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 (T-5.4.1)
Properties and Characterisation of Recycled Materials

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

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

Date of issue of this report: 29/02/2012

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	

Distribution list

Person and organisation name and/or group	Comments
D. Bradbury - Bradtec	
G.R. Elder - Bradtec	
P Homerin - GrafTech	
L Batty - GrafTech	
T Albers - GrafTech	
W von Lensa - Jülich	
F Hiltmann – SGL Carbon	
E Visser Tynova - NRG	
K Shropshire - NRG	
R Hania - NRG	
European Commission	

CARBOWASTE		
Work package: 5 **Task: :** 5.4.1	**CARBOWASTE document no:** CARBOWASTE-1202 - D-5.4.1 (e.g. May 2008 as date of issue: 0805)	**Document type:** D
Issued by: Bradtec (UK) **Internal no.:** Bradtec Report No 1107		**Document status:** Final

Document title

Properties and Characterisation of Recycled Materials

Executive summary

Work Package 5 of the Carbowaste Project is focused on creating opportunities to reuse or recycle graphite. This report forms the deliverable to Task 5.4.1 – Properties and characterisation of recycled materials. The data provided in this report has been derived from the laboratory analysis and characterisation of candidate products produced in support of the aims of Work Package 5.

The use of carbon black as a surrogate material was selected by the graphite manufacturers as a suitable material to incorporate into their pilot plant production process. In addition, the complete gasification of irradiated graphite would result in a 'syngas' (CO) which could be redeposited into a solid (carbon black) via the Sabatier Bosch reactions, thereby providing partial decontamination of the original graphite (see Carbowaste Report D.5.3.2).

The work reported includes:

- GrafTech's work on producing candidate products via that 'fast processing' route to assess the potential and limitations of incorporating recycled graphite (in the form of carbon black) into new graphite products (electrodes for waste vitrification) for use within the nuclear industry.
- SGL Carbon's work has been focused on incorporating recycled graphite (again in the form of carbon black) into new nuclear grade graphite, for potential use in new nuclear graphite for uses which include moderator graphite.
- NRG's work has been focused on the formation of Silicon Carbide from both virgin and irradiated graphite, for its potential use as a packing material for fuel wastes within a repository setting.

In addition to the data gathered under the Carbowaste project, other related work undertaken on behalf of the US DOE by Oak Ridge National Laboratory and GrafTech is covered. This work has looked specifically at the direct recycle of graphite (both virgin and irradiated) into new graphite for nuclear applications.

This report provides a summary of the data available on recycled graphite properties and characterisation undertaken to date.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	29.02.2012	Final report	Jon Goodwin	D Bradbury	D Bradbury	D Bradbury
2						

Contents

Executive Summary 3
1 Introduction 6
2 GrafTech – Graphite Electrodes 7
2.1 Candidate Products 7
2.2 Results and Discussion 8
2.3 Conclusions 12
3 SGL Carbon – Nuclear Graphite 13
3.1 Experimental Procedure 13
3.2 Laboratory Results 17
3.3 Conclusions and Recommendations 20
4 NRG – Silicon Carbide 22
4.1 Experimental Procedures 23
4.1.1 Raw Materials 23
4.1.2 Experimental Set-up 24
4.1.3 Experimental Procedure 25
4.2 SiC Formation from Virgin Graphite 27
4.2.1 SEM Analysis of Raw Materials and Formed SiC 27
4.2.2 XRD Analysis of Formed SiC 29
4.3 SiC Formation from Irradiated Graphite 34
4.3.1 SEM Analysis of SiC Formed From Irradiated Graphite 34
4.3.2 XRD Analysis of SiC Formed from Irradiated Graphite 36
4.4 SiC Formation from Irradiated Graphite for Leaching Experiments 40
4.5 Conclusions 42
5 US DOE Deep Burn Program 43
5.1 Introduction 43
5.2 Experimental 46
5.2.1 Materials 46
5.3 Results and Discussion 48
5.3.1 Bulk Density 48
5.3.2 Elastic Modulus 48
5.3.3 Electrical Resistivity 48
5.3.4 Coefficient of Thermal Expansion 49
5.4 Conclusions 49
6 Discussion 50
Glossary 52
References 53

1 Introduction

This report is in response to the Task 5.4.1, 'Properties and characterization of recycled materials', which is the first Task under the Task 5.4 - Products Evaluation of Work Package 5 (Recycling & New Products) of the Carbowaste Project.

This report provides a summary of the properties and characteristics of the recycled graphite products produced under WP5 by various contributing organizations which include GrafTech, SGL Carbon and NRG.

GrafTech's contribution has involved the production recycled graphite via their innovative, fast processing technique, also utilizing carbon black (again, to represent the recycled graphite component), to produce graphite electrodes for use in within the nuclear industry for waste vitrification [1].

