EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

Technical Report (D-5.2.3)
Graphite for New Reactors and Fuel Produced from Purified Carbonaceous Wastes

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Reporting period: e.g. 01/04/2010 – 31/03/2011

Date of issue of this report: 30/01/2012

Start date of project: **01/04/2008** Duration: **48 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the CARBOWASTE project	**X**
CO	Confidential, only for specific distribution list defined on this document	

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CARBOWASTE		
Work package: 5 **Task: :** 5.2.3	**CARBOWASTE document no:** CARBOWASTE-1201 -T-5.2.3 (e.g. May 2008 as date of issue: 0805)	**Document type:** D
Issued by: Bradtec (UK) **Internal no.:** Bradtec Report		**Document status:** Final

Document title

Graphite for New Reactors and Fuel Produced from Purified Carbonaceous Wastes

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 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.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	30th January 2012	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 Graphite Decontamination for Recycle

Various different mechanisms have been investigated as part of the Carbowaste project which are applicable to either the partial or complete decontamination of irradiated graphite. The potential benefits of graphite decontamination include the potential to reduce the radionuclide inventory of the graphite to enable its reuse through its recycle into 'new' nuclear graphite, or its potential down classification (e.g. ILW to LLW) to enable reduced management requirements for its long term storage. Other potential benefits of decontamination include the opportunity to derive valuable radioisotopes from the irradiated graphite (e.g. ^{14}C), which have potential marketable end uses such as tracers for the radiopharmaceutical industry. It is important to understand the various decontamination methods when considering the potential recycle of graphite, as:

- they are critical for firstly removing the radionuclide inventory (either wholly or partially) to simplify their inclusion in an industrial recycling process,
- they dictate the form and properties of the graphite, and
- they define the form and nature of the waste streams produced.

The following sections provide a basic summary of the various decontamination approaches which have potential applicability as a precursor to the recycle of irradiated graphite to produce new nuclear products for reactor and fuel applications.

2.1 Full Gasification

The conversion of the graphite into the gas phase results in the retention of the less labile radioisotopes such as ^{60}Co in the solid residue. This can then be packaged and grouted ready for long term storage. The gas (CO, H_2) resulting from the gasification process, will have lost a significant proportion of the radionuclides, but ^{14}C and ^{3}H remain. ^{3}H can be readily removed from the process in the form of water. The removal of the ^{14}C from ^{12}C and ^{13}C could be undertaken by applying a suitable isotope separation technique, or techniques.

There are potentially many reaction schemes to convert solid carbon (in graphite form) into gaseous oxides of carbon, of which the two principal options are:

- React the graphite with air or oxygen (incineration).
- The carbon can be reacted with steam, using the well-established "steam reforming" reaction.

Incineration of graphite is difficult; mainly because nuclear graphite is extraordinarily resistant to oxidation [2, 3]. This means that the deliberate usage of incineration to dispose of irradiated graphite by oxidation presents a considerable technical challenge for conventional incineration processes.

Of these two options, the use of the steam reforming process is probably the most suitable due in large part to its ability to be undertaken within a closed system, which when compared to the continuous air flow required for incineration and its difficulties in holding back volatile radionuclides, is a distinct advantage.

For the graphite moderator blocks to be gasified effectively, they must be size reduced in order for the feedstock to be within the optimal particle range (<50mm). This process can be undertaken by one of two mechanisms, firstly, the blocks can be removed from the reactor intact (current baseline approach) and then fed through a crusher (or crushers); or the moderator graphite could be size reduced as part of the process of retrieval from the reactor (e.g. Nibble and Vacuum approach).

The basic reaction of steam reforming involves reaction of carbon with steam according to equation 1 below:

$$C + H_2O \longrightarrow CO + H_2 \qquad \textbf{(eq.1)}$$

The CO can be separated or the gases further oxidised with oxygen to form carbon dioxide and water. The water can then be recycled, allowing the collection of the tritium released from the graphite.

$$CO + H_2 + O_2 \longrightarrow CO_2 + H_2O \qquad \textbf{(eq.2)}$$

Once gasified the carbon dioxide can then either be:

- Converted to carbon black via the Sabatier or Bosch reactions, for use as the recycled component for incorporation into new graphitic products, or
- Liquefied pending mixing with ^{14}C depleted CO_2 derived from fossil fired power stations and subsequent injection into a Carbon Capture and Storage (CCS) Scheme in a benign form [4].

