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Nuclear Fuel Compact Matrix Material Characterization

by

Robert W. Steele II

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Nuclear Engineering Idaho State University Spring 2016

Committee Approval

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Nuclear Fuel Compact Matrix Material Characterization

Abstract: As part of an effort to produce an LEU graphitic matrix based fuel compact for re-start and operation of the TREAT reactor at Idaho National Laboratory, Idaho State University was tasked with development of a method by which compact matrix material could be characterized for non-graphitic carbon phase identity and quantity present after manufacturing. The objective of this project to develop and test a method by which the identity and quantity of non-graphitic phases in fuel compacts can be determined.

To adequately characterize the fuel compact for the presence and quantity of graphitic and non-graphitic carbon structures, the following techniques were used: scanning electron microscopy (SEM) (for initial scoping analysis, allowing for identification of areas of interest, and possibly identification of graphitic structures within the amorphous carbon sugar/resin residue), Raman spectroscopy (for partial quantification based on sensitivity to types of carbon bonding and structures) and X-ray diffraction (XRD) (for determination of "degree of graphitization"). Transmission electron microscopy (TEM) (for detection of graphite "nucleation" or the beginning of graphitic stacking) and 3-D precession diffraction tomography (for 3-D reconstruction of the sample, including respective volumes of the graphitic and non-graphitic phases) will be conducted in the near term.

The analyses were performed on multiple sectioned specimens of fuel compacts, primarily from batch 13102. Additionally, Raman and XRD were performed on one of the matrix precursor materials, the natural graphite powder.

Since the accuracy of any one method and data analysis is unclear, multiple characterization techniques that provide partially overlapping data sets were used, in hopes that a single error affecting multiple methods would be minimized. Also, the techniques selected are partially or wholly complementary, with several requiring similar or identical test configurations and sample preparation.

Semi-quantitative results were obtained using Raman spectroscopy (I_D/I_G ratio), XRD (degree of graphitization) and SEM (BSE image analysis). Each quantitative estimate yielded consistent (within about 1%) results, which demonstrated the matrix material consisted primarily of graphite (~93%). Further work to refine analysis and gather more data is required.

1 Introduction

There is currently a global effort underway to reduce the amount of highly enriched uranium that is produced and used, including that which is used in research reactors. This effort is to make proliferation by state and non-state actors more difficult. Spearheading research reactor fuel conversion work in the United States is the National Nuclear Security Administration's Office of Material Management and Minimization.

As part of an overall program to convert to low-enriched uranium fuel in the Transient Reactor Test Facility (TREAT), Idaho State University was tasked with developing a method to characterize and quantify graphitic and non-graphitic phases in a new, development fuel.

The amount of graphitic (large, identified majority) and non-graphitic (small, unidentified minority) phases within the TREAT LEU conversion fuel matrix affects several physical characteristics, as well as nuclear characteristics. Some examples include porosity, strength, heat transfer capability and the nature of neutron moderation. These characteristics must be known in order to effectively model reactor behavior and to determine the range of safe operating conditions for the TREAT reactor. Currently, the INL uses a mass balance calculation with assumptions to estimate graphite content. Another aspect of the work being performed by ISU is to validate these calculations.

A review of the technical literature suggests there is no established method for this type of analysis. Further, there is no single technique from which all required information can be determined. Literature reporting the characterization of graphite matrix material was reviewed and state-of-the-art characterization techniques were assessed. As a result, multiple complementary characterization techniques were pursued.

Although there is a great body of literature on the heat treatment effect on the primary components of the conversion fuel compact, and also on characterization techniques used to describe carbonaceous materials such as graphite and glass-like carbon, none of the reported studies addressed the objectives of this project. There is a sufficient body of knowledge and set of capabilities, however, to inform the choice of a complementary series of analyses that will produce adequate data to allow phase and quantity characterization of the non-graphitic carbonaceous content of the compacts with a fair degree of certainty, with the eventual goal of scaling back the required testing for the full scale production fuel. This project focused on one of several batches of compacts provided (batch 13102) to explore the quality of information yielded by analysis. Full scale testing will require additional sampling methodology to qualify the fuel.

Part 1 of this report provides a brief introduction to the scope of work for this project. Part 2 includes discussion of the literature reviewed in support of completion of this project. Part 3 describes the experimental methodology. Part 4 discusses the results and analysis. Part 5 summarizes and discusses future work.

2 Review of Literature

2.1 TREAT Fuel Background Information

2.1.1 TREAT Historical Background

The Transient Reactor Test Facility (TREAT) reactor was initially designed to simulate accident conditions for various test materials and fuel, including high temperature fuel/coolant interactions (1). Located on what is now known as the Idaho National Laboratory (INL) and taken critical in 1959, TREAT operated and provided valuable test data until its shutdown in 1994. Testing included 6,000 reactor startups, including 3,000 transient irradiations (2) and the ability to provide a neutron source for materials testing at power. The original TREAT reactor was an air-cooled, 120 kW (steady state) power reactor, which was capable of being operated in steady-state operations, pulse type transients, or a ramped/shaped transient (2). During a transient pulse operation, the TREAT reactor was designed such that its strongly negative temperature coefficient of reactivity would cause power to quickly turn for a rise in temperature, primarily due to the effect of Doppler broadening and reduced neutron cross-sections (2). This feature, along with a rapid insertion of the control rods, limited the total amount of heat produced during a transient, thus keeping cladding temperature with design limits (3). Figure 1 illustrates a power excursion for the TREAT reactor. A typical test would begin by increasing power with a constant period to a desired pre-heat power. The pre-heat phase allowed the conditions in the test loop to be brought to prototypic conditions. The pre-heat phase was followed by

another constant period interval and a "burst" where the transient condition was created, after which rods were rapidly inserted (3).





Figure 1 Typical Power Transient for a test in the TREAT Reactor (3)

by six-foot square, which stood eight feet high, the middle four feet of

which were the fueled region. The fuel itself was Zircaloy-3 clad fuel assemblies filled with graphite blocks (the reflector region was clad in aluminum), with each located in the fueled region dispersed with U₃O₈, comprised of highly enriched uranium (HEU) (1). Each block within the assembly was four inch by four inch, making each assembly four inch by four inch by eight feet. Figure 2 illustrates the TREAT reactor configuration.



In the 1970's, a TREAT upgrade core was developed, which would have allowed testing of full 19 x 19 fuel assemblies (1). Some notable differences in design between the original TREAT core and the upgrade core include a

Figure 2 Original TREAT reactor configuration (83)

longer fueled region (five feet versus four feet) and single Inconel 625 can cladding design (versus a three can aluminum/Zircaloy-3/aluminum design) (2). The TREAT upgrade assemblies were constructed in the 1980's, but were not installed prior to TREAT being placed in a lay-up status in 1994 (2).

In 2010, the US Department of Energy (DOE) proposed re-establishing operations at TREAT at the INL or the Annular Core Research Reactor at Sandia National Laboratory to fulfill the need to resume transient testing of reactor materials and fuels (4). The DOE later identified TREAT as the preferred option and, in February 2014, approved resumption of testing at TREAT (1). As part of the National Nuclear Security Administration's Office of Material Management and Minimization, the feasibility of converting the TREAT reactor from a HEU reactor to a Low Enriched Uranium (LEU) reactor has been explored and is now entering the testing and characterization phase (5).

The LEU conversion TREAT core will be similar in many respects to the original and upgrade cores. Some notable design differences include increased graphite content (>85% as compared to approximately 59% and 72%, for the original and upgrade TREAT cores respectively) in the fuel blocks, a different carbon to uranium ratio (approximately 1,000 to 1 for the conversion core versus 700 to 1 and 10,000 to 1 for the original and upgrade cores, respectively) and the use of a single can Zircaloy-4 cladding (2). Figure 3 illustrates the three TREAT reactor fuel assembly designs.



Figure 3 TREAT Reactor Fuel Assembly Designs (2)

This project's objective is to develop a method by which the phase identity and quantity of non-graphitic carbon in a conversion LEU TREAT fuel compact's matrix can be determined. The motivation for this project is the qualification of the conversion LEU fuel for licensing. To develop a characterization method, one must first understand fuel fabrication methods.

2.1.2 Fuel Production Process

Although several methods are currently in use internationally, or have been used historically, the basic process for manufacturing graphite matrix fuel (including TRISO fuel compacts or pebbles) remains fairly standard with the exception of some key ingredient ratios and techniques. For the purposes of this report, the fuel fabrication processes for Very High Temperature Reactor (VHTR, a graphite fuel based reactor), the original TREAT reactor fuel, the upgrade TREAT reactor fuel, and the pre-full scale production LEU conversion TREAT fuel are reviewed and summarized.

