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Recycled Products for Nuclear Reactor Applications

Author(s): **D. Bradbury and J.C. Goodwin**

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Recycled Products for Nuclear Reactor Applications

Executive summary

The various participants in Work Package 5 had little or no experience of working with radioactive materials, since this is not normally required for the production of new unirradiated products. The first stage of the CARBOWASTE recycle efforts was to work with the manufacturers to try to find viable routes where they could produce recycled products without complex modifications to their facilities and excessive investment. In order to avoid unnecessary complication in conducting the testing work, it was agreed that manufacturers could (if they wished) start their work with surrogate non-radioactive intermediate materials, provided that those same materials could be readily produced from irradiated graphite [1].

The purpose of this report is to provide a summary of the work undertaken to develop recycled products for nuclear reactor applications and to assess their viability for use in a reactor setting, and also to discuss the potential limitations and subsequent optimisation of recycled products and their performance.

The work reported herewith, covers the following areas, these are:

- The selection of a non-active surrogate material (carbon black) for use as the recycled component of new nuclear graphite.
- Assessment of the behaviour of carbon black vs. typical "nuclear" coke upon heat treatment to temperatures up to 3000 ºC, (i.e. conventional graphitization temperatures).
- Reporting the results of the pilot scale study which incorporated carbon black as a surrogate for decontaminated irradiated graphite into nuclear graphite formulations.
  The production of Silicon Carbide, from both non-irradiated and irradiated graphite which has the potential for end use in HTR Fuel Pebbles.
- A discussion of the lessons learned as a by-product of the work and direction to those approaches which could lead to optimisation of the recycle process.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	31th January 2013	Final report	Jon Goodwin	D Bradbury	D Bradbury	D Bradbury
2						

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1 Introduction

Good environmental practice requires that disposal of waste should be the last resort selected only after preferable alternatives have been considered. These alternatives include minimisation of waste generation, reuse of the materials in their current form or recycling the materials through appropriate processing to form new products. CARBOWASTE's Work Package 5 is concerned with creating opportunities to reuse or recycle graphite, or constituents of graphite such as ^{14}C. It was thought that the major opportunities would be associated with recycling rather than reuse, but any opportunities identified to reuse graphite in its existing form would be included.

Before the start of CARBOWASTE there was very limited experience with recycling or reusing irradiated graphite. Conventional methods of graphite management include conversion to the gas phase and release as carbon dioxide and direct burial in the form of packaged or encapsulated waste. Significant scientific work has been done to substantiate these alternatives, which are potentially viable methods of graphite management. The purpose of Work Package 5 is to examine the potential of developing a set of new products from i-graphite in different fields. Even extraction of ^{14}C could find a market for e.g., medical purposes etc., if separation techniques like PSA and centrifuges are applied.

The various participants in Work Package 5 had little or no experience of working with radioactive materials, since this is not normally required for the production of new unirradiated products. The first stage of the CARBOWASTE recycle efforts was to work with the manufacturers to try to find viable routes where they could produce recycled products without complex modifications to their facilities and excessive investment. In order to avoid unnecessary complication in conducting the testing work, it was agreed that manufacturers could (if they wished) start their work with surrogate non-radioactive intermediate materials, provided that those same materials could be readily produced from irradiated graphite [1].

The purpose of this report is to provide a summary of the work undertaken to demonstrate the viability of utilising recycled material as part of the formulation for new nuclear grade graphite, for use as moderator new reactors or as a material for use in HTR fuel.

The work reported herewith, covers the following areas, these are:

- A summary of the potential options for the decontamination of irradiated graphite which could potential enable the graphite to be either partially or wholly decontaminated to enable recycle into new nuclear products.
- The selection of a non-active surrogate material (carbon black) for use as the recycled component of new nuclear graphite.
- Assessment of the behaviour of carbon black vs. typical "nuclear" coke upon heat treatment to temperatures up to 3000 ºC, (i.e. conventional graphitization temperatures).
- Reporting the results of the pilot scales study which incorporated carbon black as a surrogate for decontaminated irradiated graphite into nuclear graphite formulations.
- The production of Silicon Carbide, from both non-irradiated and irradiated graphite for potential end use as a robust packing material for use in a repository setting.

2 Selection of Non-Radioactive Surrogate

In principle, the simplest method of recycling graphite is to re-form new graphite from old without any intervening chemical transformation. Graphite manufacturers sometimes incorporate some scrap graphite in to their production processes already as finely-ground flour in the initial coke-pitch mix. The advantage of this option is simplicity, but it is likely to be of rather limited use, because there is limited opportunity for significant decontamination of the graphite before recycle, and the products that can be formed this way may not have suitable properties for many applications. Unless the graphite is decontaminated first, the recycle production facilities would have to be fully qualified to handle gamma emitting isotopes, which would involve considerable complication and expense.

The major limitation on decontamination of irradiated graphite without the use of the gasification process is its neutron activation and hence the presence of radioactivity throughout the structure. This means that whilst activity can be removed from the graphite surface (and the surface of open pores); activity is still retained in the remaining structure. This would result in a graphite product which has a reduced radioactive inventory, but which is still active and therefore in a form which may only be of limited use.

Various components of graphite were considered as intermediates, as follows:

2.1 Petroleum Coke

Petroleum Coke (often abbreviated petcoke) is a carbonaceous solid derived from oil refinery coker units or other cracking processes. Calcined petroleum coke (CPC) is manufactured by heating green coke to approximately 1300-1400 ºC in a rotary kiln. This affects the removal of virtually all residual hydrocarbons and moisture. The final calcined product contains only a trace of volatile matter, and 0.3-6% sulphur, depending on the petroleum base used to make the coke. Calcined and green petroleum cokes are inherently low in ash constituents. The fixed carbon content of most calcined petroleum coke products ranges from approximately 97-99.5%.

Through discussions with GrafTech it has been confirmed that they have experience of adding both graphite and lampblack to the coke mixing stage of the graphite manufacturing process. It was agreed in principle that a substitute derived in part from recycled graphite could be used in place of the petroleum coke. This would require further work and trials to demonstrate if this could work in reality.

2.2 Pitch Coke

Pitch coke is a high purity carbon residue manufactured by the destructive distillation (coking) of coal tar pitch. Coal tar pitch is a by-product resulting from the thermal distillation of bituminous coal. Because it is condensed from the gas phase, coal tar pitch is inherently low in ash and other mineral impurities. Therefore, the resultant coke is low in impurities.

Coal tar pitch is a highly aromatic feedstock and results in the formation of a coke that is highly graphitizable. Pitch coke is also inherently low in sulphur and has relatively high thermal conductivity.

Gilsonite, an asphalt naturally occurring coke which is mined in the USA is also used in the manufacture of some nuclear graphite.

The graphite's produced with Gilsonite tend to be isotropic, with higher density and strength, and lower porosities and radiolytic oxidation rates compared to equivalent graphites. The key microstructural feature of graphites produced using Gilsonite is the "onion skin" structure exhibited by the coke particles.

Through discussions with the graphite manufacturers it was agreed in principle that a substitute derived in part from recycled graphite could be used in place of the pitch coke. This would require further work and trials to demonstrate if this could work in reality.