SGL Carbon's contribution has involved the production of recycled graphite, containing a proportion of carbon black (to represent the recycled graphite component), for use as a nuclear grade graphite for moderator or other similar reactor applications [2].

NRG's contribution has been the production of Silicon Carbide (SiC), from both virgin and irradiated graphite, with various potential end uses which includes its use as a ceramic for embedding spent fuels. Further work by NRG is currently under way which is looking at the silicon carbides leaching characteristics, and these results will be reported as part of Task 6.2 'Disposal behavior of carbonaceous wastes' [3].

In addition to the work directly attributed to WP5 of the Carbowaste project; the results of work undertaken for the US DoE under their Deep Burn Project, by GrafTech and Oak Ridge National Laboratory have also been reviewed [4]. This work has considered the direct reuse of graphite (without gasification) as opposed to the route used under WP5, where the graphite is gasified, and then redeposited as carbon black thus providing partial decontamination in advance of recycle.

This report therefore provides the results of the work undertaken to date relating to the properties and characteristics of recycled graphite.

2 GrafTech – Graphite Electrodes

GrafTech International has investigated the possibility of using a so-called "fast" manufacturing process to fabricate small scale graphite electrodes to be used for the vitrification of nuclear waste. This graphite electrode has been made from a maximum fraction of carbon black that could potentially be derived from the purification of irradiated graphite waste.

GrafTech fabricated 5 different varieties of graphite material that are made with 0 to 10 % carbon black (% carbon black will be based on the dry fraction of the mix design) in order to evaluate the change in properties that occur as the fraction of carbon black within the graphite increases. They have manufactured several small billets at each of the described fractions of carbon black using their fast processing technology that allows them to reduce the standard production time required to fabricate synthetic graphite artifacts.

After manufacture, the material was characterized for coefficient of thermal expansion, sonic modulus, specific resistance, density and flexural strength. Also, optical microscopy was used to evaluate the structure of the formed artifacts [1].

2.1 Candidate Products

Small scale graphite electrodes have been fabricated using a mixture of petroleum coke, binder (coal tar) pitch and varying fractions of carbon black additive. These ingredients have been mixed together at room temperature using pitch in the solid form. The pre-made mixtures vary in carbon black content according to Table 2.1 below:

Table 2.1 – Carbon Black Content of Candidate Products [1]

Mixture	% Carbon Black (Thermax)
A – control	0
B	1
C	2
D	3
E	4
F	5
G	10

The amount of pitch in each mixture has been optimized for the manufacturing conditions and the varying fraction of carbon black. For example, artifacts made with higher amounts of carbon black require additional fractions of binder pitch. If too little binder pitch is used, the integrity of the formed artifact may become brittle and the structure questionable.

The formulations described above were processed using a proprietary fast processing technique wherein the typical processing time for the manufacture of graphite is decreased. Use of this technique minimizes the handling time of the material, and greatly reduces processing costs and lead times.

Mixture "G" was not able to be processed, as large aggregates of carbon black resulted in selected areas of the final artifact to become very brittle. The attempts at this large fraction of carbon black need to be reformulated to achieve improved results [1].

2.2 Results & Discussion

Optical microscopy images taken of representative areas of the final graphitic artifacts produced for this work are shown in Figure 2.1 overleaf. Uniform structure is evident in the artifact, aside from aggregates of carbon black that seem to appear with increased loading of the non-graphitizable particles, as seen in Figure 2.2 (overleaf). It is postulated that increased mixing time may help to correct the formation of the carbon black aggregates and in turn increase the overall processability, uniformity and quality of the final material [1].