2.1.2.1 A3-3 Fuel Compact

In the case of the VHTR reactor, a 64:16:20 ratio of natural graphite, to synthetic graphite, to thermosetting resin is proposed (6). This process requires the two graphite powders to be mixed with the thermosetting resin, and reground together using a jet mill to ensure adequate mixing and distribution of the three powders. Tri-structural isotropic (TRISO) fuel particles are over-coated with the resinated powder to enhance their crush resistance during the subsequent compaction. The over-coated fuel particles are then combined with the matrix mixture and pressed together into a cylindrical compact at approximately 150 C. The "green" compact

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is then carbonized (in this case meaning removal of volatile and non-carbon species) for one hour at approximately 800 C in an inert helium atmosphere. Following the carbonization, a final heat treatment occurs at between 1800 and 2000 C at a vacuum. The purpose of this higher temperature heat treatment is to further purify and anneal the composite (7).

2.1.2.2 Original TREAT Reactor Fuel

The first reactor core built for TREAT was manufactured by Argonne National Laboratory. The initial design was to permit a sufficient thermal neutron flux



from a power excursion as to permit meltdown studies of fast reactor fuel (8). The non-uranium materials were supplied by the Great Lakes Carbon Corporation (GLC) and uranium was supplied by Argonne. The original plan was to use UO_2 in TREAT, but the behavior of UO_2 was such that it would agglomerate during the manufacturing process, thus necessitating the use of U_3O_8 (8). Figure 4 shows a flow chart for the fuel manufacturing process.

Figure 4 Flow chart for original TREAT fuel fabrication (8)

A recreation of the original TREAT fuel design consisted of coal tar pitch (22.5 wt.%), highly enriched U₃O₈ (0.8 wt.% at 93.1% enrichment), Thermax carbon black (19.2 wt.%) and S97 grade graphite flour from Airco-Speer Carbon Company (57.5 wt.%) specifically; however, the original documentation simply states that coal tar pitch resin, graphite and carbon were used (1). Each fueled region was 4 feet long and consisted of six 4 inch by 4 inch by 8-inch blocks. The components were mixed, milled, and sieved. Then, the milled components were preheated to, and held at, 100 C for 2 hours. The fuel blocks were maintained at that temperature prior to being pressed at 5000 psi. The pressed blocks were deburred, after which they were packed in graphite for baking. The baking cycle took two weeks, with a peak temperature at 950 C. It was believed that during the baking cycle the resin would "dissociate" to carbon and the U_3O_8 would reduce to UO_2 . After baking, the blocks were unloaded and brushed in preparation for inspecting and shipping (8).

The final product was tested for fuel agglomerations, for chemical composition (specifically for neutron poisons) and for density. The average density measured was 1.73 g/cc and equivalent boron concentration was about 6 ppm (8). The amount of graphite was estimated to be about 59%, with the potential for the presence of some residual hydrogen to be present (9).

2.1.2.3 Upgrade TREAT Reactor Fuel

The TREAT upgrade fuel, developed in the 70's to replace the center 11X11 assemblies out of the full 19X19 core, was similar in many ways to the original TREAT reactor fuel (1). The external geometry of each assembly was the same; however, the fueled region of each assembly expanded to five feet from four. Additionally, instead of a single 4" X 4" block, each portion contained 16 1" X 1" blocks. The three-piece cladding was also switched to a single Inconel can (1).

Although the outer appearance of the fuel assemblies was similar, the process for manufacturing the upgrade assemblies was quite different. Each block was formed by an extrusion process, rather than compaction. The extruded fuel components used were graphite flour, Thermax carbon, UO_2 (rather than U_3O_8), wood flour and Varcum resin binder (10). A graphite to carbon black ratio of 83 to 17 by weight was used, with 93% enriched UO_2 added to achieve a composition of 1.82 to 4.78% UO_2 by weight (10). The dry components (everything except the resin) were mixed to an equal distribution and Varcum resin liquid was added. The mixture was chopped, pre-extruded at 150 tons and chopped again, with more resin added during the process to reduce viscosity. Then a final extrusion was made for each block (10).

The first portion of the heat treatment process was to slowly raise the temperature of the extruded blocks to 525 K (~252 C) over a 90-hour period. The purpose of this "curing" process was to polymerize and set the resin, as well as make the rods hard enough to subsequently handle without deformation. A second heat treatment was performed by heating the blocks to 1100 K (~827 C) in a vacuum over a 116-hour period. This "baking" period was to allow the resin to finish polymerization and setting, as well as to allow the decomposition products to diffuse out of the block. A slow diffusion was preferred to prevent internal

pressure build-up and subsequent fuel failure. The wood flour added to the porosity, and aided this diffusion (10).

The final heat treatment was performed by heating the blocks to 1550 K (~1277 C) over a three-hour period with a two-hour hold. This heat treatment could be performed in either an inert atmosphere or at a vacuum. It was important not to exceed the maximum heat treatment temperature to prevent the UO_2 from reacting into carbide, which occurs at high rates above 2100 C, but can begin to take place at lower temperatures (11). After heat treatment, the blocks were machined to size and subjected to non-destructive quality testing. The net result of this process compared to the original TREAT fuel manufacturing process was a more graphitically dense fuel block, with better fuel dispersion and thermal capabilities (10). The amount of graphite present in the extruded block was believed to be 72% (versus the 59% present in the original TREAT fuel) (1).

2.1.2.4 LEU Conversion TREAT Reactor Fuel

As part of the National Nuclear Security Agency's Office of Material Management and Minimization conversion program, work to manufacture a LEU fuel to replace the current HEU fuel is being performed. Many conceptual and trade studies have since been performed to try to recreate the old methods of TREAT fuel production, as well as develop new techniques and use new materials (12) (13) (4) (5) (14). Some challenges being faced include the need for increased graphite concentration within a fuel block to provide the proper thermal performance and prevent cladding damage due to over-heating. As stated above,

one of the main purposes of this project is to determine the amount of graphite present, so that thermal and neutronics modeling can be refined.

Several fabrication processes and design specifications have been explored for the LEU Conversion fuel (2). Statement of Work for project number 31772, titled "Method Development to Determine the Graphite Matrix Phases in TREAT LEU Fuel" lists some technical and functional requirements for the final compact design. One design aspect is fuel particle size must be less than or equal to 44 microns and graphite particle size should be between 7 and 15 microns. Another technical requirement is fuel block density should be greater than or equal to 1.85 g/cc. Additionally, the overall cross section area of final fuel block shall be approximately, but not greater than 4" by 4". Also, the final fuel block shall contain a minimum of 85% graphite and simulate the carbon to uranium particle volumetric ratio that would represent a carbon to uranium atomic ratio of not less than 1000:1 where particles are well distributed and lacking significant agglomeration. These technical requirements should be accomplished with no post fabrication heat treatment. Based on meeting these requirements, a process has been developed to fabricate a pre-full scale production fuel compact for the purposes of testing.

For the TREAT conversion fuel, a resinated-graphite powder is first formed by jet milling together the following components (13):

- Asbury Carbons No. 3482 natural flake graphite 64.0 ± 0.5 wt.%
- SGL Carbon No. KRB2000 synthetic graphite 16.0 ± 0.2 wt.%

- Durite SD-1708 novolac phenolic resin 19.0 ± 0.2 wt.%
- Hexamethylenetetramine 1.0 ± 0.1 wt.%

The four matrix components were milled to an even distribution and to target a mean particle size (d_{50}) of between 7 and 15 µm (13). The resinated-graphite matrix powder was the basis for the various batches that BWXT manufactured for the Idaho National Laboratory. For each of the batches, zirconium oxide (also known as zirconia) was used as a surrogate for UO₂ to eliminate the need for radiological, criticality safety, or special nuclear material accountability controls. Initially, it was believed the resinated-graphite powder mixed with zirconia would self-granulate, creating spherical particles that would flow and compact easily; however, testing proved that the mixture would not granulate without an additional additive (15).

The first effort to promote granulation used sieved table sugar to form the nucleus of each granule. Several risks are involved with using sugar as a nucleating agent. The first is that during the thermal decomposition of sucrose, carbon dioxide is emitted, which could cause failure of the compact if present in excess. Secondly, the "char" left behind after the thermal decomposition of sucrose is glass-like carbon, resulting in a relatively lower amount of graphite per weight within the compact, potentially making the goal of 85% or greater potentially elusive. The third risk is the relative difficulty qualifying simple table sugar as an additive to nuclear fuel (15).

Following identification of the stated risks of using table sugar, the decision was made not to use sugar as the nucleation agent. Attempts were made to use plain water in two batches, but the kernels were not fully coated and the mixture did not form granules. Following the failure of those two batches, an additional decision was made to attempt the use of a sugar water solution to promote granulation. Granulation was successful with the sugar solution and two more batches were mixed, using slight variations in the mixing process. An additional batch using graphite granules and PVP as granulation aids were also mixed (15).

Following granulation, the various batches were vacuum dried for four hours to remove water. After drying, compaction was performed. Of the five batches compacted, the compact press conditions were varied in terms of temperature, ram pressure, and ram hold time (15).