2.2 Thermal Decontamination ('Roasting')

Heating graphite can, at least in some cases, lead to selective loss of isotopes (particularly tritium and ^{14}C) from the graphite structure. This phenomenon has the potential to be utilised both as a form of partial decontamination of the graphite in advance of recycle, and for the production of a gas fraction, concentrated in ^{14}C which is applicable to further purification (e.g. isotope separation) into a form suitable for use in the radiopharmaceutical industry.

Graphite has a porous structure. A proportion of the pore volume is open, meaning it is connected with the gas atmosphere in which the graphite resides. During operation isotopes such as ^{14}C and tritium may accumulate on the surface of the reactor graphite pores through a variety of possible mechanisms:

- Isotopes formed in the bulk gas phase may diffuse into the pore volume and deposit on the pore surfaces.
- Species absorbed on the surface of the pores during manufacture, or during exposure of the graphite in air, may be activated in the neutron flux. This mechanism is particularly relevant to nitrogen species yielding ^{14}C, but may be relevant to other nuclides as well. such as the ^{14}N in the closed pores, left over from the manufacturing processes.

Any of the above mechanisms may yield a pore surface layer enriched in radioactive isotopes, which might then be released by heating either in an inert atmosphere or one which encourages gasification of carbon, such as steam. This "roasting" procedure might then yield a small fraction of the graphite in gaseous form containing a

significant proportion of the ^{14}C inventory, which would be a most desirable outcome – effectively partially decontaminating the graphite.

2.3 Chemical Decontamination

The removal of radioactivity by deliberate pre-leaching or 'washing' (enhanced by chemical and physical means) could have useful benefits in reducing the radioactive inventory of the graphite. This process could utilise known leaching kinetics possibly assisted by surfactants and sequestering agents; this process has yet to be proven although when considering the volumes of graphite involved and the generation of waste from the 'washing' process, this may not be a viable option for the majority of the activated graphite inventory.

2.4 Intercalation / Exfoliation

Intercalation / exfoliation of the graphite provides an opportunity to significantly increase the surface area of the graphite accessible, therefore providing the potential for optimised removal of key radionuclides (e.g. ^{14}C, ^{3}H), a notable percentage of which would otherwise be inaccessible within the graphite lattice.

This approach has been investigated as part of WP2 of the Carbowaste project, with a specific focus on the potential recycle of irradiated HTR graphite. One of the conclusions from this area of work, which is reported under Deliverable T-2.4.5 is that the industrial recycling of graphite separated from TRISO particles via preparation of graphite intercalated compounds (GIC's) may be an attractive way to recycle the graphitic waste for industrial and environmental applications, especially when considering the high quality of the GIC's and exfoliated graphite (EG) obtained at room temperature as part of this test programme.

2.5 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 [5].

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.

2.6 Discussion

Although it may be possible to decontaminate graphite efficiently to remove most radioisotopes, there will still be residual ^{14}C in any products manufactured from recycled graphite. In order to make these products the manufacturing plants involved will have to have appropriate design and licensing to handle mildly radioactive materials. Provided there are no significant gamma-emitting radioisotopes present, there will be no need for radiation shielding, but the manufacturing process will have to be fully enclosed to prevent the atmospheric release of ^{14}C in gaseous or small particulate form. Because of the complications involved in this, and also the licensing and administrative requirements involved, it only seems practical if the facilities involved are relatively simple and involve only a small portion of the manufacturer's total operation. Once produced the products will have to be contained in appropriate packaging and treated as radioactive material until installed in their new use.

3 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:

3.1 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.

3.2 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.

3.3 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.

4 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.

4.1 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 4.1 below)

Table 4.1 - 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 4.2).

Table 4.2 - 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 %

4.2 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 4.1 (below) and 4.2 (overleaf) show the patterns of the 002 peak for both materials with different heat treatment temperatures.