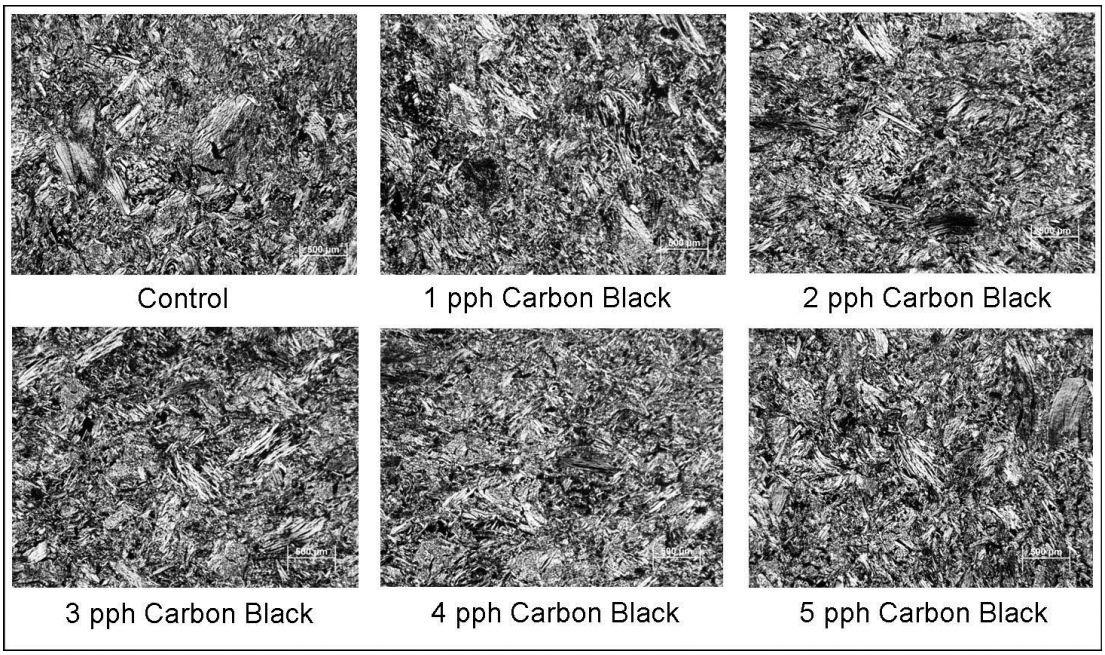


Figure 2.1 - Comparison of graphite artifacts made with varying concentrations (%) of carbon black. Images show uniform areas of graphitized material [1].

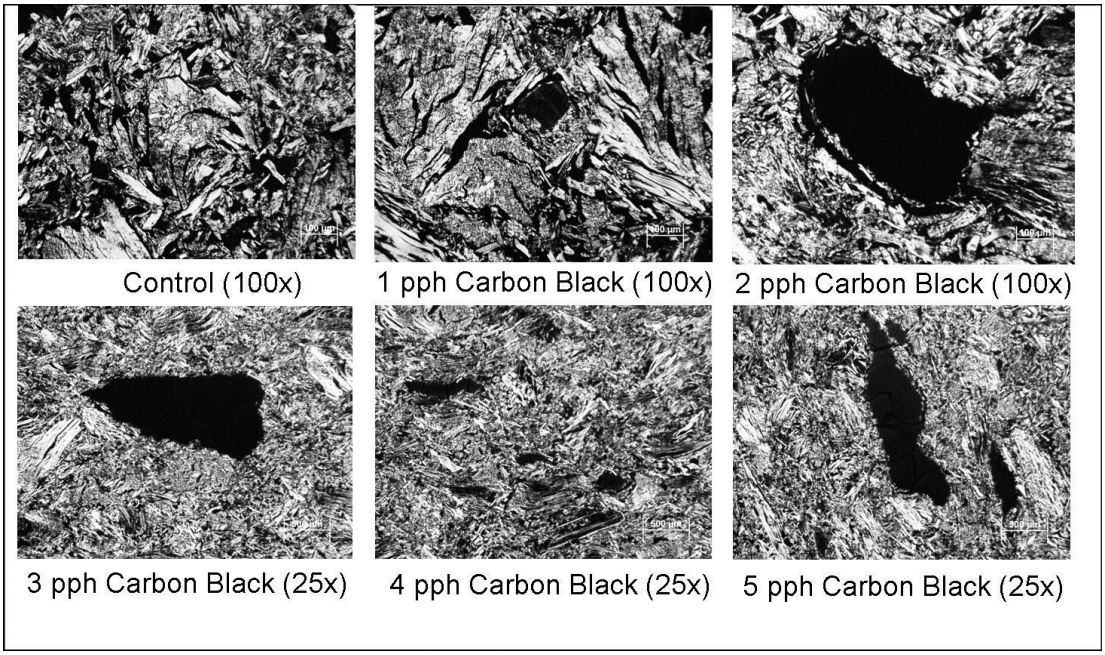


Figure 2.2 - Optical microscopy images showing aggregation of carbon black due to lack of sustained mixing. Carbon black aggregates show as dark areas in polarized light [1].

Other analysis performed on the graphite artifacts included density, flexural strength (Figure 2.3), coefficient of thermal expansion (Figure 2.4), thermal conductivity (Figure 2.5, overleaf), Young's modulus and specific resistance (Figure 2.6, overleaf). All figures show two samples tested for each value of carbon black loading [1].