When compaction was completed, the compacts were measured and subjected to the AGR Carbonization Schedule A heat treatment. The AGR heat treatment provides a gradual approach to each temperature hold, with the intent to allow

Carbonization Schedule A						
Node Temperatures ni ni+1		Ramp Rate	Hold	Step Duration	Σ Time hhmm	
20°C	-	120°C	6.0°C/min (360°C/hr)		17 min	0:17
120°C	-	1\$0°C	2.5°C/min (150°C/hr)		24 min	0:41
		1\$0°C		30 min	30 min	1:11
1\$0°C	-	220°C	1.33°C/min (\$0°C/hr)		30 min	1:41
		220°C		25 min	25 min	2:06
220°C		330°C	1.67°C/min (100°C/hr)		66 min	3:12
330°C		400°C	0.67°C/min (40°C/hr)		105 min	4:56
		400°C		15 min	15 min	5:11
400°C		560°C	1.0°C/min (60°C/hr)		160 min	7:51
		560°C		10 min	10 min	\$:01
560°C		620°C	3.0°C/min (1\$0°C/hr)		20 min	\$:21
620°C		950°C	6.0°C/min (360°C/hr)		55 min	9:16
		950°C		30 min	30 min	9:46

gases to escape from the compact without causing damage. Figure 5 illustrates carbonization schedule A, including

Figure 5 AGR Carbonization Schedule A (15)

temperatures, ramp

Department of Nuclear Engineering and Health Physics

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rates, hold times, step duration and cumulative time. The basic heating sequence includes a 30 minute hold at 180 C, a 25 minute hold at 220 C, a 15 minute hold at 400 C, a 10 minute hold at 560 C and lastly a 30 minute hold at 950 C.

The compacts formed and carbonized using the sugar solution as the nucleation agent were, with the exception of one compact, free of gross visible defects or failures. The one compact that failed was part of a lot that used a higher press pressure. Of the compacts made with granulated table sugar, the batch containing the largest amount of sugar had a 100% failure rate during the carbonization process. Another batch using less granulated sugar had fewer defects. The final product was a cylindrical compact (the production fuel will obviously be rectangular) with a mean length of 21.46 mm, a mean diameter of 12.145 mm and a mean mass of 4.455 g. Table 1 is a summary of the batches received from the INL to be included in testing for Phase I of this project (with the exception of the PVP granulated batch).

Lot/Batch	Feedstock	Notes	# of Compacts Produced	Green Mass (g, average)	Heat Treated Mass (g, average)
13105	01152014-1	Sugar solution	52	4.975	4.459
13104	01152014.1	Sugar solution	24	4.921	4.447
13103	01152014-1	Sugar solution	100	4.973	4.455
13102	10112013-2	Sugar granule	48	5.2	4.34

Table 1 Surrogate Fuel Compacts Provided to ISU for Testing

Additional compact matrix formulations are being developed and may be tested in Phase 2 (future work) of this project. One such formulation will use Asbury TC 300 graphite granulate for the nucleating agent and Polyvinylpyrrolidone (PVP) to aid in coating. TC 300 graphite is a very pure form of graphite, with a single phase (no graphitized binder), low impurities and excellent heat transfer (16). PVP is a polymer often used due to its coating enhancement and adhesive properties (17). Upon heating, PVP will thermally decompose into an amorphous carbon form (17). The proposed changes in process and materials will result in an increase in the overall percentage of graphite in the compact, because the shift is to more graphitic materials (e.g. use of a graphite seed material rather than sugar). Therefore, any characterization of the compacts made with sugar will yield a bounding (not less than) graphite percentage for the newer designs. Initial estimates based on mass balance indicate a graphite percentage of 86.6% for compacts granulated with sugar, and 88.9% for compacts granulated with PVP.

2.2 Characterization Techniques

Based on a review of technical literature regarding characterization of graphitic and non-graphitic carbon, the following analyses techniques were considered. It was known that some of the analyses would give redundant information; however, it was thought the combination of the tests would improve the overall accuracy and confidence in the results, particularly in the initial characterization phases, prior to developing a mature procedure for analysis.

2.2.1 Optical Microscopy



Figure 6 An example of the optical texture (showing anisotropic structure) of graphite and binder (20)



Figure 7 An example of the optical texture (showing isotropic structure) of graphite and binder (20)

Optical microscopy uses either reflected or transmitted non-polarized or polarized light to allow a visual indication of a material, with a potential magnification of up to 1500x

and an ability to distinguish features down to approximately 1 micrometer (18). Some sample preparation may be required such as etching, polishing, grinding, sectioning or mounting (18). Through the use of optical microscopy, the optical texture description and domain orientation may be determined (19). Figures 6 and 7 show two examples

of the optical texture of graphite composite with synthetic graphite and binder (20). The graphite example in Figure 6 was composed of elongated, needleshaped, petroleum coke particles and a binder phase. A high degree of anisotropy is visible, as well as relatively large pores (shown as the black portions of the image). The graphite example in Figure 7 shows a relatively isotropic grain configuration, and was made from similar materials. The difference in texture is primarily due to the starting size of the coke particles used, with smaller particles yielding a more isotropic texture, to where the graphite pictured in Figure 7 would be considered suitable for moderator used in a gas cooled reactor (20). The optical texture index (OTI) can be determined through the use of image analysis in conjunction with optical microscopy (19). Image analysis uses computer software to rapidly provide quantitative measurements of grain size, phase compositions and distributions using optical microscopy, scanning electron microscopy or transmission electron microscopy (21). Although the measurements and determination occur only in two dimensions, three dimensional values such as grain volume can be inferred (21).

Optical microscopy is routinely used for the characterization of materials, including graphite composites similar to the compact of interest (22) (23). The use of common software and/or polarized light will add great value to images produced by any means of microscopy, and will aid the overall characterization (24).

For this project, the use of optical microscopy was to be an initial scoping analysis. The information derived from optical microscopy would be used as a gross measure of both phase identity (e.g. graphite versus amorphous carbon) and quantity (how much of each). Additionally, optical microscopy might be used to identify any gross abnormalities or areas of interest that require further testing to characterize fully. A third potential use of optical microscopy would be the determination of the degree of homogeneity within the compact. This information would be useful in the case that a bounding assumption of homogeneity is required for an extrapolated quantity calculation.

2.2.2 Scanning Electron Microscopy (SEM)



Scanning Electron Microscopy operates by directing a beam of electrons into a sample while maintaining a vacuum on the sample. A vacuum is required to prevent electron scatter prior to reaching the



sample itself. The beam of electrons is generated from an electron gun that operates by heating a tungsten element to the point of thermionic emission (about 2500 C) (25). Three magnetic lenses (first condenser, second condenser and objective) focus the emitted electrons into a tight beam onto the sample surface. Two scan coils slightly deflect the electron beam as it is passing through the objective lens, which causes the scanning motion, and in turn allows a surface to be analyzed (25). Figure 8 illustrates the basic parts of a typical scanning electron microscope (26). Several detectors are used for capturing the image and other information. Detectors include: specimen current detector used in Electron Beam Induced Current (EBIC) measurements (used primarily for semi-conductor testing), a secondary electron detector used for image formation, an X-ray detector used for Energy Dispersive Spectroscopy (discussed below), and a backscatter electron detector used for Electron Backscatter diffraction (discussed below) and Backscatter Electron (BSE) imaging (25). Magnifications of up to 100,000x and resolutions down to 3 nanometers can be realized depending on the microscope and detector configuration (25).

SEM, in conjunction with xenon etching, has been used to determine local lamellar mesophase particle and graphitic grain orientation in a carbon-carbon composite with success (27) (22) (28) (19). Additionally, oxygen plasma etching with subsequent image analysis techniques have been used to improve the contrast between graphite and binder phases, with a resultant ability to extrapolate graphite distribution (29). Due to its enhanced resolution, SEM is an effective tool for determining the overall extent of graphitization, grain shape and size, orientation and texture of the compact (22) (30). Many SEM instruments come equipped with Energy Dispersive Spectroscopy (EDS) probes, which have the additional advantage of providing quantitative elemental detection and mapping, which will allow validation of the elemental composition of the graphite and resin. BSE allows one to image a material and view chemical compositional differences. Another feature many SEM instruments now come equipped with is an Electron Backscatter Diffraction (EBSD) probe, which enables the determination of crystal orientation and grain boundaries. Additionally, like optical microscopy, image analysis software can be used to quantitatively determine graphitic and non-graphitic phases (21) (29).

2.2.3 Dual-Beam Focused Ion Beam (DB-FIB) TomographyThe principle of operation for the FIB is very similar in many ways to SEM.Some important differences include the use of electrostatic lenses rather thanmagnetic lenses, the use of a liquid metal ion source that is a field emitter rather

than a thermionic emitter and of course, the use of gallium ions instead of electrons for its operations (31). Some high energy ions can be used to mill or remove material, whereas lower energy ions are used for image formation (32).