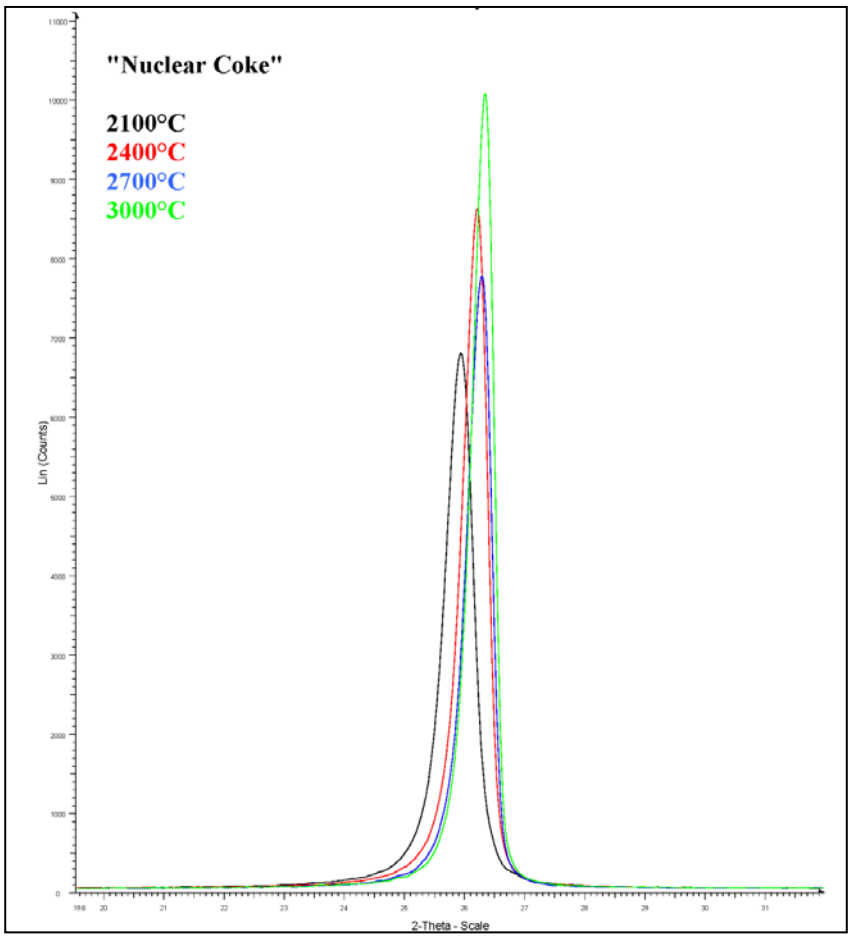

Figure 4.1 - Diffraction pattern of 002 peaks vs. Heat-Treatment Temperature for Coke

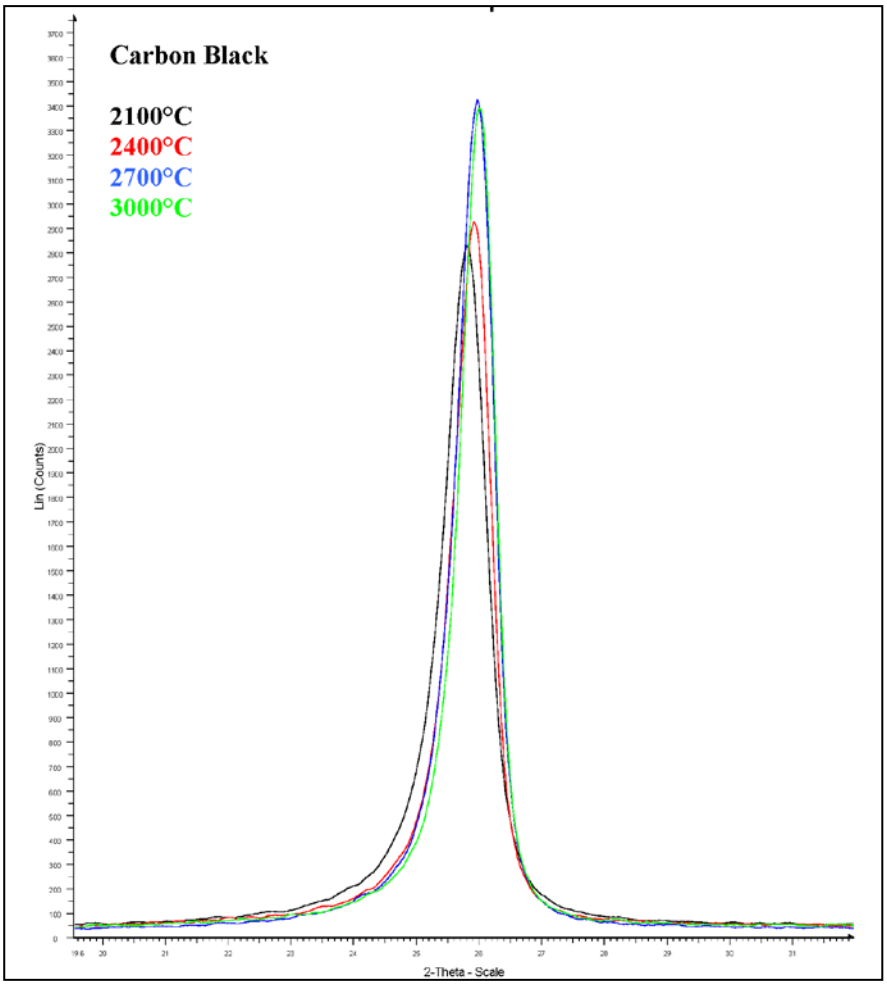

Figure 4.2 - Diffraction pattern of 002 peaks vs. Heat-Treatment Temperature for Carbon Black

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 4.3 and Figure 4.3 below).