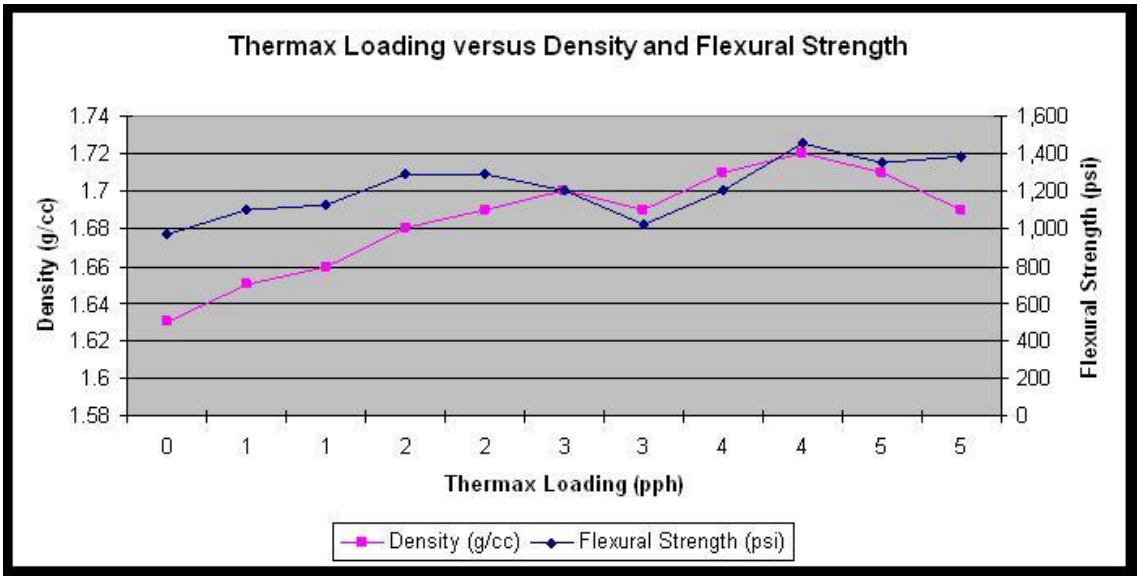


Figure 2.3 - Results of measured density and flexural strength at various levels of carbon black loading [1].

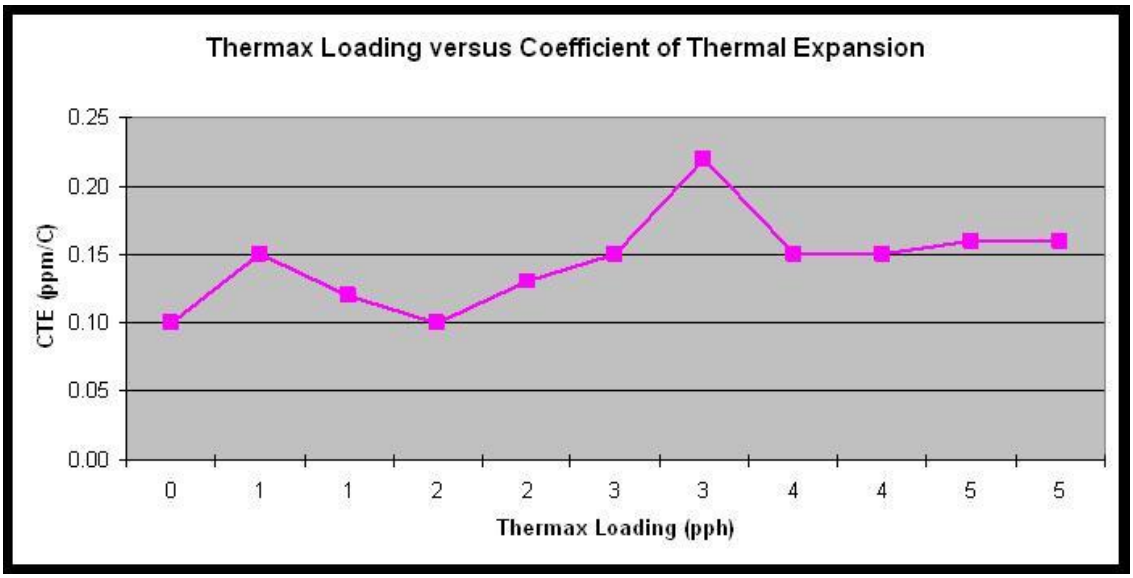


Figure 2.4 - Measurement of the slight change in CTE as a function of carbon black loading [1].