In its simplest form, FIB based instruments use a single beam of gallium ions to destructively section or image specimens (31). In many ways, the imaging capabilities of a single beam FIB are not as versatile as SEM, primarily due to the lack of EDS and EBSD capability. Thus a system using a single beam FIB combined with an SEM and associated detection equipment have been developed (31). With this system the specimen is successively sectioned and simultaneously imaged by SEM. The data is compiled to produce a complete three-dimensional tomographical image of the specimen (33). Figure 9 illustrates nano-tomography using a DB-FIB.



Figure 9 DB-FIB Tomography (33)

Although a single-beam FIB (SB-FIB) has been used successfully for milling, etching, imaging and 3-D reconstruction (also called tomography), there are many advantages to using a DB-FIB, including the ability to section a

including the ability to section a sample while performing imaging

(31). Recent FIB tomography efforts using a DB-FIB have allowed determination of microstructure, chemical composition, and crystallographic information in 3 dimensions, and through the use of software, creation of a fully 3-D

representation of the sample (32). Figure 10 illustrates an example of DB-FIB 3-D reconstruction (33).

This feature can be very beneficial for quantifying the amount of each constituent of the compact, as well as the agglomeration of each phase and has been used successfully to differentiate between various phases (32). One such study used



DB-FIB tomography to differentiate between an active material (LiCoO₂), a carbon-based binder and pores in the material, and quantify the amount of each phase (34).

Applied to the characterization of the TREAT LEU conversion compacts, DB-FIB can be a

Figure 10 Example of a 3-D reconstruction using a DB-FIB (33)

powerful tool if sufficient contrast can be created between graphitic and nongraphitic phases, such as "labeling" the graphite with a small amount of a heavy metal on its surface prior to compact production. Complemented by other analysis techniques, DB-FIB can be used to determine the volume of a particular phase within the specimen (35). If the assumption of homogeneity within a sample is validated by optical microscopy and SEM, relative volumes within a small sample can be extrapolated to the entire compact. If not, multiple samples and sample averaging may be required to accurately interpret the data. Note: this method cannot be easily used for production process.

2.2.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) operates on a basis similar to SEM and often uses the same analytical electron microscope (36). The theory of operation begins the same as SEM; however, for TEM a thin specimen is used, through which electrons are transmitted. Electrons are emitted from a thermionic source, are focused by two condenser lenses and an objective lens, and then are transmitted through a sample. As the electrons pass through the specimen, some are deflected or absorbed by the material. The electrons that pass through without interacting with the specimen are magnified through one or more lenses. The resultant transmitted electrons are used to form a visible image (36). Magnification up to 450,000x and resolution of crystalline structures as small as 30 nanometers are possible. One potential limitation of TEM analysis is the relative difficulty of sample preparation, because a sample must be thin enough to allow electrons to pass through without interacting (36).

TEM is a standard analysis performed when attempting to characterize carbonaceous, graphitic and carbon-carbon composite materials (19) (27) (37) (23) (38). The open source programming language, Python, has been used successfully in conjunction with TEM through programs such as NumPy and SciPy to aid in rapid image analysis and characterization of carbon matrix materials (23). By analyzing and interpreting the textual arrangement of the various graphene layers in a material, the anisotropy can be determined (23).

TEM is also used to determine the texture of carbon cokes and the extent of graphitization via analysis of optical texture and basal plane growth (19).

TEM performed on glass-like carbon has revealed both the development and growth of graphite-like microcrystals, and in some cases fullerene-like structures in the form of polyhedral graphite crystals have been identified (39). TEM (both bright field and dark field) cannot give much structural information for a truly amorphous carbon, but it can readily detect the "nucleation" and growth of nanocrystals (graphite or otherwise) (40).

TEM will be a key aspect in the phase identity portion of this project. By confirming or eliminating the possible formation of small amounts of graphite within the otherwise amorphous carbon resin and additive residue, a more accurate accounting of the quantity of each phase based on other analyses can be performed.

2.2.5 Precession Electron Diffraction

Precession Electron Diffraction (PED) uses very similar hardware to SEM or TEM analysis. With PED, the electron beam is precessed at an angle around the optical axis. This techniques allows a series of TEM-type images to be taken about the center axis, without the increased labor associated with sample mounting and preparation, and all the errors potentially introduced in the analysis associated with moving the sample (41). Figure 11 illustrates a simple schematic of demonstrating the theory of operation for PED.



One use of PED is Automated Diffraction Tomography (ADT), which will take a series of diffraction samples at different precession angles. The diffraction samples are then used to systematically determine the lattice structure of a material. PED-ADT has been used to determine the lattice structure of materials that are often difficult to characterize using XRD or traditional TEM such as

organic crystals (41).

Figure 11 Precession Electron Diffraction (41)

Other potential applications of PED to this project currently in use include using software to combine XRD data with data derived from PED to enhance crystal reconstruction, image bright field tomography, and TEM phase orientation imaging, which is similar to EBSD imaging, except it can be performed more rapidly and at nano-scales (42).

2.2.6 Raman Spectroscopy

Raman spectroscopy is one of several material characterization analyses that use light-scattering phenomena. In Raman spectroscopy a monochromatic beam is focused upon a material and is absorbed by the molecules that make up the material. Each molecule that absorbs a photon from the monochromatic beam either gains a vibrational or rotational quantum of energy (Stokes scattering) and emits a more energetic photon, loses a vibrational or rotational quantum of energy (Anti-Stokes scattering) and emits a less energetic photon, or the energy of the scattered photon is approximately equal to the incident photon (Rayleigh scattering) (43). Often two or three different monochrome beams are used,

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allowing multiple dispersion stages. The scattered photons are collected and analyzed (typically the Stokes scattered photons) and, based on computer programs or curve fitting, a material can be identified (43). The difference in wavelengths between an incident photon and the scattered photon is referred to as the Raman shift.

Raman spectroscopy has been used extensively in the characterization of carbon based polymers and graphite, primarily due to the changes in vibrational behaviors observed for various types of graphite and carbon bonding (43) (44) (22) (37). The resultant Raman spectra emitted are typically very sensitive to the type and quantity of carbon bonding within a sample. Laser Raman Microprobe Spectroscopy (LRMS) can be used on the micrometer scale, thus potentially aiding the effort to characterize the carbonized resin in the subject fuel compact (22).

Analysis of A3-3 matrix graphite via LRMS revealed three distinct structures representing different graphitic and non-graphitic phases, all of which could be identified by their unique Raman shift (38). The primary shift due to the presence of pure graphite occurs at about 1580 cm⁻¹, with other bands or spikes dependent upon structural and non-graphitic defects, such as a peak at about 1500 cm⁻¹ for amorphous sp² carbon-bonded material (38) (37).

Various Raman analysis studies have been performed on natural and synthetic graphites, and heat treated resin as well as non-heat treated resin. A summary of the results of the analysis is provided in Table 2.

Carbon Type	Primary Peak	Secondary Peak(s)				
	(cm ⁻¹)	(cm ⁻¹)				
Single crystal	1575	None				
graphite						
Diamond	1332	None				
Nuclear grade	1575	1355				
graphite						
Glass-like carbon	1350	1580				

 Table 2 Measured Raman Shifts for Carbon Phases (22) (40) (44)

Other forms of amorphous carbon may exhibit Raman shift peaking , usually between 1500-1630 cm⁻¹; however, the relative intensity of the peaks are small and the spectra have a sloping, disordered appearance as illustrated in Figure 12 (40). In graphite, the order-induced Raman shift peak is referred to as the 'G' peak, and the disorder-induced peak is referred to as the 'D' peak (22). In this case the terms "order" and "disorder" refer to the amount of crystalline defects within a material. For example, the Raman shift curve for single crystal graphite depicted below, has one peak (the 'G' or order-induced peak). The Raman shift curve for commercial-grade graphite has both a distinct 'G' peak and a 'D' peak, representing a material which has some amount of disorder within its crystalline structure.





Figure 12 Examples of Raman Spectra for Various Carbonaceous Materials

Quantification of various phases within a material can be challenging, but methods for doing so have been developed (45). A general way that single phases within a mixture have been quantified is through the use of statistical analysis (such as least squares regression) of the Raman spectra of the mixture relative to the Raman spectra of some standard (45). In one study that uses this technique, the concentration of a single xylene isomer was easily determined within 0.15% (45). For carbonaceous materials such as graphite, the ratio of the peak present at

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the D-band and the G-band can provide information such as the material structural disorder and phase of the material (46). Through the use of secondary band ratios, the relative volume of 2-dimensional and 3-dimensional carbon phases in a sample can also be determined (47).