Table 4.3 - 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

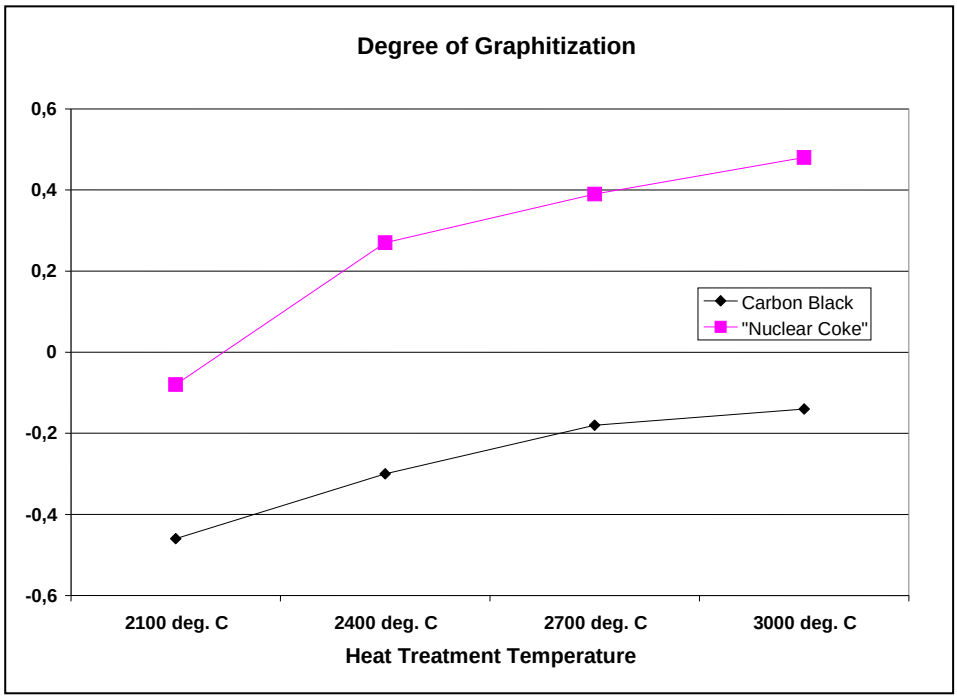

Figure 4.3 - Degree of Graphitization as a Function of Heat Treatment Temperature

4.3 Density Measurements

Samples from 3.1 were tested for density using the pycnometer method, with xylene as solvent [3]. Results are summarized in Table 4.4.

