrievable button of neptunium metal that settles to the bottom of the mixture. This process consistently produces high purity (98%–99%) neptunium metal.

2. Experimental

This work is performed using the Hot Uniaxial Press (HUP) furnace in the Casting Laboratory glovebox of the Analytical Laboratory at the Materials and Fuels Complex of Idaho National Laboratory (INL). The HUP is a water cooled well furnace that extends below the glovebox floor and is loaded from the top. The glovebox is kept under an argon atmosphere. Oxygen levels are monitored constantly within the glovebox and must be below 50 ppm in order for this work to be performed. The reagents are placed in a magnesium oxide crucible (Fig. 1b) that is custom made to fit inside the furnace insert (crucibles fabricated by Ozark Ceramics, Webb City, MO). Magnesium oxide was chosen as the crucible material because it can withstand the temperatures to which the mixture must be heated for the reduction process, and it does not react with any of the reagents being used in the process. This magnesium oxide crucible is placed inside a stainless steel crucible that is designed to ensure that the contents of the magnesium oxide crucible do not leak into the furnace itself if the magnesium oxide crucible becomes compromised during heating (Fig. 1a). The stainless steel crucible is designed to fit inside the HUP furnace stirring insert (Fig. 2). The reagents are stirred at temperature using a tantalum

* Corresponding author.

E-mail address: leah.squires@inl.gov (L.N. Squires).

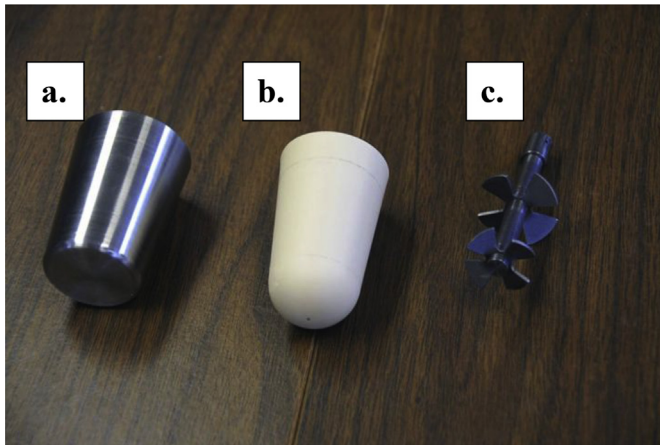


Fig. 1. Reaction vessels and stirrer. (a) Stainless steel crucible that fits into the furnace apparatus and protects the furnace well if the magnesium oxide crucible is compromised during heating; (b) heat resistant, non-reactive magnesium oxide crucible that serves as the reaction vessel for the neptunium oxide reduction process; and (c) tantalum stirrer designed with lower impellers to push reagents up and upper impellers to push reagents down in order to promote mixing of the molten material.

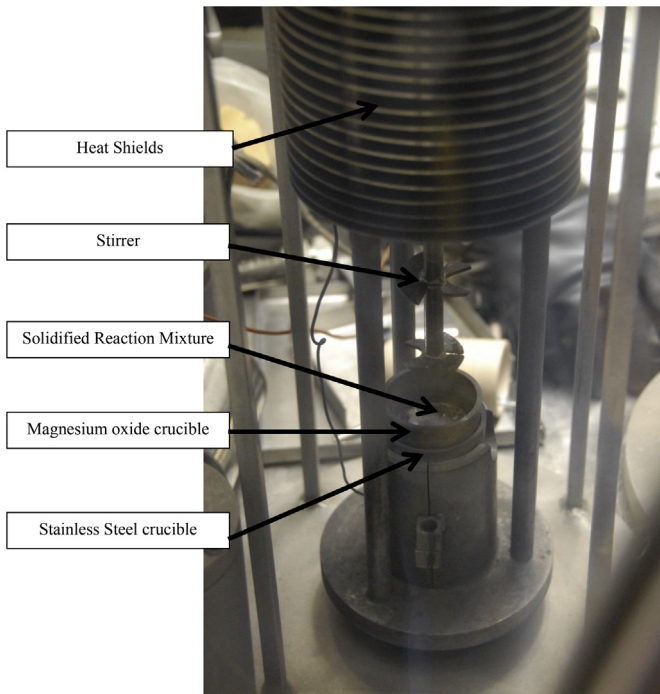


Fig. 2. The hot uniaxial press (HUP) furnace insert apparatus. Shown here is a loaded magnesium oxide crucible inside a stainless steel crucible with stirrer suspended above the reaction vessel.

stirrer that is fabricated in house at INL. The stirrer is designed with lower impellers to push material up and upper impellers to push material down in order to facilitate mixing of all reagents (Fig. 1c).

