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Recommended dispersing conditions for broths used in the preparation of uranium microspheres with carbon ☆

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ABSTRACT

Early preparations of uranium fuel kernels with carbon demonstrated the need for better dispersion of the carbon black in the aqueous feed solutions and in the subsequent microspheres. Therefore, the dispersing conditions for various carbon blacks were evaluated. A rheometer has proven to be a very useful tool in evaluation of dispersion conditions for carbon blacks (Black Pearl L and Raven 1000) with Tamol SN in the uranium and hexamethylenetetramine–urea feed solutions. The recommended dispersion conditions for Tamol SN were then used to make uranium microspheres with two carbon blacks. Optical images of these microspheres confirmed that the carbon was adequately dispersed, which supports the use of the viscosity measurements to determine appropriate carbon dispersion conditions.

1. Introduction

During the past few years, preparation of uranium oxide microspheres with carbon black has been the focus of considerable research interest within the United States (Hunt et al., 2007; Contescu et al., 2008). When these UO_2 (uranium dioxide) and UC_2 (uranium dicarbide) kernels are coated with carbon and silicon carbide, they can significantly improve the efficiency, longevity, and safety of the nuclear fuel for the next-generation commercial nuclear power systems. Moreover, the mixture of UO_2 and UC_2 can be converted to uranium nitrides (Hunt et al., in press; Lindemer et al., in press) prior to the coatings of the kernels.

With considerable difficulties, laboratory-scale amounts of UO_2 and UC_2 kernels were produced at Oak Ridge National Laboratory (ORNL) in the early 1980s using the hexamethylenetetramine (HMTA) and urea internal gelation process (Stinton et al., 1982, 1983). The formulation and process conditions were not optimized. Large carbon agglomerations formed in the uranium microspheres. These agglomerations made the conversion to UO_2 and UC_2 kernels much more difficult in terms of higher conversion temperatures and longer conversion times. Subsequent research on acid-deficient uranyl nitrate (ADUN) at ORNL has led to a much better understanding of key process variables in the internal gelation process (Collins et al., 1987). This enhanced process knowledge and equipment improvements were used to make kilogram quantities of UO_2 kernels with near theoretical density, uniform sizes, smooth surfaces, and high crush strengths (Hunt and Collins, 2004; Collins et al., 2004). While UO_2 kernels from the 1980s were prone to flaking, these new UO_2 kernels met the proposed fuel specifications for the next-generation nuclear power system.

Using these process improvements, two carbon blacks (Cabot Black Pearl L and Cabot Monarch 4750) with a ionic dispersing agent (Tamol SN) were used to produce $UO_3{\cdot}2H_2O$ microspheres with carbon (Hunt et al., 2007). These strong microspheres were not prone to leaching during washing or to cracking during subsequent heat treatments. Dense and strong uranium fuel kernels with carbon were successfully produced in argon at 1953 K when the carbon was adequately dispersed in the microspheres. The physical properties of the sintered kernels that were prepared using the different carbon blacks were indistinguishable. This study also determined that the mass ratio of Tamol SN to carbon is a key variable in the conversion and sintering kinetics. However, these tests demonstrated the need for a quick and systematic way to evaluate the dispersing process.

For Tamol SN, the Cabot Corporation has previously determined its dispersing agent requirement (DAR), which is the minimum

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amount of dispersing agent needed to produce a fluid dispersion at a specified carbon black loading in H_2O (Cabot Corporation, 1989). Too little or too much dispersing agent relative to carbon black can lead to larger carbon aggregates and compromise the stability of the broth. The viscosity of the solution will increase as the carbon aggregate size increases from too much or too little dispersing agent. Another effort demonstrated that the stability of carbon dispersion is directly related to the viscosity of the aqueous solution (Bowers and Bernards, 2003). These earlier studies indicate that the viscosity of the aqueous solution with a carbon dispersion should continue to drop until the optimal amount of dispersion agent has been added and adequately dispersed.

The pH of the solution, the type of carbon black, method of dispersion, and dispersing agent can be important factors in the determination of the best ratio of dispersion agent to carbon black. A series of viscosity tests were conducted in an effort to identify suitable the carbon dispersing conditions.

2. Experimental

2.1. Preparation of stock solutions and the feed solution

The standard concentrations for the HMTA (Fisher Scientific) and urea (Fisher Scientific) in the stock solution were 3.2 *M* each. After a stock solution was prepared and filtered, the density was measured to be 1140 kg/L and the pH ranged from 8 to 9.

The ADUN stock solutions in these runs had a density of 1860 kg/L with a pH of 1.55 or a density of 1840 kg/L with a pH of 1.66. The uranium concentrations were 2.82 and 2.77 *M* for the first and second ADUN solutions, respectively. The pH and uranium concentration (Haas et al., 1980) were used to estimate that the molar ratio of nitrate (NO_3^-) to uranium was approximately 1.6. ADUN solutions with this 1.6 M ratio can be prepared with uranium concentrations as high as 3.5 *M*. The current work has found that ADUN solutions with concentrations of 2.9 *M* and greater are supersaturated and unstable. Uranyl nitrate crystals can form, resulting in a change in the uranium concentration. Uranium concentrations of 2.6 and 2.85 *M* appear to be ideal because crystallization did not occur in these ADUN solutions.

