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Production of small uranium dioxide microspheres for cermet nuclear fuel using the internal gelation process ☆

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ABSTRACT

The U.S. National Aeronautics and Space Administration (NASA) is developing a uranium dioxide (UO_2)/tungsten cermet fuel for potential use as the nuclear cryogenic propulsion stage (NCPS). The first generation NCPS is expected to be made from dense UO_2 microspheres with diameters between 75 and 150 μm. Previously, the internal gelation process and a hood-scale apparatus with a vibrating nozzle were used to form gel spheres, which became UO_2 kernels with diameters between 350 and 850 μm. For the NASA spheres, the vibrating nozzle was replaced with a custom designed, two-fluid nozzle to produce gel spheres in the desired smaller size range. This paper describes the operational methodology used to make 3 kg of uranium oxide (UO_x) microspheres.

1. Introduction

A nuclear cryogenic propulsion stage (NCPS) based on nuclear thermal propulsion (NTP) is under development by the National Aeronautics and Space Administration (NASA) (Hickman et al., 2012). Many believe that NTP is the best near-term propulsion option for manned missions to the Moon and Mars. The viability of NTP was firmly established by NASA and the Atomic Energy Commission's space nuclear rocket program in the 1960s (Koenig, 1986). The current NASA effort focuses on uranium dioxide (UO_2)/tungsten cermet fuel. An extensive overview of the fabrication technology behind this type of cermet fuel has been reported elsewhere (Burkes et al., 2007). The initial focus of this effort at Oak Ridge National Laboratory (ORNL) was the hood-scale production of UO_2 microspheres with diameters between 40 and 150 μm using an existing internal gelation system with relatively simple modifications. In the initial or proof of principle experiments, the objective was to generate batches in which most of the dense UO_2 microspheres had diameters smaller than 75 μm. To make and capture the small uranium gel spheres, several modifications to the internal gelation equipment were made. Several experiments were performed to determine suitable operational conditions, which provided a reasonable percentage of gel spheres in the targeted size range. As the size of the gel spheres decreased, the collection and washing of the very small gel spheres became more challenging. During the heat treatment of the microspheres, the smaller spheres would form agglomerations, which were difficult to break apart and led to some surface damage. Therefore, NASA requested that ORNL change the target size range for the production runs so the final diameters of the UO_2 microspheres would be between 75 and 150 μm.

For decades, the internal gelation process has been used in the production of UO_2 kernels with diameters on the order of 100 μm. Initially, KEMA used a vibrated spray nozzle (Kanij et al., 1974). The droplets from the nozzle were collected in horizontally flowing streams of mixed hydrocarbons at 353–372 K. The observed standard deviation of this technique was 40 μm at a pilot-scale production rate. The use of spinnerets resulted in a reduction in the standard deviation to 10 μm. To make UO_2 kernels with a diameter of 10 μm, KEMA used an emulsion technique (Kanij et al., 1974; Notz, 1977). The uranium solution was dispersed in cold Freon 113 using an ultrasonic vibrator. When the Freon was warmed to 313 K, the droplets gelled. Next, the Freon and the gel were transferred into ammonium hydroxide (NH_4OH) solution at 333 K, and the Freon was evaporated. After the gel spheres were washed, calcined, and sintered, dense UO_2 fines with a wide size distribution were produced. It was speculated that the use of a turbulent

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shear nozzle in 2-ethyl-1-hexanol (2EH) could also be used. However, the rate of production or uniformity would be impacted negatively (Lackey and Steele, 1978). This speculation was confirmed at least partially in a recent study, which used 2EH to make uranium oxide (UO_x) microspheres with diameters between 5 and 120 μm (Deptula et al., 2010). Unfortunately, details about the researchers' process were not reported. Alternatively, the internal gelation process and the jet entrainment technique to prevent agglomeration have been used to make small, dense mixed oxide (MOX) particles with UO_2 as a component (Pouchon et al., 2003; Hellwig et al., 2006; Bart et al., 2007), but published information about the experimental system and optimized parameters was lacking. Fortunately, equipment development and optimized process conditions to obtain dense UO_2 particles with diameters of 80–120 μm have been provided (Ganatra et al., 2008). After the size requirements for the UO_2 particles are further refined during the development of the NCPS, it is expected that future internal gelation experiments will use a system similar to ones used at Bhabha Atomic Research Center (Ganatra et al., 2008) and Paul Scherrer Institute (Pouchon and Ingold, 2009) if the desired diameter is 100 μm or above.

2. Experimental

2.1. Preparation of stock solutions and the feed solution

The acid deficient uranyl nitrate (ADUN) stock solutions for these tests had densities between 1879 and 1890 kg/m^3 and pH values from 1.2 to 1.3. The densities were used to estimate the uranium concentrations using an empirical relationship determined elsewhere (Spencer and Whatley, 1990; Collins et al., 2004). The uranium concentrations were estimated to be between 2.89 and 2.93 M. As shown elsewhere (Haas et al., 1979), the uranium concentration and pH of a solution can be used to estimate the nitrate-to-uranium molar ratio, which is a measure of the acid deficiency. All ADUN stock solutions had nitrate-to-uranium molar ratios between 1.70 and 1.75. The uranium concentration for each ADUN stock solution was lowered to 2.76 M through the addition of deionized water. The concentrations for the hexamethylenetetramine (HMTA) (Fisher Scientific) and urea (Fisher Scientific) in the other stock solution were both 3.2 M, and the density of the HMTA/urea solution was 1140 kg/m^3.