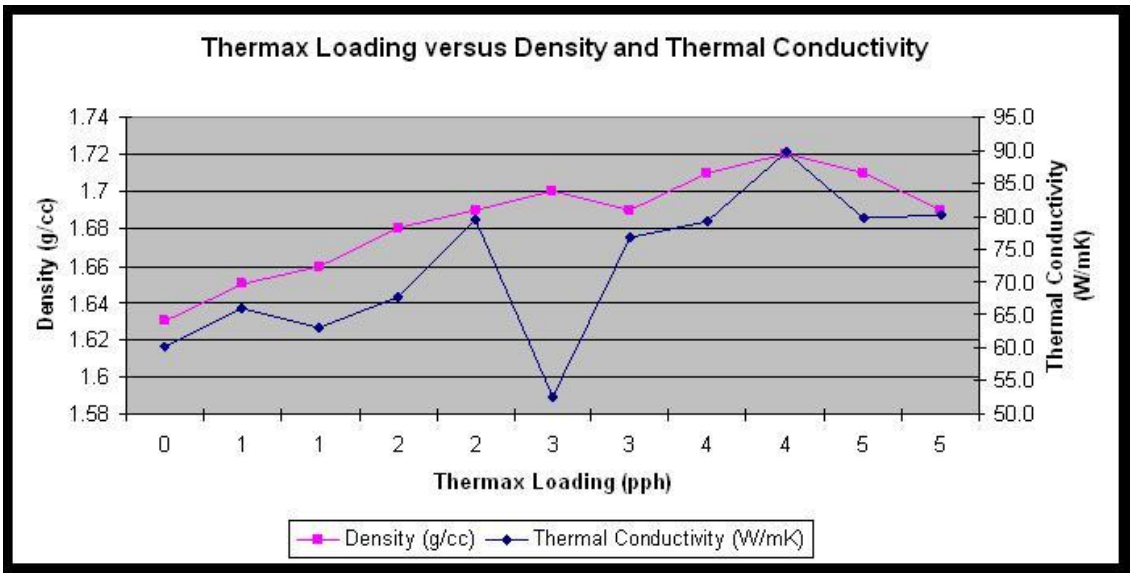


Figure 2.5 - Measurement of the density and thermal conductivity of graphite made with varying levels of carbon black [1].

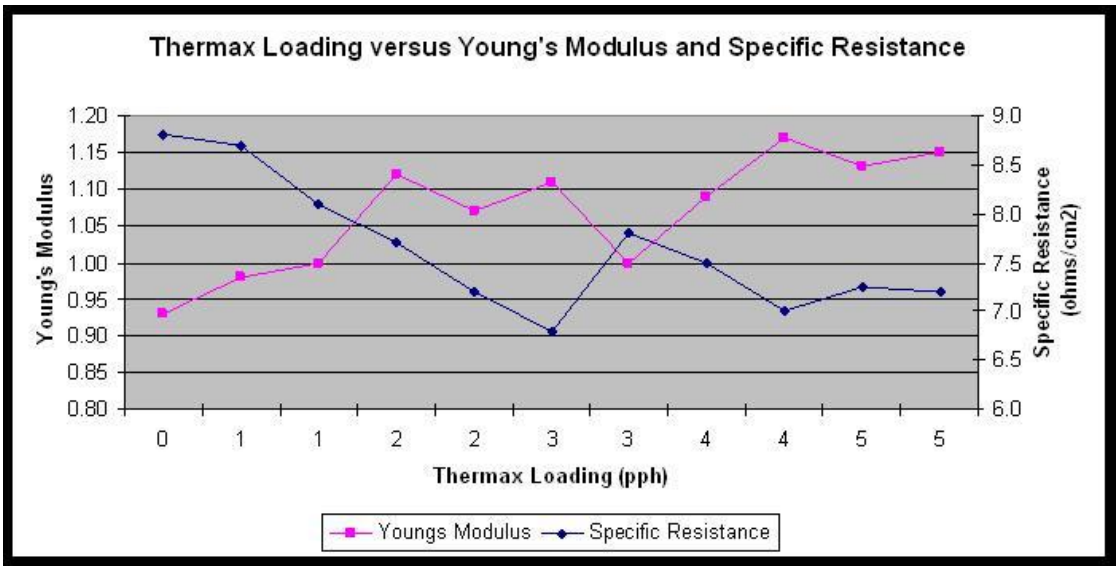


Figure 2.6 - Variation in Young's modulus and SR with varying levels of carbon black loading [1].

While some variations are measured for the properties of the graphite artifacts, no significant deviations out of the range of acceptable properties were realized [1].

2.3 Conclusions

Carbon black can be utilized as a filler material in new graphite artifacts. These materials can be manufactured using a fast-processing technique that reduces the total amount of material handling, as well as the total processing time. This process is of a significant advantage to the nuclear industry when considering the possibility of using previously irradiated, and processed materials into new artifacts for re-use.

The work completed under this program has demonstrated that carbon black loading can easily be accomplished up to 5pph of the dry fraction of the material. Higher loading could probably be achieved by focusing on other methods to ensure more homogeneous mixtures prior to forming the artifact. Work in this area could help to alleviate significant aggregates of carbon black material that are seen via optical microscopy in the final product.

The final properties of the graphite manufactured for this project are within the range of 'acceptable' graphite material for the purpose of vitrification of nuclear waste. Further development work could also be done to significantly strengthen this material and improve the other basic properties of the graphite [1].

3 SGL Carbon – Nuclear Graphite

SGL Carbon has investigated the incorporation of carbon black into the production process of nuclear graphite for use in graphite moderated reactors. Carbon black represents their chosen intermediate material which can be reached through the gasification or graphite, and subsequent redeposition via the Sabatier Bosch reactions, and is therefore a potential route for partially decontaminated graphite to be recycled through its inclusion in new nuclear graphite.

The production of candidate products was undertaken at SGL Group's Raciborz facility in Poland. For both legal and technical reasons decontaminated i-graphite for the trails was not available, and therefore all trials used carbon black as a substitute. Specific formulations based on SGL Group's industrial grade NBG-18 were tested in pilot plant scale and were analysed by standard quality control methods appropriate for synthetic graphite [2].