2.2. Carbon blacks and dispersing agents

A number of carbon blacks and dispersing agents were compared in this study. The carbon blacks included Raven 1000, Raven 1040, and Raven M from Columbian Chemical Company as well as Black Pearl L. The dispersing agents used with these carbon blacks included Tamol SN from Rohm and Haas, Tergitol XD from Dow, and Borchi Gen 12 from Borchers. The dispersing agents and the fluffy carbon blacks were used as received. The Cabot Black Pearl L, which arrived in the form of 24-nm pellets, was first passed through a 150 mesh sieve to exclude all particles with diameters greater than 105 μm.

2.3. Carbon dispersion in HMTA–urea

The dispersing agent was typically added to 75 mL or 85.5 g of HMTA–urea, and the resulting solution was mixed by hand until the dispersing agent went into solution. In some cases, the amount of dispersing agent was varied in order to determine the DAR. Next, 2.79 g of carbon black was added to the HMTA–urea solution, which was then chilled to 273 K in an ice water bath. The carbon black in the chilled solution was next dispersed using a Hielscher Ultrasound Technology model UP200S ultrasonic probe. Attempts to use a less energetic mixing such as a vortex mixer were not effective with the carbon blacks in these tests. After an 8 h conversion at 1823 K in dilute carbon monoxide, the microspheres from the ultrasonic probe preparation were at least 35% more dense than the microspheres from the less energetic techniques. For a production system, a common alternative to the ultrasonic probe is a mixing pump system.

The carbon black must be uniformly dispersed throughout the solution, and its particle size must be kept as small as possible. The ultrasonic probe was used in 30-min increments. The use of the ultrasonic probe was sometimes problematic because the probe would become hot and increase the solution temperature. During sonication, the temperature of the carbon solution would increase from 273 K to 303–313 K even though the sample bottle was kept in an ice water bath. After the carbon was dispersed and the temperature of the carbon solution was returned to 273 K, a 16-mL sample of this solution was transferred to a small-sample adapter of a Brookfield DV-III rheometer. The sample temperature in the adapter was set at 278 K. With the aid of a refrigerated recirculator, the same temperature was used to produce $UO_3 \cdot 2H_2O$ microspheres with carbon at ORNL. After the sample was permitted to equilibrate in the small-sample adapter, the viscosity of the carbon solution was measured. Each solution was further dispersed in 30-min segments until the total dispersion time was 90 or 120 min. After each 30-min period with the ultrasonic probe, the carbon solution was chilled, and its viscosity was measured. Once the viscosity exceeded 25 cP, then no further dispersions were performed. All of the carbon solutions were non-Newtonian; thus, the measured viscosities are a function of the shear rates imposed by the Brookfield rheometer. Therefore, the shear rate for each viscosity measurement was provided.

2.4. Uranium broth preparation and subsequent analysis

Another HMTA–urea–carbon black solution with a dispersing agent as needed was prepared using the recommended dispersion conditions. After the dispersed solution was chilled to 273 K, 12.79 g of carbon black solution was added to 16.98 or 17.16 g of a chilled ADUN sample and mixed well to form the broth. The broth characteristics were as follows: an HMTA-to-uranium molar ratio of 1.35, a urea-to-uranium molar ratio of 1.35, a nitrate-to-uranium molar ratio of 1.55, a carbon-to-uranium molar ratio of 1.3, and a uranium concentration of 1.3 *M*. Our tests have indicated that the urea-to-uranium molar ratio should be between 1.20 and 1.37 when the uranium concentration is 1.3 *M*. If the HMTA-to-uranium molar ratio was higher than 1.37, the microspheres were prone to cracking. If the HMTA-to-uranium molar ratio was lower than 1.20, the surface of the microspheres would tend to erode. As the uranium concentration in broth increases, the ideal zone for the HMTA-to-uranium molar ratio decreases. Because the optimal mass ratio is known to be a function of pH for ionic surfactants, Tamol SN was also added to the ADUN to increase the mass ratio of the Tamol SN to carbon in the broth. It should be noted that uranyl nitrate crystals formed when the ADUN and Tamol SN were chilled to 273 K. When the ADUN and HMTA–urea solutions were well mixed to form the broth, all solids went back into solution. The viscosity of the chilled broth was then measured. The spindle for the rheometer was chilled to 278 K in order to reduce the potential for precipitation during the viscosity measurements. No signs of precipitation in the small-sample adapter were observed in any of the viscosity tests. The pH of the chilled broth was measured via a model 611 digital pH meter from Orion Research. Next, 0.5 mL of the chilled broth was heated in a water bath at 333 K to determine its gel time, which is another important process control variable. For our gelation system, a gelation time of 5–10 s is ideal. Another common gelation temperature is in 363–368 K range. However, the uranium microspheres made at this higher temperature are more likely to crack during subsequent heat treatment.