2.3 Carbon Black

This a powdered form of carbon produced by pyrolysis (thermal decomposition in a limited amount or in the absence of oxygen) of hydrocarbons, wood or other carbon containing materials.

Carbon black is sometimes called amorphous carbon: however, this is not correct as its structure is crystalline. The powder particles are finely divided graphite micro-crystals having dimensions in the range 8 nm - 400 nm (3.2*10-6 - 1.6*10-5 inch). Besides carbon, carbon blacks may contain small amounts of oxygen, hydrogen, nitrogen and sulphur.

Carbon black (lamp black, acetylene black, furnace black, gas black, thermal black, channel black) is used for manufacturing tyres and other rubber products, as a pigment in inks, paints and toners, as active carbon and for fabrication electrodes and cell battery cores.

The potential exists to incorporate carbon black (lampblack) derived from the pyrolysis stage of the gasification of reactor graphite into new manufactured graphite. Its use as the recycled component of new graphite was discussed with the graphite manufacturers and was agreed in principal as a viable opportunity, although further work would need to be undertaken and the end use of the graphite produced would have to be limited to nuclear applications only.

Initial discussions were held with the graphite manufacturers as to what form of intermediate would be most convenient as a starting point for recycling efforts. Both GrafTech and SGL indicated that they had a preference for carbon black, since this can most readily be produced from gasification routes.

Although both manufacturers have considerable experience of incorporating non-radioactive graphite in products, they were concerned about the practicality of working with un-decontaminated graphite itself. On the other hand NRG chose to investigate the recycle of graphite directly into silicon carbide, because of the availability of an appropriate synthesis route and the availability of fully-radiation-shielded small scale SiC production facilities on the NRG site.

Despite this preference other possible intermediates have not been ruled out from consideration. There is a possibility that recycled carbon could be used to form compounds such as high molecular weight aromatic hydrocarbons which could be incorporated in pitch formulations for graphite manufacture.

Note – since the original selection of the intermediates for the WP5 recycle work, significant development of decontamination methods have taken place with a result that there may now be a case for re-considering the direct recycle of graphite much more seriously. If the decontamination processes are sufficiently effective, the restrictions on manufacturing activities due to the presence of gamma emitting radionuclide's may be significantly reduced.

3 Behaviour of Carbon Black towards Heat Treatment

In order to understand the limitations of incorporating recycled graphite (or in this case carbon black as a surrogate for decontaminated i-graphite) it is critical to understand the behavior of carbon black compared to that of typical "nuclear" coke upon heat treatment to temperatures up to 3000 ºC, i.e. conventional graphitization temperatures.

For both legal and technical reasons, decontaminated i-graphite for the trials was not applicable; all trials therefore used carbon black as a substitute. In order to determine maximum acceptable carbon black content in the formulation for nuclear graphite, heat-treated materials were investigated via X-Ray diffraction to reveal the degree of graphitization, backed by density measurements.

3.1 Experimental Procedure

For the test program, the following raw materials were selected:

a) Isotropic pitch coke, as typically used for nuclear graphite production

b) Carbon black, grade P-803, from Konimpex, Poland (properties provided in Table 3.1 below)

Table 3.1 - Product properties for Carbon Black P-803

Parameter	Value
Specific Surface Area	14 – 18 m^2/g
DBP Absorption	86 – 100 $cm^3/(100\ g)$
Ash Content	Max. 0.5 %
Sieve Residue (45 µm)	Max. 0.08 %

The coke was milled down to a maximum grain size of 63 microns, whereas the carbon black was used as received from supplier.

50-gram samples of the materials each were heated up in a graphite resistance furnace at a rate of 400ºC/h up to the final heat treatment temperature. After a 2 hour soaking time, samples were left to cool down to room temperature in about 3 hours. After cooling down, mass loss was determined by comparing sample weight before and after treatment (Table 3.2).

Table 3.2 - Mass Losses of the Samples after Heat Treatment.

Heat Treatment Temp.	Coke	Carbon Black
2100 ºC	3.0 %	1.5 %
2400 ºC	3.3 %	2.3 %
2700 ºC	3.5 %	2.0 %
3000 ºC	3.8 %	2.0 %

3.2 XRD Results

Samples after heat-treatment were measured in a powder diffractometer (Siemens D500) with Cu-Kα radiation. Diffraction patterns were recorded for the different materials. Figures 3.1 (below) and 3.2 (overleaf) show the patterns of the 002 peak for both materials with different heat treatment temperatures.

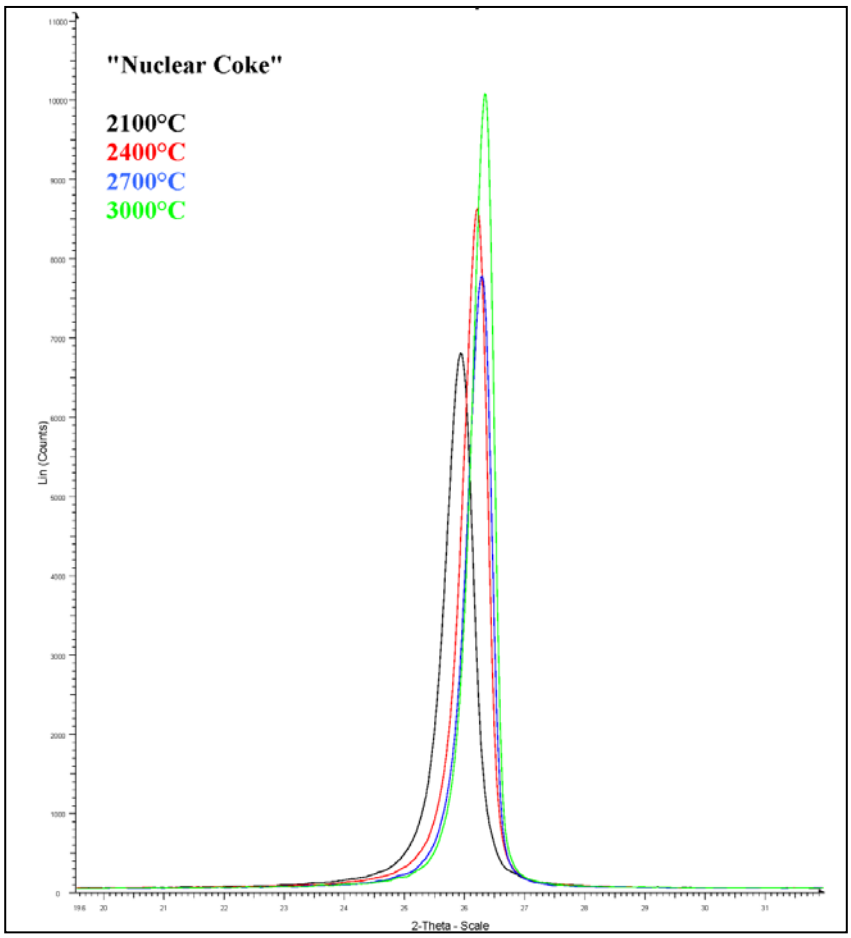

Figure 3.1 - Diffraction pattern of 002 peaks vs. Heat-Treatment Temperature for Coke