Although Raman spectroscopy can be used to identify carbonaceous phases, for this project it has been primarily used for quantification. The heat treated graphite and resin materials were analyzed separately to develop baselines to which the fuel compact analysis results can be compared. A precise method for interpolating the results (using one of a number of different mathematical processes), must be used/developed to interpret the data.

2.2.7 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is used to better understand the crystalline structure of a material, including but not limited to, the quantitative determination of phases in a multi-phase material, unknown phase identification, and crystal orientation (48). X-ray Powder Diffraction (XRPD) is the same technique applied to a powdered material, thus aiding in elimination of "preferred" phase orientation that can be a problem with samples comprised of large crystals (49). The basic theory of operation for XRD is that a crystalline material is bombarded by X-rays, and the subsequent X-rays diffracted from the material planes are detected, and the degree of diffraction is analyzed to determine the geometry of a unit cell (50).

XRD and XRPD have been used extensively for the characterization of graphite, carbonaceous materials and carbon-carbon composites (19) (37) (51) (52) (53)

(54). XRD has been used to determine the degree to which a carbonaceous material has graphitized, including the effect of Heat Treatment Temperature (HTT) on graphitization (19). Additionally, physical characteristics such as graphene layer spacing, the degree of distortion for turbostratic carbon, degree of basal (in-plane) plane growth, and orientation of planes within a crystallite can be determined using XRD (52). The data derived from performing XRD may aid in the characterization of the two main graphitic grain types (natural and synthetic) due its ability to distinguish between 3R and 2R structures and could also potentially provide additional insight into the structure and characteristics of the carbonized thermosetting resin (22).

Studies have shown that the XRD diffraction patterns for glass-like carbon exhibit a more graphite-like pattern as the final heat treatment temperature rises (55) (56). Similar data have shown that interlayer spacing tends to decrease for heat treated phenolic resins as the coherent domain (the area of a micro-crystal within a material) increases for higher treatment temperatures (57) (58). XRD can be used to determine the change in crystal size (via layer spacing d_{002}) and coherent domain, layer distortions, and the structure of nano-crystal graphite stacks (59). Analysis of XRD derived data can allow the calculation of the degree of graphitization (59) (19).

Table 3 provides a summary of values for interlayer spacing, as well as coherent lengths (a one-dimensional measurement of a microcrystal within a material, where L_a is basal length and L_c is thickness) for various carbonaceous materials (54) (19) (55). Interlayer spacings of around 3.36 to 3.37 indicate a fully

graphitized sample, whereas spacings between 3.37 to 3.40 are considered partially graphitized. Spacings greater than 3.40 indicate a non-graphitizable carbon (19).

 Table 3 Interlayer Spacing and Coherent Lengths for Selected Carbon Based Materials (19)

Material	D ₀₀₂ Spacing	Coherent lengths L_a and L_c
Pure Graphite	3.354	
Composite Graphite	3.361	233, 317.3
Glass-like Carbon (HTT	3.660	Not given, 14.3
Resin)		

For this project, XRD acted as a complement to the other analyses. XRD gave important, but not fully quantifiable evidence to suggest the presence and quantity of graphitic and non-graphitic carbonaceous phases. It will help to provide corroboration and add certainty to data derived from analyses such as Raman spectroscopy and SEM (image analysis).

2.2.8 High Energy X-ray Diffraction

Much like XRD, High Energy XRD uses the reflection of X-rays off of a material to gain characterization information. As the name would suggest, High Energy XRD uses higher energy X-rays, with correspondingly shorter wavelength, to get a more refined data set, particularly for low atomic mass materials, such as carbon (60). The main drawback is the specialized equipment required for the analysis. Typically a synchrotron, or other high energy source is required to generate high enough energy X-rays.

2.3 Phases Expected in Fabricated Compact

2.3.1 Carbon

Carbon is a versatile element in many compounds and present in several allotropes. The most common forms of carbon are diamonds, graphite fullerenes, nanotubes and amorphous carbon, but it can also be found as diamond-like carbon, glass-like carbon and carbon fibers (61).



Figure 13 Carbon Electron Orbital Hybridization (19)

Many of the differences in structures and compounds that can be formed by carbon are due to electron orbital hybridization. A carbon atom can bond by sp^3 , sp^2 , or sp electron orbitals resulting in tetragonal, planar, or linear geometries, respectively (61), as

depicted in Figure 13. Carbon in the form of pure diamond contains solely sp³ bonds, whereas pure, single crystal graphite is comprised solely of sp^2 bonds. Certain polymers are bonded linearly using sp bonds.

A six-carbon ring is also referred to as an "aromatic" ring and forms the basis for many carbon-based structures including graphite (19). Many forms of carbon are defective or derived forms of graphite, also known as paracrystalline structural forms (19). Some examples include glass-like carbon, cokes, carbon blacks and pyrocarbons (19). Turbostratic carbon describes the long-range disorder of groups and layers of graphite material, having a random orientation relative to each other (19). In Figure 14, various parameters used to describe turbostratic carbon are illustrated, including: L₁ (the defect-free length), L₂ (the real layer size), L_a and L_c (the coherent lengths within a stack), and N (the number of layers within a stack). Figure 15 illustrates the difference between turbostratic layers and pure graphite.



Figure 15 Turbostratic Stacks of Carbon Layers (19)

Amorphous carbon is a disordered form of carbon that is comprised of both sp² and sp³ bonds. The proportion of sp² to sp³ bonds affects the physical properties and







appearance of the material, ranging from amorphous carbon high in sp³ bonding (diamond-like) to more sp²

Figure 14 Turbostratic Structure versus Graphite Structure (58)

34 | P a g e Department of Nuclear Engineering and Health Physics bonds (glass-like carbon) (61). Often a material is not truly amorphous, but rather is a paracrystalline material, as previously described, consisting of disordered stacks of defective graphite material that as a whole are referred to as amorphous due to the long range disorder (19).

Various forms of amorphous carbon films and structures have been identified, such as a-C (soft amorphous carbon formed at low temperatures), a-C:H (soft carbon with hydrogen), ta-C (amorphous carbon with tetrahedral sp³ bonding), ta-C:H (amorphous carbon with tetrahedral sp³ bonding and hydrogen), glass-like carbon (disordered carbon comprised of entangled graphite ribbons) and polymeric a-C:H (polymer sp bonded carbon with hydrogen), as well as others (40) (62).

As discussed above, TEM is used extensively in carbon and graphite phase identification. Using TEM imagery, four distinct stages of graphitization can be identified (19). Each stage describes a process of increasing order. The four stages from least ordered to most ordered are the green-coke stage, the columnar stage, the coalescence stage and the graphitization stage (19).

2.3.1.1 Green-Coke Stage

The green-coke stage is the stage that a carbonaceous material acquires when a solid carbonized product is formed during heat treatment. The product contains small coherent domains consisting of 2 to 3 aromatic graphene layers. This stage is important because many physical features of the solid product are fixed during this stage, including density, porosity and the structure allowing full

graphitization. One can see at this stage, that graphitizable materials have a larger domain, whereas non-graphitizable carbons will have relatively small domains (19). The green-coke stage lasts until a temperature of 800 C is reached during heat treatment.

2.3.1.2 Columnar Stage

The columnar stage of graphitization occurs in the temperature range from 800 C to 1500 C (19). Carbonaceous material in this stage tends toward more aromatic graphene layers than the green-coke stage (about 10 versus 2 to 3). Adjacent layers tend to be more or less parallel, and at this heat treatment temperature range, large interlayer defects begin to anneal. Based on the heat treatment temperature for the TREAT LEU conversion fuel, graphitization of the resin or additives is not expected beyond this stage.

2.3.1.3 Coalescence Stage

From 1500 C to 2000 C, the various graphene layers within the carbonaceous material will begin to coalesce. The number of layers within a stack increases and many defects are locked into place until higher heat treatment temperature. The overall structure becomes linked disordered layers (19).

2.3.1.4 Graphitization Stage

At temperatures above 2000 C, the coherent domains of the disordered layers and stacks increase at an exponential rate. True graphitization and the annealing of defects takes place at temperatures in the approximate range of 2800 to 3200 C (19). The graphites used to create the TREAT LEU conversion fuel matrix

material have been purified at similar high temperatures. It should be noted that some carbonaceous materials are considered non-graphitizable even at these higher temperatures. The resin and other additives used in the compacts fall into this category.

2.3.2 Graphite



Figure 16 Flow Chart for Synthetic Graphite Manufacturing Process (7) Typical graphitic matrices for particle fuel are manufactured using natural graphite and synthetic graphite, as well as a binding agent. Although both are fully graphitized, the natural and synthetic graphites differ in microstructure. Typically, natural graphite has larger flake-like grains and

synthetic graphite has fine, needle-like grains (22).