Table 4.4 - 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

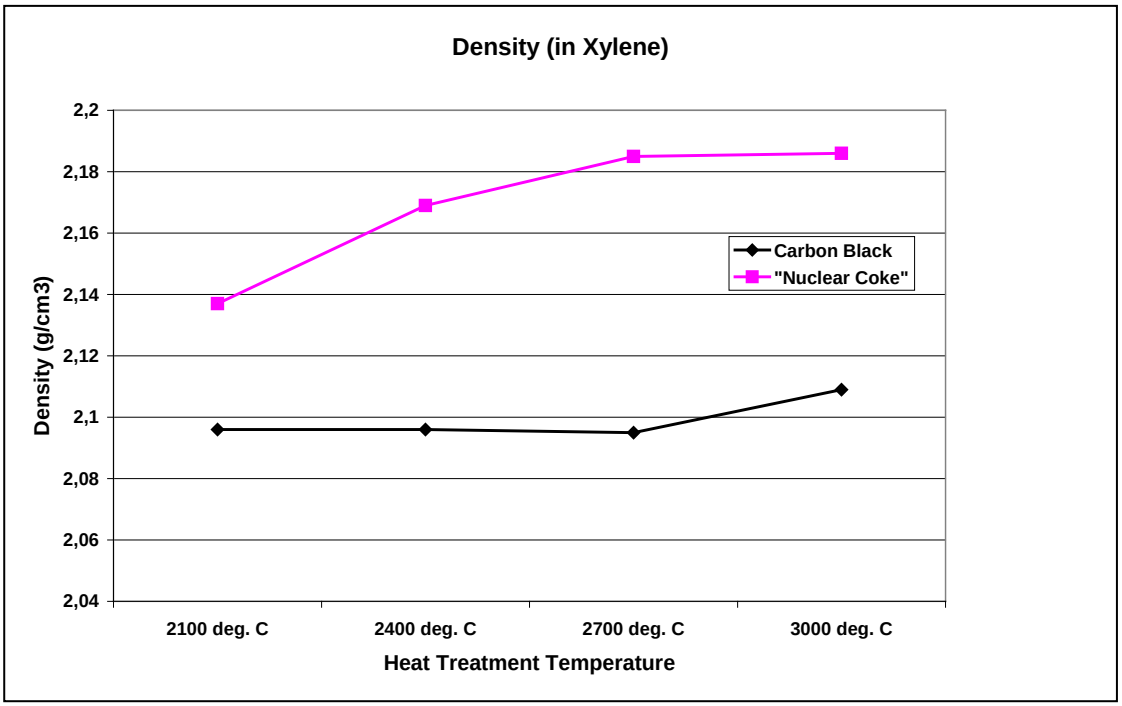

Figure 4.4 - Evolution of Density as a Function of Heat Treatment Temperature

4.4 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 [6].

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.

5 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 5.1 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

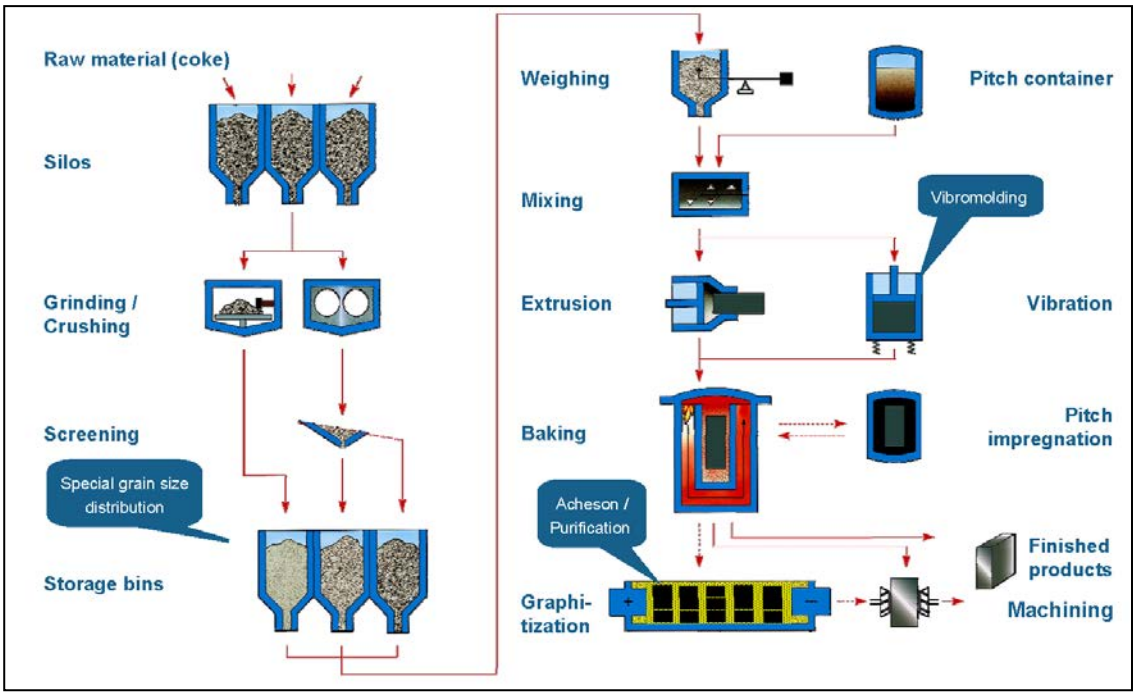

Figure 5.1 - Industrial Nuclear Graphite Production Process (schematic)

The pilot plant process utilized followed the principle way of industrial nuclear graphite production (Fig. 5.1 and [7]), 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 5.2) by uniaxial hydraulic block-pressing. Trial 2 required approx. 15 % more binder addition.

Figure 5.2 - 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 5.3, Table 5.1).

Figure 5.3 - 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 5.1 - 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

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.

6 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. [8].

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.

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

CCS	Carbon Capture and Storage
CPC	Calcined Petroleum Coke
DBP	Dibutyl Phthalate
EG	Exfoliated Graphite
GIC	Graphite Intercalated Compound
HTR	High Temperature Reactor
ILW	Intermediate Level Waste
LLW	Low Level Waste
NBG	Nuclear Block Graphite
pph	Parts per hundred
PSA	Pressure Swing Adsorption
SiC	Silicon Carbide
TRISO	Tristructural-isotropic
US DoE	United States Department of Energy
XRD	Powder X-ray Diffraction

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