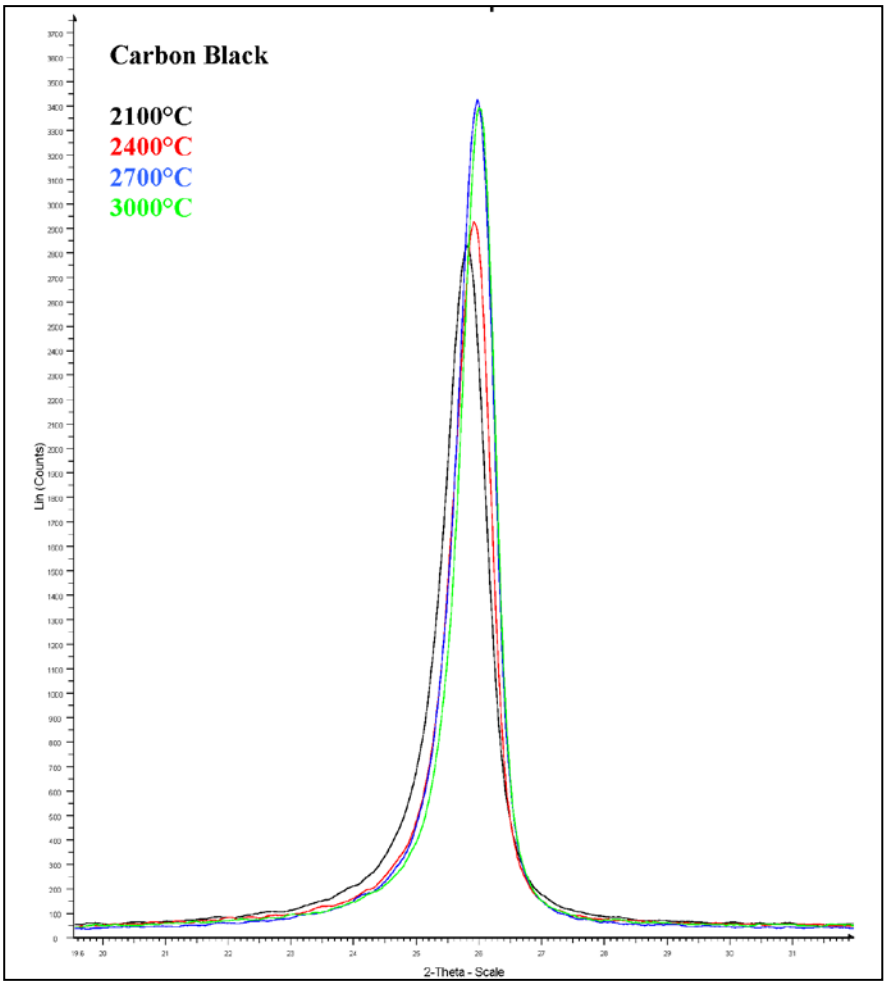

Figure 3.2 - Diffraction pattern of 002 peaks vs. Heat-Treatment Temperature for Carbon Black

The degree of graphitization is calculated according to Maire and Méring [2], based on the interlattice spacing derived from the 002 diffraction peak. To determine the 2-theta reflexion angle of the 002 peak, the peak area is horizontally divided into two parts with same area (Stokes method). The lower cut with the diffraction curve gives the 2-theta value used for calculation of d(002).

The degree of graphitization g is then calculated as

$$g = [0.3440 - d(002)]/0.0086 \qquad (1)$$

where d(002) is the lattice spacing from the 002 peak in nm.

References are Ceylon natural graphite with d(002) = 0.3354 nm and g = 1 and turbostratic graphite, i.e. perfectly disordered graphite, with d(002) = 0.3440 nm and g = 0. The d(002) value for turbostratic graphite is historically based on a specific (graphitizable) polyvinyl chloride coke [2]. Based on these historical assumptions, negative g values are not defined, at least not for graphitizable carbons. Hence, there is limited significance for low g values, as being far away from graphite, but trends are possible to be identified.

For coke, the degree of graphitization increased from -0.08 to 0.48 when going from 2100 to 3000ºC, whereas carbon black only increased from -0.46 to -0.14 (see Table 3.3 and Figure 3.3 below).

Table 3.3 - Degree of Graphitization after Heat Treatment

Heat Treatment Temp.	2100 ºC	2400 ºC	2700 ºC	3000 ºC
Coke	-0.08	0.27	0.39	0.48
Carbon Black	-0.46	-0.30	-0.18	-0.14

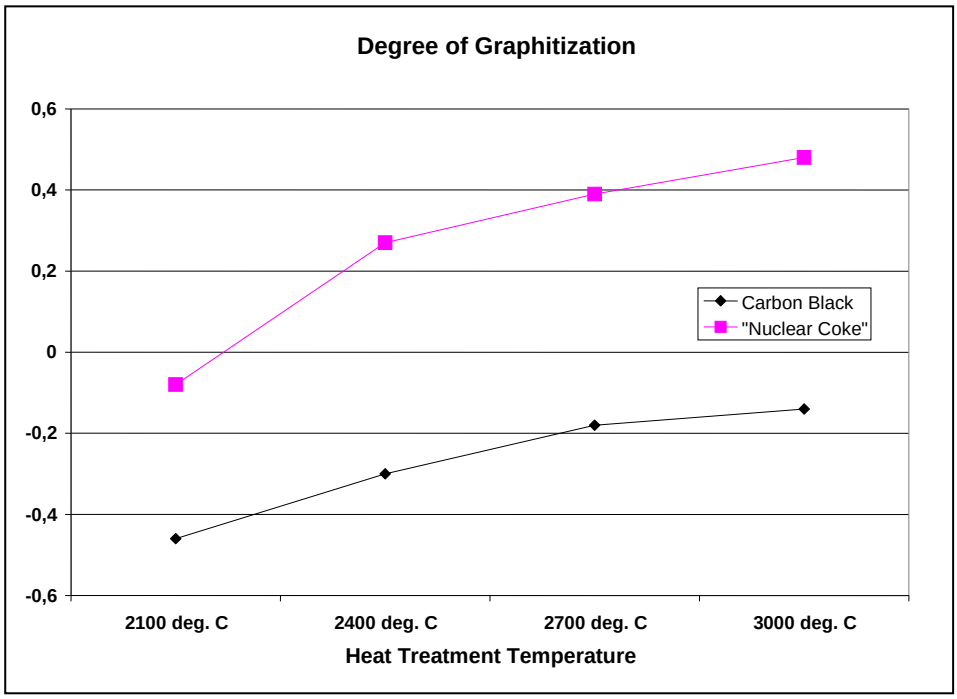

Figure 3.3 - Degree of Graphitization as a Function of Heat Treatment Temperature

3.3 Density Measurements

Samples from 3.1 were tested for density using the pycnometer method, with xylene as solvent [3]. Results are summarized in Table 3.4.

