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Straight-chain halocarbon forming fluids for TRISO fuel kernel production – Tests with yttria-stabilized zirconia microspheres

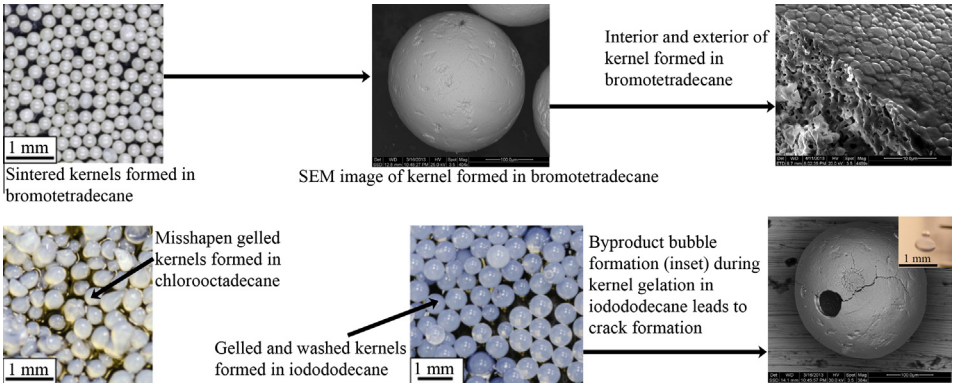
M.P. Baker [a], J.C. King [a,*], B.P. Gorman [b], J.C. Braley [c]

[a] Nuclear Science and Engineering Program, Metallurgical and Materials Engineering Department, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, United States
[b] Metallurgical and Materials Engineering Department, Colorado Center for Advanced Ceramics, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, United States
[c] Nuclear Science and Engineering Program, Chemistry and Geochemistry Department, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, United States

HIGHLIGHTS

- YSZ TRISO kernels formed in three alternative, non-hazardous forming fluids.
- Kernels characterized for size, shape, pore/grain size, density, and composition.
- Bromotetradecane is suitable for further investigation with uranium-based precursor.

GRAPHICAL ABSTRACT



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ABSTRACT

Current methods of TRISO fuel kernel production in the United States use a sol–gel process with trichloroethylene (TCE) as the forming fluid. After contact with radioactive materials, the spent TCE becomes a mixed hazardous waste, and high costs are associated with its recycling or disposal. Reducing or eliminating this mixed waste stream would not only benefit the environment, but would also enhance the economics of kernel production. Previous research yielded three candidates for testing as alternatives to TCE: 1-bromotetradecane, 1-chlorooctadecane, and 1-iodododecane. This study considers the production of yttria-stabilized zirconia (YSZ) kernels in silicone oil and the three chosen alternative formation fluids, with subsequent characterization of the produced kernels and used forming fluid. Kernels formed in silicone oil and bromotetradecane were comparable to those produced by previous kernel production efforts, while those produced in chlorooctadecane and iodododecane experienced gelation issues leading to poor kernel formation and geometry.

1. Introduction

A Tri-structural ISOtropic (TRISO) particle consists of a 200–500 μm diameter sphere of uranium oxide (UO_2), uranium carbide (UC), or uranium oxycarbide (UCO), coated with carbon and silicon carbide (SiC) layers applied via chemical vapor deposition in a fluidized bed. The carbon buffer layer absorbs the kinetic energy of ballistic fission fragments, provides void volume for gaseous fission products, and accommodates kernel swelling. The silicon carbide layer acts as a pressure and diffusion barrier of fission products, and the two pyrolytic graphite layers protect the silicon carbide layer during production and aid in rigidity. Although layer

* Corresponding author. Tel.: +1 303 384 2133; fax: +1 303 273 3795.
E-mail address: kingjc@mines.edu (J.C. King).

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Nomenclature

Latin symbols

A_p	projected surface area calculated by ImageJ
d_{max}	maximum kernel diameter measured by ImageJ
d_{min}	minimum kernel diameter measured by ImageJ

thicknesses vary between manufacturers, the buffer layer is around 100 μm, the silicon carbide layer around 35 μm, and the pyrolytic carbon layers around 40 μm, for fuels developed and being qualified in the United States [1].