3.1 Experimental Procedure

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

- Isotropic pitch coke, as typically used for nuclear graphite production
- Carbon black, grade P-803, from Konimpex, Poland (properties see Table 3.1)

Table 3.1: Product properties for Carbon Black P-803 [2]

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 pilot plant process utilized followed the principle way of industrial nuclear graphite production (Fig. 3.1 and [5]), which consists of raw material preparation by crushing and screening, mixing in defined proportions with pitch, shaping by extrusion or vibromolding, 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 vibromolding 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. Isomolding was not considered as this requires a completely different raw material preparation and green process, and moreover, no internal reference was available [2].

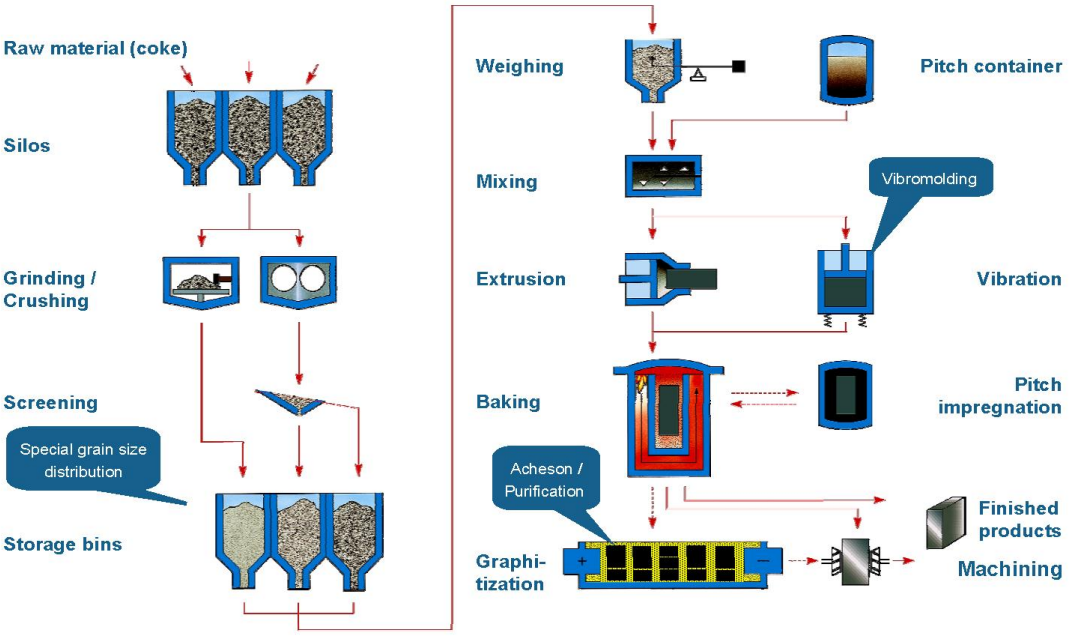


Figure 3.1 - Nuclear Graphite Production Process (schematic) [2]

The coke was prepared in the conventional way, i.e. crushing, milling, and screening into defined grain fractions with a maximum grain size of 1.6 mm. Part of the coke was milled down to flour with an approximate maximum particle size of 200 microns. Carbon black replaced this flour fraction, in order to keep the overall granulometry constant. Carbon black was used as received from supplier.

As concluded from graphitization tests with coke and carbon black [6], the maximum content of carbon black was set to 15 %, which resulted in dry aggregate compositions for the trials, as listed in Table 3.2 (overleaf). Reference formulation was SGL GROUP's grade NBG-18.

Table 3.2 - Dry aggregate compositions for pilot plant trials [2]

	Reference	Trial 1	Trial 2
Coke	100 %	92.5 %	85 %
Carbon Black	-	7.5 %	15 %

30 kg of the dry raw material mixes each were mixed with conventional coal-tar binder pitch (softening point 84 ºC (KS)) in a sigma-blade mixer for 50 minutes at 160 ºC. The binder contents were determined empirically with regard to the plasticity of the resulting carbonaceous paste. The pitch amount increased with increasing carbon black content in the formulation (Table 3.3). The relative binder amount considerably increased by 13.6 % from reference to Trial 2 (15 % carbon black addition).

Table 3.3 - Coal-tar pitch binder content in green mixes [2]

	Reference	Trial 1	Trial 2
Dry Aggregate	84.6 %	83.4 %	82.5 %
Binder Pitch	15.4 %	16.6 %	17.5 %

The resulting carbonaceous paste was transferred to the mould of the pilot plant hydraulic block press and shaped at a pressure of 28 MPa under vacuum of 150 mbar. The green blocks of approximate dimensions 200 x 200 x 220 mm were measured for geometrical apparent density (Table 3.4).