Table 3.4 - Density in g/cm3 of Heat-treated Coke and Carbon Black

Heat Treatment Temp.	None	2100 ºC	2400 ºC	2700 ºC	3000 ºC
Coke	2.004	2.137	2.169	2.185	2.186
Carbon Black	1.870	2.096	2.096	2.095	2.109

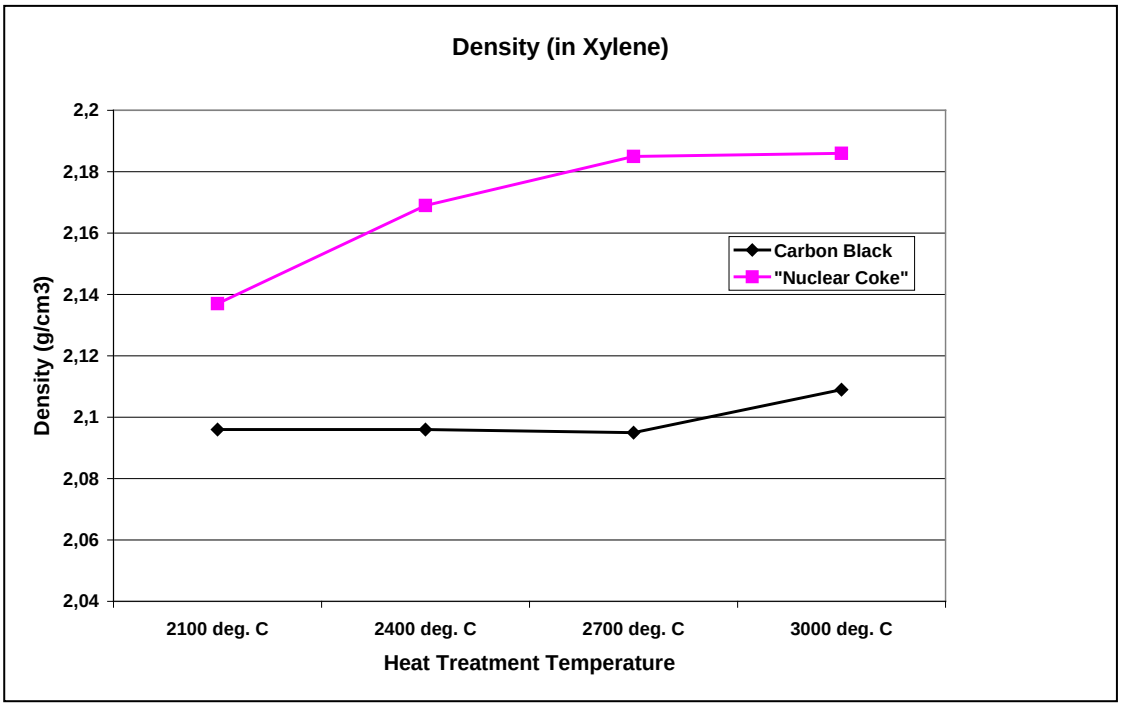

Figure 3.4 - Evolution of Density as a Function of Heat Treatment Temperature

3.4 Conclusions

The behaviour of carbon black vs. coke upon heat treatment shows, that this material cannot replace coke due to its poor graphitizability and anticipated negative impact on thermal conductivity.

Upon thermal treatment at 3000 ºC, a noticeable graphitization of the coke sample can be observed whereas the carbon black sample only marginally responds, resulting still in a calculated negative degree of graphitization. Therefore, carbon black can indeed be considered as "non-graphitizable", i.e. unable to contribute to the desired pronounced graphite character of nuclear graphite, reflected in its high thermal conductivity.

In addition, the measured density of carbon black does not considerably change from 2100 to 3000 ºC heat treatment temperature. A typical graphitizable coke shows behaviour as the tested "nuclear coke": density increases with temperature, with levelling out around 3000 ºC. Synthetic graphite based on well-graphitizable needle coke typically shows a density value of around 2.24 g/cm3 [9].

Furthermore, due to the very low particle size and different pitch take-up and wetting behaviour compared to coke dust, there will be a practical limit of carbon black addition for producing nuclear graphite for moderator and fuel. This limit is expected in the range of 10-15% in the dry material aggregate, taking also into consideration that coke flour will be replaced by carbon black, where replacement is constrained by overall (coke) flour quantity in the formulation.

Therefore, pilot plant trials in the scope of this task within WP 5 utilized 7.5 and 15 % carbon black, replacing coke flour in a standard nuclear graphite formulation.

4 Recycling of Carbon Black into Nuclear Graphite

The (calculated) negative degrees of graphitization for carbon black show that this material has to be considered as "non-graphitizable" and cannot fully replace coke in the formulation because it will hardly contribute to the thermal properties required in nuclear graphite. The same curve for coke shows the expected behaviour with continuous increase up to g = 0.48 after heat treatment at 3000 °C.

Furthermore, the very low particle size and therefore higher pitch take-up and worse pitch wetting behaviour of carbon black compared to coke flour constitutes a practical limit of carbon black addition for producing nuclear graphite for moderator and fuel. This limit was estimated in the range of 10-15 % in the dry material aggregate, taking also into consideration that coke flour will be replaced by carbon black, where replacement is constrained by the overall (coke) flour quantity in the formulation.

Therefore, the pilot plant trials utilized 7.5 and 15 % carbon black, replacing coke flour in a standard nuclear graphite formulation. As base formulation, SGL's standard nuclear graphite NBG-18 with 1.6 mm maximum grain size of isotropic coke was selected. Three variants were produced using comparable processes to that of industrial production (see Figure 4.1 overleaf), these were:

- Reference: standard NBG-18 formulation, i.e. 100 % coke in dry aggregate
- Trial 1: 92.5 % coke, 7.5. % carbon black in dry aggregate
- Trial 2: 85 % coke, 15 % carbon black in dry aggregate

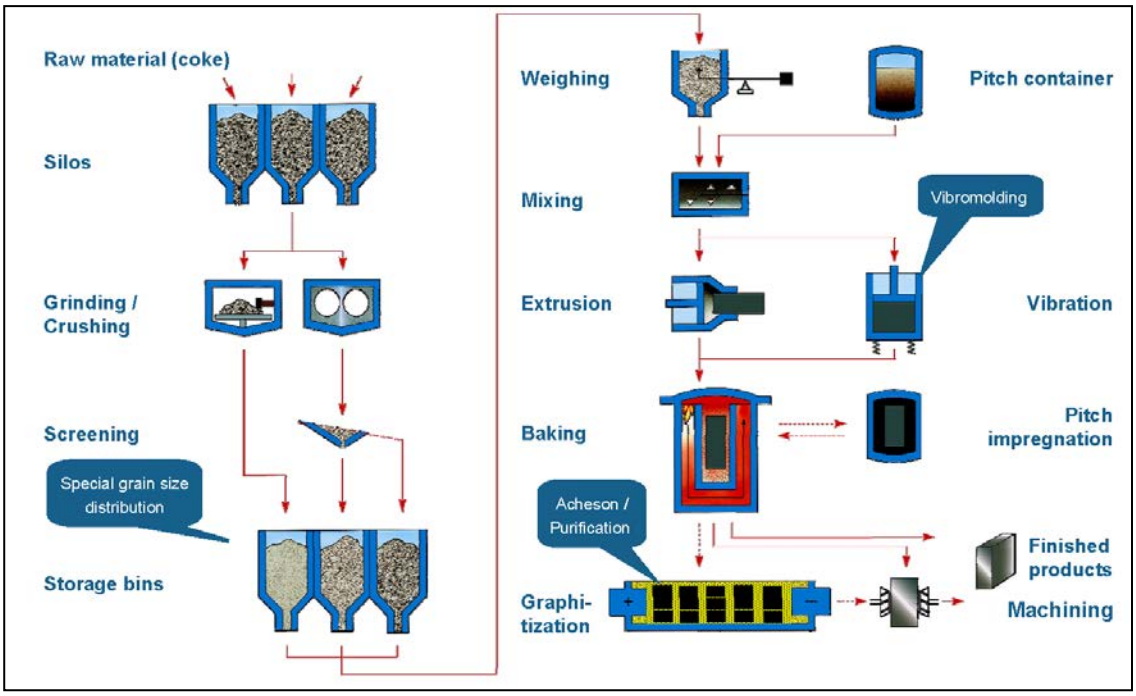

Figure 4.1 - Industrial Nuclear Graphite Production Process (schematic)