Natural graphite is produced when carbonaceous minerals are heated geothermically, whereas synthetic graphite production is a multi-step process typically starting with a petroleum coke product and highly graphitizing binder (7). In the case of the synthetic graphite, steps are taken to ensure that a highly graphitic, pure product is produced, often by employing multiple baking, milling

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and purification stages (7). Figure 16 shows a basic flow chart for the synthetic graphite manufacturing process. Both natural and synthetic graphites are selected for use based on physical, chemical and nuclear properties.

As previously stated, during fuel compact construction, the graphite is milled, resin is added and fuel particles are added to the mixture before compaction. The compacted product is heat treated. During the heat treatment process, some structural instabilities present in non-heat treated graphite are removed. For example, graphite layers that form a rhombohedral structure in an ABCABC pattern (also known as the 3R structure) convert to a more pure and stable ABABAB pattern (also known as the 2H structure) as evidenced by a change in XRD results (22). Figure 17 depicts 3R and 2H graphite structures.



Figure 17 2H and 3R Graphite Crystalline Structure (7)

characterized in this project is manufactured by Asbury Carbon (No. 3482, natural flake carbon) (13). The weight percentage of the No. 3482 natural graphite in the resinated mixture described below is 64.0 ± 0.5 wt. % (13). The lot provided had a carbon content of 99.8% of total weight (63). Previous analysis by Oak Ridge National Laboratory indicated this graphite had a low total level of specified impurities (~ 79.3 ppm), but a relatively high concentration of Al and Fe (29 and 38 ppm, respectively) (30). Additionally, of the seven natural graphites tested by

Oak Ridge National Laboratory for suitability of use in a fuel compact, Asbury Carbon No. 3482 was the densest (30).

The synthetic graphite used in the fuel compact to be characterized is manufactured by SGL Carbon (KRB2000 synthetic graphite) (13). SGL Carbon KRB 2000 has been used successfully in manufacturing of Advanced Gas Cooled Reactor (AGR) Experiments 1 and 2 fuel compacts. Of the twelve synthetic graphites tested by Oak Ridge National Laboratory for use in the AGR test fuel compacts, KRB2000 had the highest density and the lowest levels of specified



impurities (4.53 ppm) as tested by GDMS (30).

2.3.3 Thermosetting Resin Historically, resin used as the binding agent for graphitic matrix material has been primarily linked phenols with minor amounts of formaldehyde and other additives (30). Phenolic resins can be further subdivided into novolac and resole resins. Novolac



phenol to formaldehyde molar ratio than resole phenolic resin (7). Figure 18 illustrates the reaction scheme for the formation of novolac phenol resin.

Phenolic resin is considered to be non-graphitizable in bulk even up to high temperatures (3000 C), primarily due to the highly crosslinked nature of the polymer (27). Its highly linked nature ensures that it remains solid during the heat treatment process, which means unlike some petroleum products that form a mesophase on heating (7). Figure 19 illustrates a crosslinked novolac phenol resin.





The thermal decomposition characteristics of phenol resins have been extensively studied, not only for their use in the nuclear industry, but also for the many uses of phenolic resin in aerospace applications such as an ablative (controlled disintegration) composite

for atmosphere re-entry vehicle heat shields (64). It was found that at lower temperatures, the resin would thermally decompose, releasing water, free gaseous phenol, and xylenol, and at higher temperatures would release benzene, toluene, methane, carbon dioxide, carbon monoxide, and hydrogen gas. In one study, after heat treatment to 850 C, the remaining char contained 92.6% carbon, 0.9% hydrogen and 6.5% oxygen, with significant amounts of hydrogen gas and carbon monoxide released (64). The structural result of heat treatment is a highly linked, three dimensional, non-graphitic carbonaceous structure.

As demonstrated in Figure 20 phenolic aromatic rings are linked through





The para

position is considered twice as reactive as the ortho position; however, because there are two possible ortho positions, the number of phenolic aromatic rings linked in each position is approximately equal (65). Phenol rings that carry one methylene bridge are considered "attached", those that carry two bridges are considered "bridging" and phenols that carry methylene bridges in all three possible locations are referred to as "cross linking" (66). Common resins have 10 to 20 phenol rings linked in this manner in the raw product.

In novolac resins, a catalyst is needed to promote "setting" by forming additional cross links. Industry often uses hexamethylenetetramine ($C_6H_{12}N_4$), also known as hexa, hexamine, or HMTA (65), which is illustrated in Figure 21. The HMTA degrades at temperatures consistent with resin curing, directly supplying formaldehyde directly to fully link all the available phenolic rings, without creating excess free formaldehyde (65). The heat treated HMTA will thermally



Figure 21 Hexamethylenetetramine (HMTA) (84)

decompose in a manner not inconsistent with the resin itself, through the release of hydrogen gas, carbon dioxide and carbon monoxide (64).

The resinated graphite matrix material used for the compacts to be characterized is comprised of 19.0 ± 0.2 wt. % of Durite D_SD-1708 novolac

phenolic resin (13). It has been determined that this resin has a char yield (meaning material left after carbonization to 950 C in this case) of 41% (30).

2.3.4 Expected Matrix Characteristics

Based on the review of relevant literature, including manufacturer specifications, the following characteristics of the raw materials or finished fuel compact matrix material were expected:

- For the graphites and binding agents selected, few impurities were expected within the compacts.
- Due to the relatively low final heat treatment temperature (950 C) for the fuel compact, little to no large-scale graphitization was expected;

however, through the use of TEM, stacks of about 10 graphene layers may be observable (about 1 nm).

• Little to no mass loss from the graphite powder precursor material during heat treatment, therefore most of the mass lost during carbonization should be in the form of volatile gas released in the thermal decomposition of other components, such as the HMTA, resin and PVP.

In summary, due to the relatively low heat treatment temperature for the compacts and the materials used, little to no additional graphitization mass expected. With no additional graphitization within the resin, hardener (HMTA), or nucleation agent (sugar, sugar solution or PVP), the mass percentage graphite in the compact after heat treatment can be conservatively estimated by calculating the mass percentage graphite in the mixture of precursor materials. Such an estimate would provide the lower limit or bounding value for graphite content.

Of the batches provided, batch 13102 was likely to contain the lowest percent by mass of graphite (estimated to be 86.6% by mass balance). This is due to the amount of granulated sugar added during the fuel manufacturing process, which thermally decomposes into amorphous carbon during heat treatment. The batches that used a lesser amount of dissolved sugar should contain a higher amount of graphite by weight, with the proposed PVP/graphite granule compacts having the highest amount (estimated to be 88.9%). Ideally, to maximize graphitic content, any additive used during the granulation process will either be graphite or easily graphitizable.

Due to the lack of information about the feedstock and batch mixing process, performing a mass balance calculation to determine a bounding graphite percentage (assuming no additional graphitization) is difficult to perform at this point. However, for full scale production, the specific amount of each additive used within a compact can be identified, tracked and certified. This certified amount can then be used as a bounding estimate for a given compact. This method would need to be qualified with empirical evidence and testing.

3 Characterization Methods

3.1 SEM

As previously stated, SEM was used for overall visual characterization, such as identification of areas of interests and irregularities within the matrix material. Additionally, for any SEM analysis performed where a difference in the resin residue and graphite can be discerned, image analysis can be applies to perform a rough characterization.

SEM was performed using both ISU's in-house capabilities and those at the Center for Advanced Energy Studies (CAES). Various sample preparation techniques were used to improve the contrast between the graphitic and carbonized resin phases, such as sample polishing. Specific detection methods for SEM used are as follows:

3.1.1 Secondary Electron

Standard secondary electron SEM was performed at both ISU and CAES. At ISU, a LEO 1430 with Oxford EDS instrument was used for both secondary electron and EDS analyses. At CAES, a JEOL JSM-6610LV SEM, with EDAX TEAM EDS was used.

Secondary electron analysis was primarily used for bulk optical characterization of the matrix material. Analysis was performed on a sectioned compact from batch 13102.

3.1.2 EDS

EDS was performed at ISU using the LEO 1430 with Oxford EDS instrument described above. Likewise, the analysis performed at CAES used the JEOL JSM-6610LV SEM, with EDAX TEAM EDS as described above.

EDS was used to determine what, if any, impurities were present within the compact, and also to determine if potential slight elemental differences between the graphitic and non-graphitic phase can be analyzed to visually distinguish between phases. Again, analyses were performed on a compact from batch 13102.

3.1.3 BSE

The analysis performed at CAES used the JEOL JSM-6610LV SEM, with EDAX TEAM EDS.

BSE was performed to determine the crystalline structure of the material, the idea being that a distinction between crystal structure of the graphitic and nongraphitic phases can be made. If such a distinction could be made, image analysis would be applied to determine approximate quantity, if possible.

3.2 XRD

XRD analysis was performed at the Molecular Analysis Facility (MAF) at the University of Washington, as well as Idaho State University. The analysis at MAF was performed on a sectioned piece of a compact from batch 13102. Analysis at ISU was performed on a compact from batch 13102, as well as raw (i.e. unheated) natural graphite from Asbury (Type 3482), such as that used in all of the compacts provided to ISU.