Table 3.4 - Green apparent density of pilot plant blocks [2]

	Reference	Trial 1	Trial 2
Green Apparent Density	1.65 g/cm^3	1.64 g/cm^3	1.61 g/cm^3

The green blocks were embedded in coke breeze and baked in a Nabertherm® chamber furnace with a cycle time of 325 hours with a maximum temperature of 850 ºC held for 16 hours (Figure 3.2).

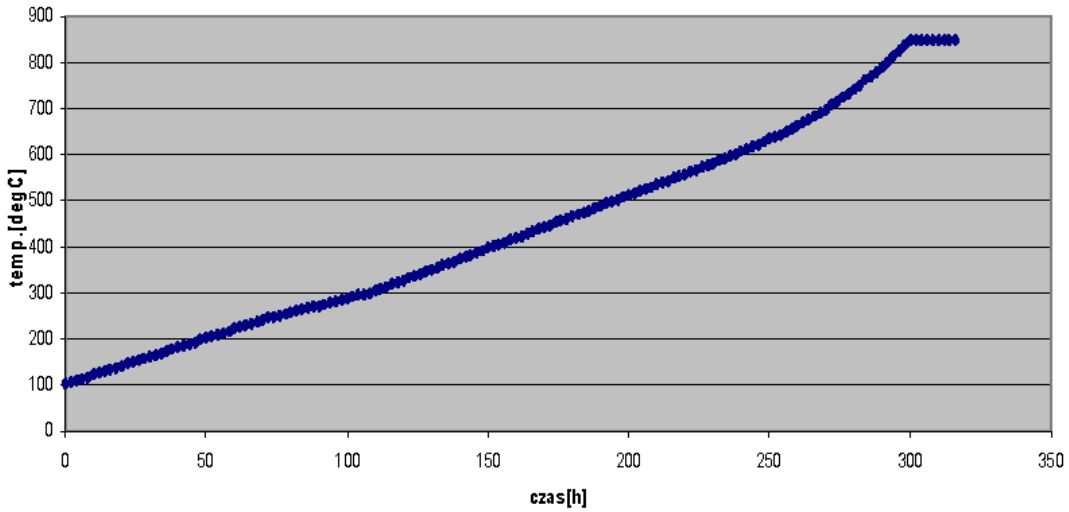


Figure 3.2 - Baking cycle (temperature vs. time [h]) [2]

After baking, the blocks were impregnated twice with conventional coal-tar impregnation pitch (softening point 60 ºC (KS)) to improve mechanical strength and provide a good thermal conductivity after graphitization. After heating the samples to 300 ºC in an autoclave, vacuum (50 mbar) was applied for 15 minutes. After immersing the samples in the autoclave in liquid impregnation pitch with a temperature of 210 °C, a nitrogen pressure of 7 bar was applied for 2 h to secure impregnation of the entire sample. After each impregnation step the samples were embedded in coke breeze and carbonized at 850 ºC (162 h cycle, soaking time 12 h) in a Nabertherm® chamber furnace. The reduction in baking cycle time for baking a baked/impregnated vs. a green body is typical due to the lower sensitivity of an already baked material.

As final heat treatment step, the blocks were loaded in an Acheson lab graphitization furnace and heated up to 2900 ºC. After cooling down, cores were drilled from the lab samples for lab analyses. The visual appearance of the blocks and core samples was normal (Figure 3.3, overleaf) [2].

Figure 3.3 - Samples after graphitization (from left to right: Reference, Trial 1 with 7.5% carbon black, Trial 2 with 15% carbon black) [2]

3.2 Laboratory Results

The bulk density of the trial blocks was measured after each process step. After the final graphitization step, differences from previous process steps basically levelled off, i.e. the resulting Bulk Density was practically the same, as shown in Figure 3.4.