The pilot plant process utilized followed the principle way of industrial nuclear graphite production (Fig. 4.1 and [6]), which consists of raw material preparation by crushing and screening, mixing in defined proportions with pitch, shaping by extrusion or vibro-molding, baking the resulting green product, densifying by pitch impregnation/rebaking, and finally graphitising the artefact in an Acheson graphitization furnace. In contrast to the industrial process, block-pressing was used in pilot plant scale instead of vibro-molding to avoid additional experimental scattering through the forming process and no purification technique was applied during graphitization. With regard to the task, these aspects are considered non significant for the objective of this activity. Iso-molding was not considered as this requires a completely different raw material preparation and green process, and moreover, no internal reference was available.

The dry components were mixed with coal-tar pitch to form a carbonaceous paste which was shaped into rectangular blocks of dimensions 200 x 200 x 220 mm (Figure 4.2) by uniaxial hydraulic block-pressing. Trial 2 required approx. 15 % more binder addition.

Figure 4.2 - Samples after block-pressing (from left to right: Reference, Trial 1 with 7.5 % carbon black, Trial 2 with 15 % of carbon black)

After baking at 850 °C, blocks were twice impregnated with coal-tar pitch and rebaked to improve mechanical strength and provide a good thermal conductivity after graphitization. Finally, the blocks were graphitized in an Acheson lab graphitization furnace at 2900 °C. After cooling down, cores were drilled from the lab samples for lab analyses (Figure 4.3, Table 4.1).

Figure 4.3 - Samples after graphitization (from left to right: Reference, Trial 1 with 7.5 % carbon black, Trial 2 with 15 % of carbon black), with core samples already taken

Table 4.1 - Laboratory data for pilot plant trial materials

Base Grade	Recipe	No of sample	Apparent density	Specific resistivity	Compressive strength	Flexural strength	Thermal conduct.(at 30°C)	Coeff. of lin.ther.exp. (20-200^{0}C)	Young's Modulus
			g/cm^3	Ω·µm	MPa	MPa	W/m.°K	µm/(K·m)	kN/mm^2
NBG-18	Reference	1 - with grain	1,78	7,9	62,1	23,4	153,1	3,8	10,3
		3 - against grain	1,78	8,2	53,1	18,7		4,1	9,4
	7.5 pp of carbon black	1 - with grain	1,77	9,5	50,6	11,7	136,1	3,8	9,5
		3 - against grain	1,78	10,7	50,6	11,3		4,1	7,6
	15 pp. of carbon black	1 - with grain	1,79	13,1	43,3	5,5	104,5	3,8	6,8
		3 - against grain	1,79	13,6	43,2	6,9		4,1	5,5

4.1 Summary

There is considerable impact on the mechanical and thermal properties of the graphite material. The addition of 15 % carbon black considerably decreased mechanical strength – both compressive and flexural – by up to about 70 % and thermal conductivity by 32% vs. Reference. Apparent Density remained practically unaffected from the addition of carbon black.

Overall, one can conclude from the trials that maximum only 5-10 % of carbon black can be tolerated from process requirements, in particular in industrial scale, and product properties point of view.

Mechanical characteristics might still be improved through a secondary raw material preparation, i.e. producing a precursor from carbon black and pitch, baking and crushing the baked product for using it as raw material component for nuclear graphite production instead of plain carbon black. However, the thermal properties would only be marginally affected, keeping the addition limit for carbon black (and hence i-graphite decontaminated via the gasification route) still at around 10%.

Direct use of i-graphite or material from other decontamination routes were not considered due to the presence of critical radionuclide's which constitutes a particular issue when producing moderator/reflector graphite in industrial scale of several hundred tons. Chances exist that the response to graphitization is better than for carbon black (-type) materials. This would remain to be investigated with actual i-graphite – pure or decontaminated – which would require handling and thermal treatment in adequately equipped lab facilities.

5 Fuel and core products

Tristructural-isotropic (TRISO) fuel is a type of micro fuel particle utilised in high-temperature reactors. It consists of a fuel kernel composed of UOX (sometimes UC or UCO) in the centre, coated with four layers of three isotropic materials. The four layers are a porous buffer layer made of carbon, followed by a dense inner layer of pyrolytic carbon (PyC), followed by a ceramic layer of SiC to retain fission products at elevated temperatures and to give the TRISO particle more structural integrity, followed by a dense outer layer of PyC.(see Fig 5.1 below)

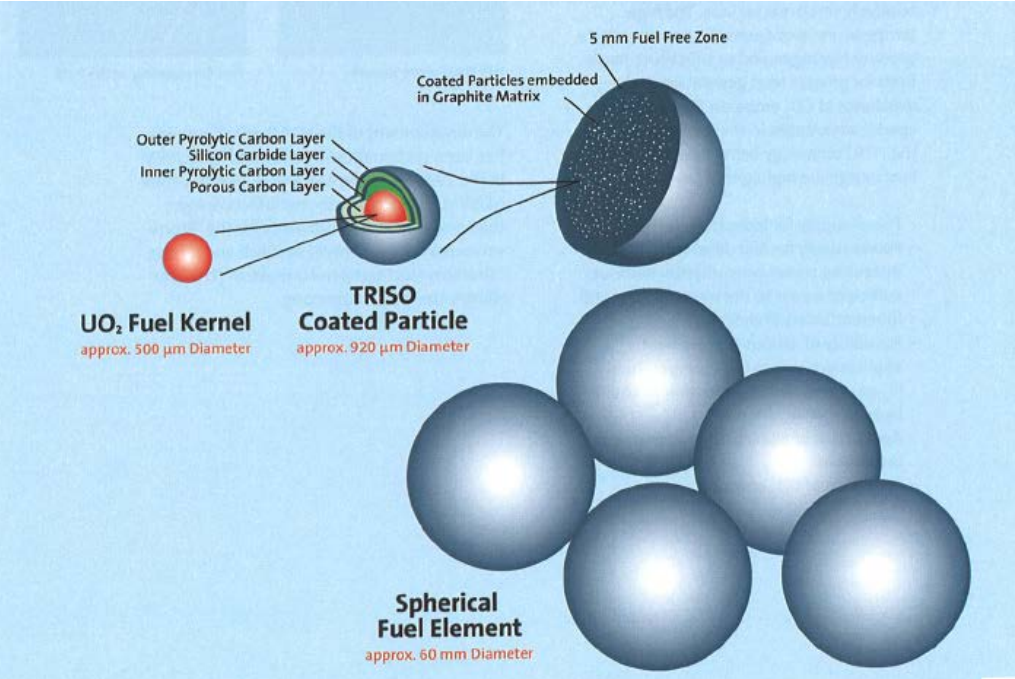

Figure 5.1 - Diagrammatic representation of the TRISO Fuel Particles [7]