The XRD testing at MAF was performed in October 2015. A Bruker D8 Discover with GADDS 2-D XRD System Diffractometer was used for this analysis. The Bruker D8 features a Cu (with a wavelength of 1.54056 nm) anode X-ray source and a large area 2-D detector, which allows the detection of strain and orientation within a sample to be detected, something traditional diffractometers cannot do (67).

XRD was also performed at ISU using a Bruker Model D8 Discover diffractometer. Specific XRD analysis was performed on non-heat treated Asbury natural graphite, such as that used in the compact manufacturing process.

XRD was performed to learn more about the overall crystalline structure of the matrix material, determine key characterization measurements such as interlayer spacing, and estimate graphite content based on the measurements.

3.3 Raman Spectroscopy

Raman spectroscopy was performed by the MAF at UW and by ISU. The analyses performed at MAF were on portions of a batch 13102 compact. The analyses performed at ISU include a batch 13102 compact, non-heat treated natural graphite (Asbury 3482) and non-heat treated, non-compacted, granulated matrix material.

A Renishaw InVia Raman Microscope using a 514 nm laser was used to sample four points on one compact using a 60 second integration time. Raman analysis at ISU was performed using a Horiba Jobin Yvon, Olympus bx41 Raman spectrometer. Data was collected from a batch 13102 compact, non-heat treated natural graphite (Asbury 3482) and non-heat treated, non-compacted graphite/resin matrix material.

Raman spectroscopy was performed primarily as a quantification tool based on the magnitude of key, graphite characteristic, intensity peaks.

4 Results/Findings

4.1 SEM

Overall most objectives were met in regards to information yielded from SEM. One notable exception is that small elemental differences between the graphite and the resin residue were not sufficient to distinguish between phases using EDS. Specific SEM results follow:

4.1.1 Secondary Electron

For images taken at both ISU and CAES, an attempt to distinguish between graphite and non-graphitic phases within the compact was made, however, no clear distinction was seen. Progressive sample polishing failed to improve image contrast. Figures 22 and 23 are images taken using SEM at ISU with a sample prepared with very little polishing. All SEM analyses were performed on a compact from batch 13102. Figure 24 is an optical image of a sample after polishing prior to SEM analysis at CAES. Figures 25 and 26 are SEM images taken of polished samples at CAES.



Figure 22 SEM Image (Secondary Electron) of a batch 13102 compact taken at ISU (1,730X Magnification)



Figure 23 SEM Image (Secondary Electron) of a 13102 batch compact taken at ISU (2,140X Magnification)



Figure 24 Optical Image of a batch 13102 compact sample after polishing (2,500 grit)



Figure 25 SEM image (Secondary Electron) of a polished batch 13102 compact taken at CAES (500X Magnification)



Figure 26 SEM image (Secondary Electron) of a polished batch 13102 compact taken at CAES (2,000X Magnification)

Many of the images above have indications of a granular component, which safely can be surmised to be the ingredient graphites. One cannot see a clear distinction between the heat-treated resin and additive materials and the graphite; therefore, without employing sample preparation techniques such as plasma oxygen etching (29), xenon etching or heavy metal plating of one or more compact ingredient, SEM is not effective contrasting graphitic and non-graphitic phases with the subject compacts. The zirconium oxide component of the compact is clearly visible as bright white spots in Figures 25 and 26.

4.1.2 EDS

The compacts were determined to be highly carbonaceous, as expected. Visual contrast between phases was not seen in the images, however, EDS did show the zirconia fuel surrogate to be irregularly sized and shaped. Table 4 lists the relative elemental concentrations as determined at ISU. Figures 27, 28 and 29 are EDS based images (captured at CAES) that demonstrate both the zirconia irregularities and the lack of phase contrast.

	С	0	Na	Si	K	Ca	Fe	Br	Zr	Total
Spectrum 1	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 2	99.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	100
Spectrum 3	97.97	0.00	0.00	0.00	0.00	0.21	0.00	0.00	1.82	100
Spectrum 4	97.02	2.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 5	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 6	93.84	6.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 7	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 8	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Spectrum 9	73.65	22.72	0.29	2.45	0.26	0.08	0.17	0.38	0.00	100
Spectrum 10	98.62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.38	100
Spectrum 11	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
Average	96.44	2.90	0.03	0.22	0.02	0.03	0.02	0.03	0.31	

Table 4 EDS results from ISU showing relative elemental concentrations as measured from a batch 13102 compact

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As shown in Table 4, most EDS measurements yielded a relative elemental concentration comprised entirely or mostly (>97%) of carbon. Spectrum 6 (with a carbon concentration of 93.84%) and spectrum 9 (73.65%) were notable exceptions. It was expected that oxygen and zirconium would be present within the compact and they were identified. Additional trace elements included sodium (Na), silicon (Si), potassium (K), calcium (Ca), iron (Fe) and bromine (Br). Based upon the variation observed (most likely due to localized non-homogeneities), a more extensive and randomized method of sampling would be needed to achieve a high statistical confidence in the quantities of elements present.



Figure 27 CAES EDS image of a batch 13102 compact (100X Magnification)



Figure 28 CAES EDS image of a batch 13102 compact (500X Magnification)



Figure 29 CAES EDS image of a batch 13102 compact (1000X Magnification)

Figures 27, 28 and 29 show a background of carbonaceous material, contrasted by zirconia, which appears white. The heat-treated graphite/resin matrix appears to contain small pores, typically only a few micrometers in diameter. The zirconia appears well distributed, with no significant agglomeration. As noted above, the zirconia present does not have a uniform shape or size. Most zirconia particles observed are significantly non-spherical and vary in size from only a few micrometers to greater than 20 micrometers or more in diameter.

4.1.3 BSE

BSE analysis was performed at CASES as an additional attempt to improve contrast between graphitic and non-graphitic phases using SEM. Although there is some indication of crystalline structure variations within the images captured using BSE, a clear contrast was not apparent. Figures 30, 31 and 32 are the BSE images captured at CAES.



Figure 30 CAES BSE image of a batch 13102 compact (100X Magnification)



Figure 31 CAES BSE image of a batch 13102 compact (500X Magnification)



Figure 32 CAES BSE image of a batch 13102 compact (1000X Magnification)

Zirconia appears as a bright white component in images in Figures 30 to 32. The matrix itself is comprised of composite of light and darker grays. Based on the known quantities of the matrix precursor materials and the faint indication of layering in the structure, it would appear the light grey material is comprised of the graphitic component of the matrix and the darker gray is comprised of the non-graphitic resin residue phase.

Based on the assumptions that the lighter colored material represents graphite and the darker gray represents the non-graphitic binder phase, a program such as MatlabTM, (specifically the image segmentation and analysis toolboxes), can be used to process the image and determine the relative quantities of each visual "phase". The image shown in Figure 31 was analyzed in this manner. A filter was applied to select the zirconia in the image, as well as other artifacts (e.g. overlayed settings information, etc). Figure 33 shows the image resulting from this analysis.



Figure 33 CAES EBSD Image with Zirconia and Artifacts Selected (1000X Magnification)

The green areas highlighted in the image in Figure 33 represent the lightest (in greyscale) portions of the image, which can be associated with the zirconia and image artifacts. Matlab[™] refers to this process as masking, where areas of an image lighter than a given pixel threshold value are "masked".

Figure 34 is the result of converting the "masked" image seen in Figure 33 into a binary image (also performed with MatlabTM, threshold set at ~170).



Figure 34 Binary Image of Zirconia and Artifacts

The area by pixel for the zirconia and artifacts was calculated (calculated using the "sum" function, which is used to find the number of white pixels) and divided by the total area of the image (found using the "numel" function, which counts all pixels), yielding 7.38%. Next, a new "mask" was created to encompass the graphitic phase, as well as the zirconia. Figure 35 shows the image with the overlay (threshold set at ~105).


Figure 35 EBSD Image with Overlay over Graphite, Zirconia and Artifacts

Figure 35 was then converted into a binary image as shown in Figure 36.



Figure 36 Binary Image of Graphite, Zirconia and Artifacts

The resultant calculated area including graphite, zirconia and artifacts makes up 98.37% of the total image area. When the zirconia and artifacts are subtracted, it can be said 92.5% of the imaged area is comprised of graphite.

This simple form of image analysis does have potential weaknesses such as using a non-representative image, using an incorrect threshold (the level of contrast used by the software to determine phase difference) or misidentifying phases. Most of these weaknesses can be effectively mitigated through the use of trained personnel, more advanced software and using a statistically representative sample size.

4.2 XRD

As stated previously, XRD was performed at the MAF, as well as by ISU. Specific results follow:

4.2.1 MAF Analyses

XRD was performed by the MAF on a batch 13102 compact. Figure 37 is a plot

of the results of the analysis.