2.1. Calcining

The first step of the process is a calcining heat treatment of the neptunium oxide starting material. In this step, approximately 20 g of neptunium oxide powder is placed in the magnesium oxide crucible that is then placed in the stainless steel crucible and next placed into the furnace insert. The entire insert is then lowered into

the well furnace and heated to 800 °C. The material is held at temperature for 6 h. The purpose of the calcining step is to drive off volatile impurities before the reduction. While no specific analysis has been performed on the starting material, it is most likely that a very small amount of water is being driven off during the calcining process. The furnace is turned off after 6 h, and the contents are allowed to cool overnight. The following day the material is removed. The neptunium oxide is reweighed and the magnesium oxide crucible is examined for damage. If the crucible is not found to be damaged it is used for the reduction process. If any damage is detected, a new crucible is used for the reduction step.

2.2. Reduction

The crucible is then refilled for the reduction step of the process. First the tantalum stirrer (Fig. 1c) that is designed to ensure thorough mixing of the material is placed in the crucible. It is important to place the stirrer in first because, once the crucible is full of reagents, it is not possible to insert the stirrer. Approximately 9 g of calcium metal (Fisher Scientific-Alfa Aesar) is placed in the bottom of the crucible, followed by a thin layer of approximately 1 g of ultra-dry calcium chloride (Fisher Scientific-Alfa Aesar). The calcined neptunium oxide is then placed on top of the thin calcium chloride layer, and the remaining volume of the magnesium oxide crucible is then filled with ultra-dry calcium chloride salt (approximately 100 g).

The furnace insert is placed inside the furnace well and the furnace is heated at a ramp rate of 50 °C per minute to the maximum heat capacity of the furnace (1000 °C). When the internal temperature measured by a thermocouple placed just above the reaction mixture reaches 850 °C, the external gear on the motor is engaged with the gear on the stirrer to begin turning the tantalum stirrer (Fig. 3). The rate of stirring is 100 RPM. The reaction is allowed to sit at temperature for 6 h with stirring. Once the time has elapsed, the stirrer is removed from the molten mixture before the furnace is shut off to ensure that it does not become lodged in the re-solidified material. After the stirrer is removed the mixture is left at temperature for at least 1 additional hour in order to allow the components of the reaction mixture to settle and separate by density before the furnace is turned off. The crucible and contents

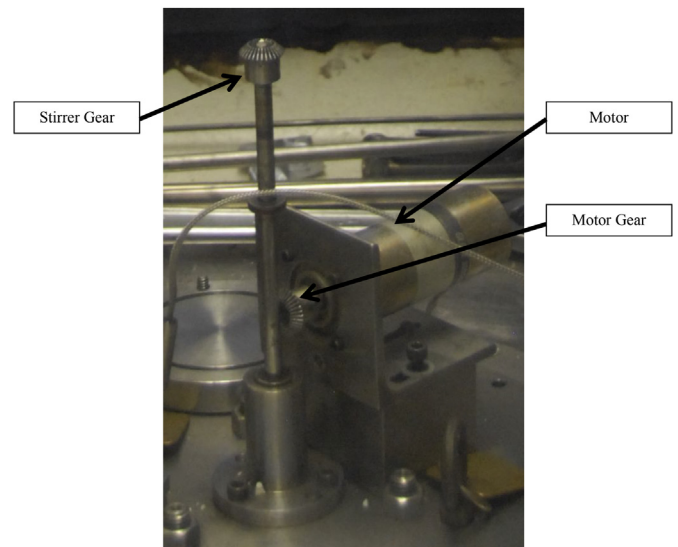


Fig. 3. Stirrer and motor. The motor to run the stirrer is located above the furnace well. The stirrer is positioned when reagents are molten and the gear on the stirrer is engaged with the gear on the motor.

Download English Version:

<https://daneshyari.com/en/article/1564733>

Download Persian Version:

<https://daneshyari.com/article/1564733>

[Daneshyari.com](https://daneshyari.com)