TRISO fuel particles are designed not to crack due to the stresses from processes (such as differential thermal expansion or fission gas pressure) at temperatures beyond 1600°C, and therefore can contain the fuel in the worst of accident scenarios in a properly designed reactor. Two such reactor designs are the Pebble Bed Modular Reactor (PBMR), in which thousands of TRISO fuel particles are dispersed into fuel pebbles, and the prismatic-block gas-cooled reactor (such as the GT-MHR), in which the TRISO fuel particles are fabricated into compacts and placed in a graphite block matrix [7].

The potential exists to use recycled graphite (at least in part) in place of virgin graphite for the TRISO fuel particles, either as a component of the pyrolitic carbon, or as the following section supports, its conversion into Silicon Carbide.

The flow chart below (Fig 5.2) highlights the production process of the TRISO fuel particles which is instigated with the supply of graphite. The radiological inventory of the recycled graphite would need careful consideration as to its potential affects on the fuel particles.

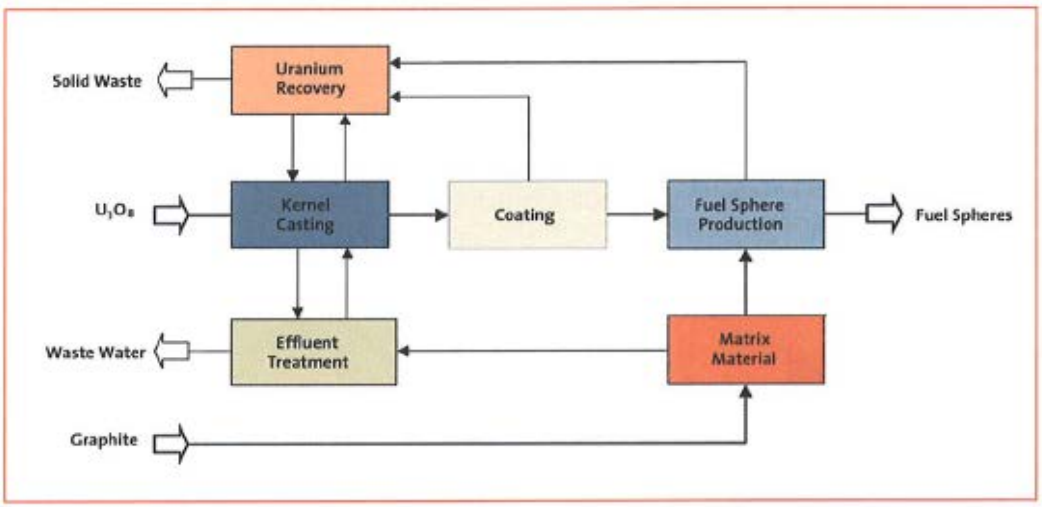

Figure 5.2 - Flow chart showing the production process of the TRISO Fuel Particles [7]

6 Silicon Carbide Production from Recycled Graphite

Under Work Package 5, NRG participated in sub-task 5.2.3 “Carbonaceous ceramics for waste management” and concentrated on SiC formation from graphite primarily for use in disposal sites as backfill, encapsulants, etc., without oxidation of the carbon and providing safety during processing. The potential also exists to combine irradiated graphite with silicon to form Silicon Carbide, a key component of the TRISO fuel particles covered in the previous section.

6.1 Introduction

SiC is the most widely used non-oxide ceramic material. It was first synthesized by Acheson in 1891 by heating a mixture of clay and carbon up 1600 °C in a carbon arc (“carborundum,” a name still used today for abrasive and refractory grade SiC). Most SiC (α-SiC) is still synthesized via the Acheson process (carbothermal reaction of quartz). Only for SiC (β-SiC) platelets or whiskers other processes are used, e.g. pyrolysis of rice hulls, spinning from organosilicon polymer precursors, chemical vapor deposition (CVD) and the so-called vaporliquid- solid (VLS) process, using liquid catalysts.

Due to the small electronegativity difference between C and Si, the covalent bond dominates (88%), i.e. strong, directional bonds that are responsible for high decomposition temperature and hardness of SiC. SiC occurs in two general crystalline forms: cubic β-SiC (low-temperature) and α-SiC (high-temperature). The latter has a special type of one-dimensional polymorphism called polytypism (i.e. various stacking sequences in the c-direction) and can be cubic (zinc blende structure) or hexagonal (wurtzite structure). Usually, α-SiC is obtained by carbothermal reduction of quartz (Acheson process), while β-SiC forms by direct reaction of Si and C (self-sustaining reaction), vapor phase routes or using plasma or laser heating.

Table 6.1: Typical properties of SiC

Property	Value
Density	3.2g/cm^3
Hardness	21-25 GPa
Fracture toughness	3-6 MPa·m$^{1/2}$
Young's modulus	420 GPa
Bend strength	450-650 MPa
Thermal expansion coefficient	4-5·10^{-6} K^{-1}
Thermal conductivity	in order of 50 W/mK

Because of its high hardness (see Table 6.1), SiC is extensively used as abrasives and in grinding wheels. SiC is also used as a refractory (high thermal conductivity, high decomposition temperature, chemical inertness, low wettability by molten metals and slags), heating element (appropriate electrical properties) and high-temperature semiconductor (only ultra-pure, doped SiC), as well as a structural material in contact with corrosive liquids such as concentrated HF and NaOH (due to its excellent corrosion resistance) and in heat engine components (due to its excellent wear resistance; its low coefficient of friction reduces wear in contact with itself or other materials).

6.2 SiC Formation

Literature research on SiC formation from graphite was done, several suitable methods were found and finally a technique published by A. Morancais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956 [8], was chosen as method to be tested. In the paper, the method is called "a process involving an SHS stage."

The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite has been studied. Products with very high pore contents (≈80%) were obtained using a process, shown in Figure 6.1 overleaf, which consisted of heating the reactive pellets in purified argon, at 15 °C min−1, up to 1430 °C and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of a SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the

formation of silicon carbide, during heating from about 1325 up to 1430 °C, is associated with a large sample expansion, which mainly determined the final pore volume fraction. The pore transfer mechanisms, which occur during the SHS stage at 1430 °C, have a specific influence on the pore development. Since the final pore size distribution is strongly related to silicon grain size distribution, the porosity of the porous SiC ceramic, obtained by this process, can be easily modulated.