Figure 37 XRD performed at MAF on a batch 13102 compact

It can easily be seen the largest diffraction peak is at approximately 26.5 degrees 2Θ , which correlates to the 002 plane, the plane representing the "B" layers of the ABAB pattern. Additionally, peaks representing the 101 and 004 planes are also visible (at ~44.5 and ~54.5 degrees, respectively) (68). Bragg's law can then be used to calculate interplanar distances using a relationship between the incident X-ray's wavelength, the interplanar distance and the sine of the incident angle (69). Equation 1 and Figure 38 illustrate Bragg's law, as well illustrating a physical interpretation of Bragg's law.

$$\lambda \cdot n = 2 \cdot d_{hkl} \cdot \sin \theta$$
 [1]



Figure 38 X-ray diffraction physical representation (70)

When Bragg's law is applied to the XRD results from MAF (e.g. using a measured 002 peak at 26.504 degrees), a d_{002} interplanar distance of 0.3360 nm is given. Further, a semi-quantitative measure of the degree of graphitization of the sample is given by equation 2 (73).

$$g(\%) = \frac{0.3440 - d_{(002)}}{0.3440 - 0.3354} \times 100$$
 [2]

The value of 0.3440 nm in equation 2 represents the interplanar distance found in a disordered or amorphous carbon substance, whereas the value of 0.3354 nm represents the interplanar distance in ideal graphite. The degree of graphitization

calculated by the above equation relates to the degree a material represents a purely graphitic material, versus one comprised of turbostratic carbon (71). Applying Equation 2 to the data captured by MAF, the degree of graphitization for the compact sample is 93.02%.

4.2.2 ISU Analysis

This analysis yielded results similar to those from the heat treated compact, with the 002 plane reflection at approximately 26.5 degrees, thus indicating a pure, highly graphitized material.

4.3 Raman Spectroscopy

As stated previously, Raman spectroscopy was performed at the MAF and by

ISU. Specific results follow:

4.3.1 MAF Analyses

The resulting spectra indicated a highly graphitic material, as expected. Figure 39 shows the four spectra plotted together.



Figure 39 Raman spectroscopy analysis at UW on four sections of a batch 13102 compact using a 514 nm laser with a 60 sec integration time

As Figure 39 illustrates, there is a clear G-peak for each sample taken at about 1575 cm⁻¹ and a D-peak at about 1355 cm⁻¹, both of which are indicative of graphite. The additional large peak at 2700 cm⁻¹ (2D-peak) is also expected. A semi-quantitative calculation often used when characterizing graphite is the I_D/I_G ratio, which has been shown to be inversely proportional to the in-plane crystallite size. Table 5 shows the I_D/I_G ratio for each sample, as well as the average ratio using peak intensities.

	ID	IG	Id/Ig ratio
Sample 1	11,785.70	47,459.20	0.25
Sample 2	4,561.64	41,644.00	0.11
Sample 3	7,066.18	49,125.40	0.14
Sample 4	9,555.37	56,942.00	0.17
Average	8,242.22	48,792.65	0.17

Table 5 Id/Ig Ratio Calculation for MAF Raman Analysis

For perspective, the I_D/I_G ratios have been calculated by Magampa et al. (23) for synthetic graphite, 0.12, natural graphite, 0.18, and carbonized novolac phenolic resin, 0.9. If one assumes the synthetic graphite is pure (i.e. 100%) multi-crystalline graphite, the carbonized resin is non-graphitic (e.g. 0% graphite), and an approximately linear relationship, the relative graphite content of the compact analyzed by ISU can be estimated.

$$(1\% of the Magampa matrix) = \frac{|0.9 - 0.12|}{100} = 0.0078,$$
 [3]

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therefore,
$$graphite(\%) = 1 - \frac{(0.17 - 0.12)}{0.0078} = 93.6\%$$

Obviously, any non-linearity or other major deviations from the restrictive assumptions would alter or null the calculated graphite percentage from the I_D/I_G ratio; however, this exercise does give a rough idea of the amount of graphite in the compact samples.

4.3.2 ISU Analyses

Figure 40 illustrates the plotted spectra of the three materials analyzed (with arbitrary y-axis units).



Figure 40 Raman spectra from powdered Asbury 3482 natural graphite, graphite/zirconium granulate and a batch 13102 compact (Black, Blue and Red Lines, respectively)

Figure 40 shows spectra with shapes as expected and are consistent with other similar studies, as shown in Figure 41. Figure 41 illustrates the Raman spectra variation associated with heat-treated and compacted graphite/resin matrices comprised of different ingredient mixtures.



Figure 41 Raman Spectra for Various Combinations of Natural Graphite (NG), Synthetic Graphite (SG), and Novolac Phenolic Resin (7)

Additionally, as part of future ISU work, the I_D/I_G ratio will be calculated for each

of the three materials using the D and G peaks using ISU Raman data.

5 Conclusions/Summary

5.1 Summary of Analyses

The characterization techniques performed provided complementary data and, together, provided a data set significantly stronger than that possible from any one test. Indirect or semi-quantitative methods based on three very different analytical techniques have yielded estimates of graphitic and non-graphitic content that are within about 1% of each other. Additionally, the estimates found from this work were not overly dissimilar from the mass balance estimate. Table 6 summarizes the analysis techniques performed (or scheduled) and the information derived (or that will be derived) from each.

Analysis	Information Derived	Graphite Content (%), if determined
Optical Microscopy	Grain size, morphology, identification of areas of interest (Planned)	
SEM	Zirconia dispersion and morphology, graphite/resin distribution, percent graphite	92.5% graphite
TEM	Identity of structure and composition of nano crystalline structures, including fullerene-like graphitic structures. Phase identification. (Planned)	
Raman Spectroscopy	Crystallite size, disorder. Phase quantification.	93.6% graphite
XRD	Degree of graphitization, distortion and nano crystal size.	93.02% graphite
Mass Balance Estimate		86.6% graphite

Table 6 Summary of Analyses

5.2 Future Work at ISU

Work on this project will continue at ISU, including ensuring repeatability of the analyses, refining data analysis, analyzing the compact matrix ingredients, and analyzing a new prototype compact design. Discussion of specific analyses follows.

5.2.1 Future SEM Work

Although ISU does not have any SEM work planned for the near-term, as demonstrated by the use of image analysis techniques, SEM, may have be worth pursuing. Additionally, EBSD and other forms of SEM may be found more effective through the use of an etching (xenon or oxygen plasma) sample preparation technique.

5.2.2 Future XRD Work

XRD has provided a semi-quantitative measure of the degree of graphitization within the compacts, and may continue to be useful in the future should refined data analysis techniques be used or developed, or as an informational analysis for full-scale fuel production. Future XRD work planned by ISU includes the use of high energy XRD, as described elsewhere in this report. The high energy XRD may allow for identification of non-graphitic structures and potentially crystal quantification due to its ability to more accurately analyze structures of low atomic mass materials. 5.2.3 Future ISU Raman Spectroscopy Work

ISU intends to continue Raman spectroscopy analysis of additional compact batches and for Phase II compacts. In addition, Raman data will be analyzed to determine degree of graphitization per a method described by Cançado, et al. (47) and Barros et al. (72), who have shown that secondary G peaks in Raman spectra coming from 2D (sp² bonded carbon as in graphite) and 3D (sp³ bonded carbon) carbon phases coexisting in same sample can be "nicely distinguished" and the relative volumes of 3D and 2D carbon phases present in samples can be estimated.

5.2.4 Other Planned ISU Work

ISU currently has TEM, PED and high energy XRD planned for the near-term. TEM will reveal small, localized graphene stacking that may occur in otherwise amorphous carbon, thus informing the overall understanding of the graphite present in a compact. TEM will act as a complementary analysis to XRD and Raman by giving information about the microstructure of the graphitic material under analysis (73) (74).

As previously stated, PED has many of the same analytical benefits as TEM but, due to the circular scanning motion, eliminates potential pitfalls inherent to TEM (e.g. ion channeling) and may provide better data overall. PED should be a valuable analysis for the identification of very low quantity non-graphitic phases.

Additionally, high energy XRD will provide useful data such as that from traditional XRD, with the additional benefit of higher sensitivity for lower Z materials, such as carbon. With a higher sensitivity, calculations such as the degree of graphitization would only become more accurate.

5.3 Recommendations

In order to increase the accuracy of the methods used to quantify the amount of graphite present, the following methods may be employed.

- More accurately tracking the masses used during fuel production. Most of the mass lost during production will be from non-graphite sources (such as volatile off-gas or moisture loss), and little to no additional graphititization is expected. Such a "mass balance" approach will provide a limiting (i.e. not less than) value representing the minimum amount of graphite present. This method will need to be qualified using empirical evidence and testing.
- If cost effective, develop a set of standards with known graphite and nongraphitic phase amounts to act as a calibration standard for future analyses.

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