For a typical test, 174.6 g of the 2.755 M ADUN stock solution and 120.3 g of HMTA and urea stock solution were chilled separately in an ice bath for a minimum of 30 min. To prepare the feed solution or broth, the HMTA and urea solution was slowly added to the ADUN solution. The feed was mixed by hand until clear of any localized precipitate. Generally, there was little or no noticeable amount of precipitate formed. The uranium, HMTA, and urea concentrations in each broth preparation were 1.30, 1.69, and 1.69 M, respectively.

2.2. Experimental apparatus and conditions

As shown in Fig. 1, a hood-scale apparatus, which has been used for numerous preparations of gel spheres with either the vibrating (Collins et al., 2004) or the two-fluid nozzle (Hunt et al., 2005) techniques, was used in this work. However, due to the small droplet size in this effort, changes to the internal gelation apparatus were needed. A key modification involved the use of a custom designed, two-fluid nozzle. Subsequent testing indicated that it was critical to clean the nozzle with dilute nitric acid and then water after each run. The nozzle consisted of two static mixers (Stratos Tube Mixers by Kaflo), which were connected to opposite ends of a stainless steel Swagelok® tee. The lengths of the static mixers on the inlet and outlet sides were 7.62–19.05 cm, and their respective internal diameters were 0.335–0.194 cm. A 0.476 cm to 0.635 cm stainless steel Swagelok® adapter was used to attach the tee to the larger diameter static mixer. A 10.16 cm long, 0.15 cm outer diameter, 17-gauge blunt-end hypodermic needle (Cadence) was positioned in the side connection of the tee using a small section of Tygon® R-3603 tubing. In addition to being a good seal, this tubing provided for easy insertion and removal of the needle. A section of thin-walled rigid plastic tubing was used as a sleeve on the needle to act as a stop which provided consistent positioning of the tip of the needle near the center of the channel when it was inserted. During a run, the flow of the hot 2EH (Sigma–Aldrich) in the channel of the tee caused small droplets of broth to rapidly form when the chilled broth exited the needle. Flow through the series of fixed alternating right and left hand helical elements in the static mixer kept the droplets separated.

At the start of a run, the chilled feed solution was transferred to a jacketed Pyrex® broth pot mounted on a variable speed magnetic stirrer (VELP Scientifica). The temperature of the broth solution was maintained near 273 K, which enhanced broth stability time to a minimum of 60 min. The broth pot and the head of the digital gear pump (Cole–Parmer) were chilled using of ethylene glycol and a refrigerated circulating bath (Neslab). The digital gear pump was used to transfer the feed solution from the broth pot to the hypodermic needle in the nozzle at a rate of 11.5 cm^3/min. A different digital gear pump (Micropump) was used to transfer heated 2EH from its reservoir to the top of the static mixer at a rate of 179–190 cm^3/min. Most of the tests were performed using a 2EH flow rate of 180 cm^3/min.

At a typical flow rate of 350–450 cm^3/min, a centrifugal pump (Eastern Centrichem) was used to pump hot 2EH, which contained Span™ 80 (Sigma–Aldrich) at a concentration of 0.002–0.004 g/cm^3 of 2EH, from the reservoir to a glass fitting at the bottom of the vertically positioned gelation column. The Span™ 80 is a sorbitan monooleate ester and a surface-active compound, which minimized coalescence of droplets once they were formed in the nozzle.

Once the gel spheres were formed in the gelation column, the spheres and the 2EH were transported through a 1.8 m long, 0.375 cm inner diameter Tygon® R-3603 serpentine delivery tube into the first Pyrex® collection vessel located in the reservoir. Typically, gravity caused about 95% of the gel spheres that entered the first collection vessel gravity to settle to the bottom and remain there. Two additional collection vessels were connected in a series so the overflow from the first would go into the second Pyrex® collection vessel, and the overflow from the second would go into the third collection vessel, which was made of stainless steel wire mesh (140 mesh). Typically, less than 3% of the gel spheres were collected in the second Pyrex collection vessel. The amount of gel spheres that escaped the collection vessels was minimized when flow through the system was maintained at a reasonable rate. However, a fraction of very small gel spheres escaped the collection system and settled in various locations in the gelation system or remained suspended, resulting in an increase in the turbidity of the 2EH. Eventually, the turbidity was observed to increase to the point that the 2EH could no longer be used because of operational problems such as plugging and a significant decrease in the size of the gel spheres. At this point, replacement of the 2EH was required.

The 2EH was heated with two 450 W stainless steel heating blades. A thermocouple in the reservoir and a temperature controller for the heating blades were used to maintain the temperature of the 2EH at 333–336 K. A Lightnin® mixer with its stainless steel shaft positioned between the two heating blades and its stainless steel impeller located near the bottom of the reservoir was used to mix the 2EH and help maintain it at the desired temperature. A large removable stainless steel wire mesh (100 mesh) basket,