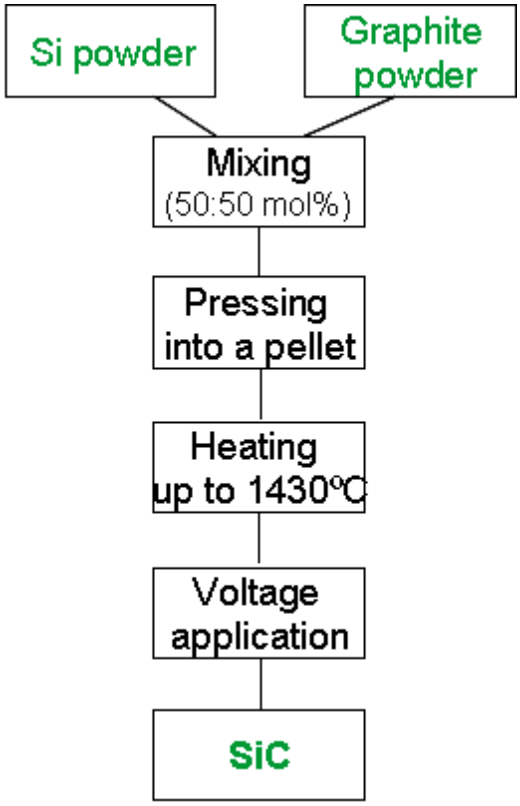

Figure 6.1: Flowchart showing the SiC formation method

This method has been applied for the fabrication of SiC directly from silicon and graphite. Many tests were performed to establish the right conditions, and it was found that the voltage applications were not necessary for the SiC formation. First, the method was tested with virgin graphite. When the procedure was established, the formation of SiC from irradiated graphite could start. In this report, only the part of the SiC formation from irradiated graphite is presented.

6.3 Raw Materials

The raw materials used for the production of SiC were:

- Silicon powder (Alpha Aesar) – crystalline, 325 mesh, 99,5 % metal basis.
- Irradiated graphite – irradiated graphite from Carbowaste WP3 – RRT test was used, this graphite originates from UNGG, EdF.
- Ethanol/methanol.

6.4 Experimental Set-up

A new setup for the experiment was built, as shown in Figure 6.2. This setup was designed to avoid pressure on the molybdenum wires during movement of the pellet to the middle of the ceramic tube in the high temperature oven (HTTF) – because during testing of the original setup wires were often broken. This setup consists of a ceramic tube with a length of 1 meter with 2 bores (an internal diameter of 1 mm). A ceramic dish was fixed to the ceramic tube using an aluminium oxide mixture (ceramic paste), which was slowly sintered to 1000°C to harden. Afterwards the two molybdenum wires were placed through the bores and cut to length. After forming the ends of the molybdenum wire so that the two graphite plates could move freely, the space between the bore and the molybdenum wire was filled up with ceramic paste. This ensured that there would be no gas leakage through this end.

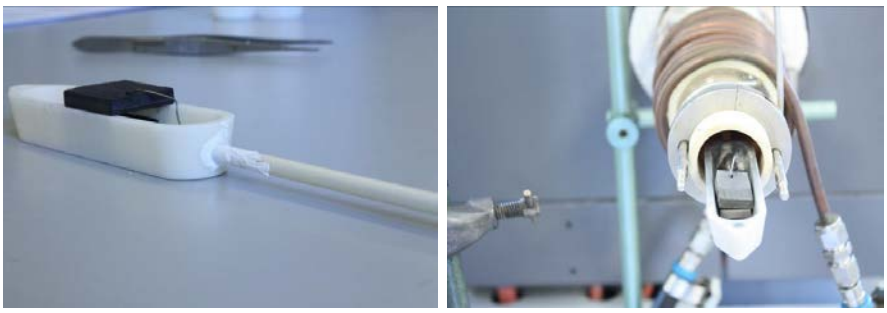

Figure 6.2: Fixed dish to tube (left) and setup placed in the HTTF oven (right)

6.5 Experimental Procedure

Reactive samples were prepared from a stoichiometric ratio of graphite and silicon (30wt% of C – 70wt% of Si) mixed in an ethanol/methanol solution for 30 min. in a ball mill IKA mixer.

When the mixing was finished, the ethanol/methanol was evaporated and the powder mixture was pressed at low pressure into a pellet suitable for the reaction setup. The sample was placed into the oven where a temperature program was applied. The following temperature program was used as the starting basis but was modified as experiments proceeded:

1. 100°C/h to 200°C
2. 200°C for 10 h
3. 200°C/h to 1430°C
4. (voltage application)
5. 1430°C for 40h
6. 200°C/h to RT.

When finished, the sample (see Figure 6.3) was taken from the setup and analyzed by XRD and SEM.

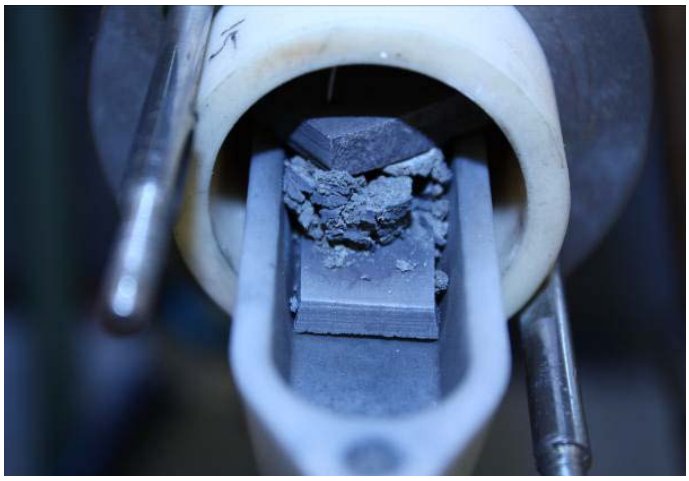

Figure 6.3: A SiC pellet after the Morancais SHS method

To optimize the formation process, different reaction conditions were tested. Various times and values of voltage were used, several ratios of Si/C in starting mixture, different sintering time and two different atmospheres – argon and noxal (95% argon+ 5% hydrogen) or their combination – were tested. Further data from laboratory testing of the SiC is provided in T.5.4.1.

6.6 Conclusions

The method for formation of SiC directly from graphite and silicon was established within Carbowaste – WP5. This method was applied first to virgin graphite; when the method was modified and established, irradiated graphite was used. The same procedure was applied to irradiated graphite; unfortunately these two graphite types seem not to react in the same way. Reaction conditions were varied to optimize the procedure to get pure SiC using the irradiated graphite. However, besides the SiC a small amount (less than 5%) of free carbon was always still present after the reaction process.

Further work would be required in this area to align the laboratory testing to the requirements of HTR Fuels. Given the exit of PBMR early on in the Carbowaste Project, it has not been possible to develop this area of recycle further. However, dependant on the development of the HTR reactor designs and their associated fuels, this remains the most applicable area for applying graphite recycle. It is therefore a key area in which applicable recycle pathways needs to be investigated further.

7 Direct Recycle without Decontamination

In addition to GrafTech's work under Carbowaste, they have also been involved in the Deep Burn project, working closely with Oak Ridge National Laboratory on behalf of the US Department of Energy.