In the United States, TRISO fuel fabrication usually takes place by internal gelation with trichloroethylene (TCE) as the forming fluid [2]. As a chilled uranium-based precursor solution falls through the hot trichloroethylene, the internal temperature of the precursor rises, which decomposes hexamethylenetetramine (HMTA) into ammonia and formaldehyde. This change increases the kernel's pH, which drives metal decomplexation to form a solid sphere during free-fall at terminal velocity [2,3]. The used formation fluid eventually needs replacing and the disposal of this mixed hazardous waste is a costly environmental concern. Replacing the TCE with a non-hazardous alternative may save an estimated $112,500 per ton of TRISO fuel kernels [4,5]. In the United States, the Resource Conservation and Recovery Act (RCRA) identifies hazardous wastes by several means, including waste characteristics ("characteristic waste") or by the inclusion of the material on a hazardous materials list ("listed waste"). TCE is a listed waste; therefore, identifying a replacement that is not on the hazardous materials lists, and does not meet any of the hazardous waste characteristics, ensures that the spent forming will not be considered a mixed hazardous and radioactive waste. While TCE and the proposed alternatives are both halogenated hydrocarbons, they are structurally quite different and the identified replacements do not result in a hazardous waste by either the listed or characteristic waste criteria.

Previous evaluation and testing of alternative forming fluids identified three fluids as potential replacements for TCE in TRISO kernel production: 1-iodododecane, 1-bromotetradecane, and 1-chlorooctadecane [5]. In the previous study, fluid selection was based on the forming fluids' physical properties and assuring the new fluid is not listed as a hazardous chemical. Densities, viscosities, and surface tensions values at elevated temperatures were used to estimate the settling velocities of forming UCO kernels and the time required to bring the center of the kernel to $5/6^{th}$ of the forming fluid temperature. Using the estimated values also provided a minimum column height. This paper presents the results of production and characterization of surrogate zirconia kernels in silicone oil and the three potential alternative fluids.

This study uses yttria-stabilized zirconia (YSZ) as a surrogate material to avoid radioactive materials handling. The YSZ precursor solution is less dense than TCE, which prevents TCE from acting as a forming fluid for zirconia formation. Silicone oil is the most commonly used forming fluid for YSZ microspheres [6–10], and was also one of the first formation fluids used in the production of TRISO fuels [11–14].

The overall goal of this study is to eliminate the mixed hazardous waste resulting from kernel fabrication with TCE. The previous study identified three potential non-hazardous alternative fluids based on fluid physical properties [5]. This study aims to use the proposed fluid in lab-scale kernel production to determine their usefulness as forming fluids. Successful kernel production will replicate the microstructure, geometry, composition, and density of the kernels produced in silicone oil.

2. Experimental setup

A properly sized formation column with temperature control and a pump capable of delivering a precise amount of fluid to a well controlled vibrating orifice are required to achieve a narrow kernel size distribution. Previous calculations provided sizing information for the equipment in this study [5] and the operational set points selected for zirconia surrogate production are presented in this section.

The formation fluid within the column should be kept at a constant temperature to allow each kernel to gel at the same rate. Formation columns may be constructed of any material capable of keeping the formation fluid at the desired temperature without introducing adverse chemical reactions. The ability to watch the forming particles and monitor their settling velocity is desirable, which leads to a preference for high temperature plastic or glass columns. High temperature plastics may result in unknown chemical reactions with the alternative forming fluids, while glass columns are inert to many chemicals and are more transparent, allowing easy viewing or kernel formation. Fig. 1 presents the top and bottom of the custom-built glass column created for this research built by Allen Scientific Glass. The column is approximately 45 cm in total height, including the attached flask, which is larger than the minimum heights calculated for UCO production [5], and is near the maximum height available given the glass blower's ability with the given geometry.

The jacketed glass column is equipped with a 32 mm upper opening, a heating fluid inlet/outlet, a formation fluid return spout, a 100 ml removable collection flask, a 6 mm stopcock, and a 1 mm measuring stencil (see Fig. 1). Digital video recording of the kernel formation and the movement of the gelling spheres in reference to the stencil allows for accurate terminal velocity measurement. The heating jacket allows a constant temperature-recirculating bath to keep the formation fluid at the specified operating conditions while monitoring the temperature via a remote thermocouple probe. The forming fluid return spout allows excess fluid displaced by the kernels to be collected.

To aid the natural laminar flow breakup of the precursor solution needed for the production of consistently sized kernels, the precursor broth needs to be delivered continuously at a specified flowrate to a precise orifice diameter in conjunction with a vibration mechanism (Fig. 2 [15]). A Cole Parmer screw-driven pump with an attached 50 ml syringe allows for precise flow control though 1/16″ (1.59 mm) inner diameter Viton® tubing. The production facility includes blunt-ended electropolished hypodermic needles and 1/16″ (1.59 mm) needle-tubing coupling units from Cadence Scientific.

An electrodynamic shaker (LW132.151-7) connected to a servo controller (SC-121), and power amplification unit (PA-151) purchased from Labworks Inc. provides the necessary frequency for kernel diameter control. The vibration controlling unit is capable of 1–10,000 Hz operation with 1/2″ (12.7 mm) of travel, and a needle holding attachment allows for varying needle angles and distance from the vibration source. The equipment allows the formation of almost any size kernel if the proper orifice size is used in conjunction with the appropriate frequency. The vibration unit