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# Selection of water-dispersible carbon black for fabrication of uranium oxicarbide microspheres

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## Abstract

Fabrication of uranium oxicarbide microspheres, a component of TRISO fuel particles for high temperature nuclear power systems, is based on the internal gelation of uranium salts in the presence of carbon black. In order to obtain a high quality product, carbon black should remain dispersed during all phases of the gelation process. In this study, the surface and structural properties of several commercial carbon black materials, and the use of dispersing agents was examined with the goal of finding optimal conditions for stabilizing submicron-sized carbon black dispersions. Traditional methods for stabilizing dispersions, based on the use of dispersing agents, failed to stabilize carbon dispersions against large pH variations, typical for the internal gelation process. An alternate dispersing method was proposed, based on using surface-modified carbons functionalized with strongly ionized surface groups (sodium sulfonate). With a proper choice of surface modifiers, these advanced carbons disperse easily to particles in the range of 0.15–0.20 μm and the dispersions remain stable during the conditions of internal gelation.
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## 1. Introduction

The nuclear fuel for Generation IV very high temperature gas cooled reactors (VHTR) is based on microspheres containing a mixture of uranium oxide ($UO_2$) and uranium carbide ($UC_2$) coated with carbon and silicon carbide. This structure represents a significant improvement in efficiency, longevity, and safety of nuclear fuels. The interest in production of $UO_2$–$UC_2$ kernels has been revived in the last few years. In the late 1970s, laboratory-scale ($UO_3 \cdot 2H_2O$–C) gel spheres were first prepared at Oak Ridge National Laboratory (ORNL) [1,2]. The process was based on the sol–gel reaction between an acid-deficient uranyl nitrate (ADUN) aqueous solution (pH 1.9–2.0) and a solution of hexamethylenetetramine (HMTA) and urea in water (pH 10–10.5), a process referred to as internal gelation. In the early studies at ORNL, carbon black was dispersed with a surfactant and was introduced in the process before the gelation step. Several batches of dried gel spheres were prepared with C/U mole ratios of 0.8–1.2:1, which were sintered to make uranium 'oxicarbide' ($UO_2 + UC_2$) kernels. However, no optimization of formulation or of process conditions was attempted at that time. Subsequently, more in-depth studies on the chemistry of internal gelation in the ADUN–HMTA/urea system [3,4] led to a better understanding of process variables, and made possible production of several batches of good quality $UO_2$ kernels at ORNL in 2004 [5].

Production of high quality carbon-containing kernels was not without difficulty. A key requirement to obtain

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high kernel density is the uniform distribution of carbon in the $UO_2$ gel spheres before the thermochemical step; i.e. during the gel formation step. Uranium carbide is formed by direct reduction of $UO_2$ with carbon, and therefore the presence of large carbon particles or agglomerates is undesirable because they will create voids during sintering. It was proposed that, in order to obtain good kernel density, carbon particles should be dispersed to smaller than 5 μm in size, and preferably smaller than 1 μm in size. Carbon dispersions must withstand large pH variations between the initial pH of HMTA/urea solutions (pH 10–10.5), or alternately that of ADUN solutions (pH 1.9–2.0), and the final pH in the mixed broth at gelation conditions (pH 4.4–4.5). Dispersions must also withstand a large background ionic concentration from dissolved electrolytes (about 2.6–2.9 M for $UO_2^{2+}$ and about 4.4 M for $NO_3^-$ in the ADUN solution) and competition from high concentrations of HMTA and urea (about 3.18 M each in the initial solution).

The correct choice of carbon black and of dispersing conditions is critical for producing dispersions with the required properties and high stability needed for preparation of uniform uranium oxicarbide kernels. Stabilizing the dispersions through all stages of the sol–gel process requires a good match of surface properties of carbon black with the solution parameters and the nature of the dispersing agent used. This paper reports on the results of a thorough characterization of several types of carbon black, selected as possible candidates for the process. Characterization of the surface chemistry of carbon black by potentiometric titration measurements ($pK_a$ spectra) provided a comprehensive picture of pH effects on the factors influencing the dispersion stability. The results were complemented by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy. The best results were obtained by using surface-modified carbons with strongly ionized surface functions chemically grafted on their surface [6].

## 2. Background

Carbon blacks consist of nanometer-size particles which are bound together into aggregates of various shapes and structures. The aggregates, which are the characteristic units of carbon black, may cluster into larger agglomerates forming fluffy free-flowing powders, or may be bonded into beads. Under ideal dispersion conditions, the agglomerates are broken down into primary aggregates (usually of submicrometer sizes). Methods to stabilize dispersions against re-agglomeration include promotion of surface wetting of aggregates, development of electrostatic repulsions, or coating with adsorbed bulky polymer molecules.

Both physical and surface chemical properties of carbon black affect its dispersability. Carbon blacks with small particles (high surface area) are more difficult to disperse. Carbons with a compact structure of aggregates ('low-structure carbons') are more difficult to disperse than carbons with open, complex structures ('high-structure carbons'). The presence of polar chemical groups on the carbon's surface (carboxyls, phenols, lactones, and quinones) is beneficial because they improve wetting and aid in the development of electrostatic charges. All physical factors being constant, carbon blacks with higher volatile content would disperse easier. Some carbons are specially treated (oxidized) in the manufacturing process to improve water dispersability. However, not all surface groups are identical: the pH response of surface groups (or their acid–base character) is an important, but often overlooked, factor that should be considered in a discussion of carbon black dispersability.

Traditionally, dispersability is improved by using dispersing agents (surfactants). Their action is based on dynamic adsorption of the surfactant's non-polar tail segments at the hydrophobic surface of carbon black, and solvation of the hydrophilic heads oriented outwards. Surfactants with ionisable groups (weak acids or bases) develop a pH-dependent charge at the carbon–water interface; their effectiveness is strongly pH-dependent, such that anionic surfactants can only be used in basic solutions, and cationic surfactants are limited to acidic solutions. Non-ionic surfactants contain polar groups (e.g., polyethers) and their dispersing action is not pH-dependent; the drawback is that these bulky surfactant molecules must be used at high concentrations because of the lower hydrophilizing effect of non-ionic polar groups [7]. A newer alternative to the traditional dispersing methods based on dynamic surfactant adsorption is the use of surface modified carbons with suitable chemical groups grafted on their surface by strong chemical bonds. This makes possible a better tuning of surface properties through selection of grafted chemical groups, and allows better control of the surface concentration of modifiers. Because surface modifiers are chemically bonded to carbon the dispersions are more stable against variation of solution conditions (pH, ionic strength).

## 3. Materials and methods

The materials selected for this study were low surface area, high purity carbon blacks available commercially from Columbian Chemical Company (Raven 1000, Raven 1040, and Raven M) and from Cabot Corporation (Black Pearls L). Dispersion of these carbons was aided by the addition of surfactants; several types of surfactants were tested, including ionic (anionic) and non-ionic. The results were compared against several types of surface-modified carbons developed by Cabot Corporation using diazonium salts [8]. A demonstration kit of carbon black samples modified with various surface groups was obtained from Cabot Corporation. It included the unmodified carbon (sample A), an oxidized counterpart (sample B), and carbons modified with aliphatic amino groups (sample E), carboxyl groups (sample F), and sodium sulfonate functions (sample G).

The surface properties of several carbon black samples selected for this study were characterized by $N_2$ adsorption