Deep Burn reactors can handle a variety of fuel sources and be of several reactor designs, but all require nuclear grade graphite as a moderator. Over the life of the reactor the significant quantities of nuclear graphite components will need to be replaced, creating a radioactive materials management issue: storage, transportation, and burial, all with associated costs and environmental implications. One method for addressing the irradiated graphite management issue is to reuse/recycle the graphite. Reuse of irradiated graphite could be as straightforward as shuffling the graphite components within the reactor to maximize the useful life of that material, or to use an expended block as the raw material for making a new graphite component. This latter option is essentially the production of a new graphite component through a true recycle process.

The primary goal of this project was to determine if nuclear graphite, formed through the normal graphite forming process but using crushed previously irradiated nuclear graphite, could be formed with sufficient mechanical integrity to warrant further investigation.

Initial results from the work to date suggest that, within the narrow parameter range studied, the materials could be formed with a level of density, strength, and thermal conductivity to suggest that the recycling process is viable. It is noted that the irradiated materials used in this study were in a moderate range of irradiation associated with graphite densification, and that recycling would likely include graphite irradiated to a higher irradiation dose [4].

It should be stated that whilst this work is very promising, the approach to graphite recycle will be of limited application due to the carryover the full radionuclide inventory from the used irradiated graphite moderator block to the new nuclear graphite product, and thereby requires significant radiological containment for the full process of

retrieval, processing, manufacture and installation. The potential use of non destructive decontamination techniques prior to recycle, such as ‘roasting’ or chemical decontamination, may enable the radiological protection measures required, to be downgraded in line with reduction of the graphite radionuclide inventory resulting from its partial decontamination.

8 Discussion & Conclusions

At the start of the Carbowaste project, discussions were held between the Work Package 5 leadership and the graphite manufacturers (SGL and GrafTech) in order to assess what the most applicable intermediate would be for use in demonstrating the inclusion of recycled graphite as a key component of new graphite for use in nuclear applications.

The graphite manufacturers had little or no experience of working with radioactive materials, since this is not normally required for the production of new un-irradiated graphite products. Therefore the key driver for any recycle route was to find an intermediate from which they could produce recycled products without complex modifications to their facilities and excessive investment, and also for which a suitable simulant (non-active) could be derived. [10].

The intermediate chosen was selected due to two key criteria; firstly the path to recycled intermediate by passing through the gas phase enables the intermediate to be largely free of active contamination, with the exception of ^{14}C and ^{36}Cl. Secondly, the intermediate (carbon black) is readily achievable through a process of full gasification (steam reforming) of the irradiated graphite followed by re-deposition through the Sabatier and Boschh reactions.

Whilst the use of a carbon black intermediate for graphite recycle addresses in large part the issues associated with the use of radioactive materials being used in the manufacturing process, there would still be the requirement for the working/manufacturing areas to be radiologically controlled. This requirement would realistically limit the size and complexity of the potential recycled products which could be produced.

As a result of the very fine particulate nature of the carbon black, optimisation in the approach for incorporation of the carbon black into the recipe formulation would need to be addressed, due to its tendency to ‘clump’ or ‘aggregate’ and not distribute evenly throughout the formulation. Improvements in the dispersion of the carbon black within

the formulation would enable a limited increase in the proportion of carbon black which could be incorporated.

The behaviour of carbon black vs. coke upon heat treatment shows that this material cannot replace coke due to its poor graphitizability and anticipated negative impact on thermal conductivity. This is therefore a major limiting factor for its large scale inclusion in 'new graphite artefacts'.

Parallel work undertaken outside of the Carbowaste Project which has focused on the direct reuse of irradiated graphite into 'new graphite' without decontamination (Deep Burn – USDoE Project), indicates that the use of recycled graphite rather than carbon black supports the inclusion of a significantly higher proportion of recycled material. However, this would be subject to much tighter radiological controls and shielding, both for the manufacturing process and the subsequent transport of the active graphite products.

From the work undertaken under WP5, it is clear that the ideal intermediate to support recycle would be in the form of graphite, which has been successfully decontaminated to a sufficient degree to support the manufacture of new products with only minimal shielding requirements. Work undertaken outside of Carbowaste, as well as experience of the graphite manufacturer's indicates that recycling graphite without transformation produces a material with much great graphitization characteristics. This in turn enables a substantially larger proportion of the formulation to be composed of recycled material with no adverse effects on the properties and characteristics of the resulting product. The key to this approach is both the optimisation of the decontamination approach, to minimise the radionuclide content of the recycled graphite and its corresponding effect on the shielding/process requirements associated with the production of recycled graphite products.

A primary target area for graphite recycle would be the HTR reactors, and specifically the fuel pebbles of design similar to that demonstrated in Section 5. Given the large quantities of waste generated by the high turnover of fuel pebbles, one potential option to minimise waste through recycle could be the conversion of irradiated graphite to

silicon carbide for use in the SiC layers of the fuel pebbles. Whilst under WP5 the conversion of i-graphite with silicon into SiC has been successfully demonstrated at Laboratory scale, further work is now needed to develop this further.

Key areas which need further investigation include the assessment of the SiC produced and its viability for use in Fuel Pebbles, and also development of the lab scale process to an industrial scale.

In summary, the work undertaken under WP5 has demonstrated that the recycle of graphite is achievable, although further work is required to optimise the recycle process. The primary target area for graphite recycle would be the HTR reactors given the large quantities of waste generated, and the requirement for continuous supply of fuel pebbles.

Glossary

CPC	Calcined Petroleum Coke
EdF	Électricité de France
GT-MHR	Gas Turbine Modular Helium Reactor
HTTF	High Temperature Tube Furnace
HTR	High Temperature Reactor
NBG	Nuclear Block Grade
NRG	Nuclear Research and Consultancy Group
PBMR	Pebble Bed Modular Reactor
PSA	Pressure Swing Adsorption
PyC	Pyrolytic Carbon
SEM	Scanning Electron Microscope
SHS	Self-Heat Sustaining
SiC	Silicon Carbide
TRISO	Tristructural-isotropic
UCO	Uranium oxycarbide
UNGG	Uranium Naturel Graphite Gaz
UOX	Uranium Oxide
USDoE	United States Department of Energy
VLS	Vapor-Liquid-Solid
XRD	X-Ray Diffraction

References

[1] Carbowaste Report No5.2.1 Identification of Requirements for Intermediates Needed for New Products Synthesis

[2] J. Maire, J. Méring, in: P.L. Walker Jr. (Ed.), Chemistry and Physics of Carbon, vol. 6, Marcel Dekker, New York, 1970, p. 125

[3] Standard for pycnometric density, xylene method (DIN 51901)

[4] Burchell, T., Pappano, P. 'The Characterization of Grade PCEA Recycle Graphite Pilot Scale Billets', (Rep No. ORNL/TM-2010/00169). August 27th 2010.

[5] Internal communication with author, SGL Carbon GmbH, 2010

[6] Nightingale, N.E. (Ed.)., 1962, Nuclear Graphite, New York and London, Academic Press

[7] NUKEM HTR Fuel Technology Brochure

[8] A. Morancais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956

[9] Burchell, T., Pappano, P. 'The Characterization of Grade PCEA Recycle Graphite Pilot Scale Billets', (Rep No. ORNL/TM-2010/00169). August 27th 2010.

[10] Hiltmann, F., Carbowaste Technical Report, Carbowaste-1102-T-5.2.1-SGL-01