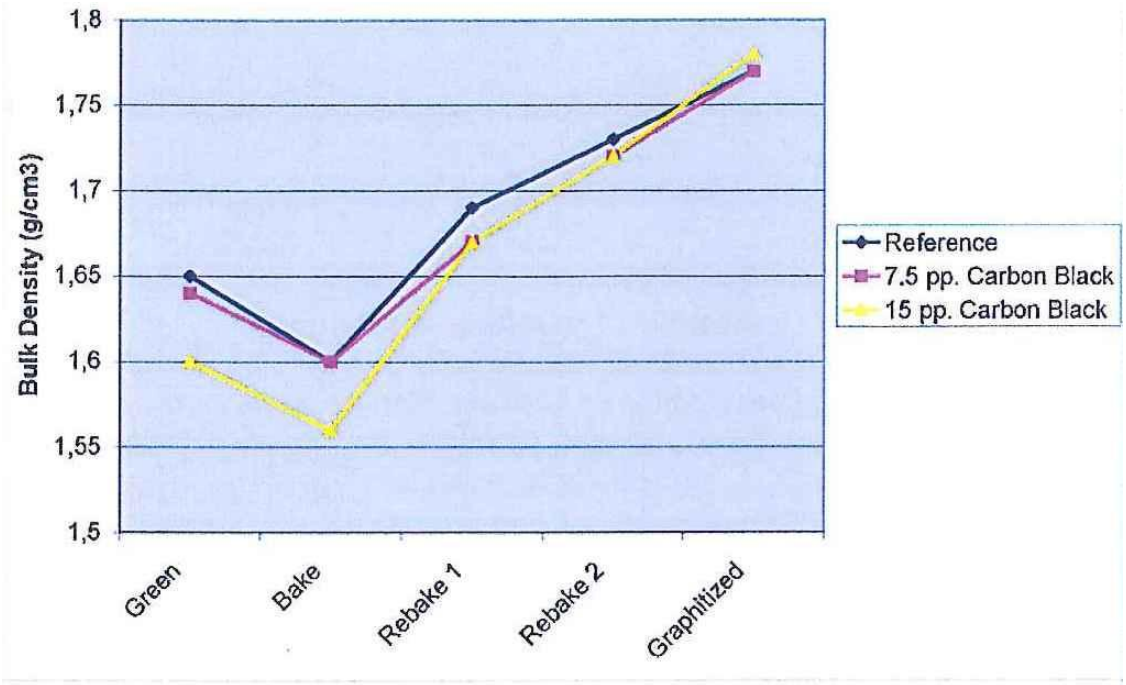


Figure 3.4: Evolution of Bulk Density of the Pilot Plant Trial Materials [2]

Core samples were taken from the blocks, as shown in Figure 3.3 and submitted to lab analyses in Quality Lab of Raciborz plant (Table 3.5, overleaf).

Table 3.5 - Laboratory data for pilot plant trial materials [2]

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°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

It became obvious, that there is considerable impact on the mechanical and thermal properties of the graphite material. The addition of 15 % carbon black dramatically decreased mechanical strength – both compressive and flexural – by up to about 70 % and thermal conductivity by 32 % vs. Reference.

The measurements on Apparent Density confirmed the results measured on full blocks, i.e. no particular impact of carbon black addition.

The trends on mechanical strength (Figure 3.5) and thermal conductivity (Figure 3.6) become even more prominent when plotted against the content of carbon black. For smoothness, against- and with-grain figures were averaged [2].

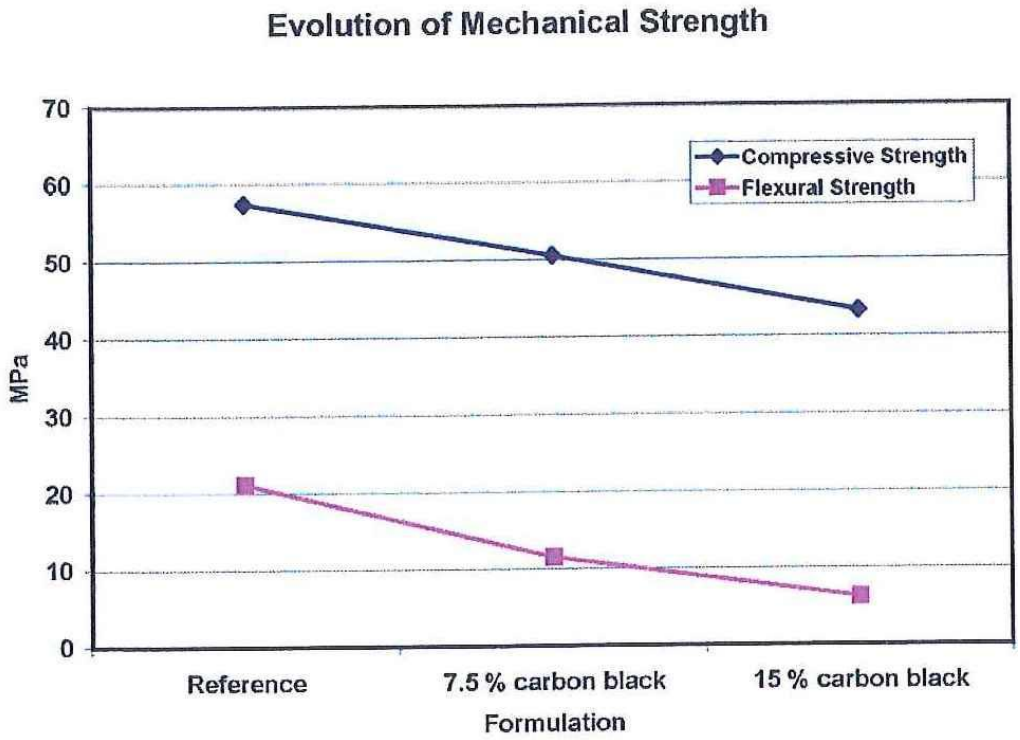


Figure 3.5 - Evolution of mechanical strength with amount of carbon black addition [2]

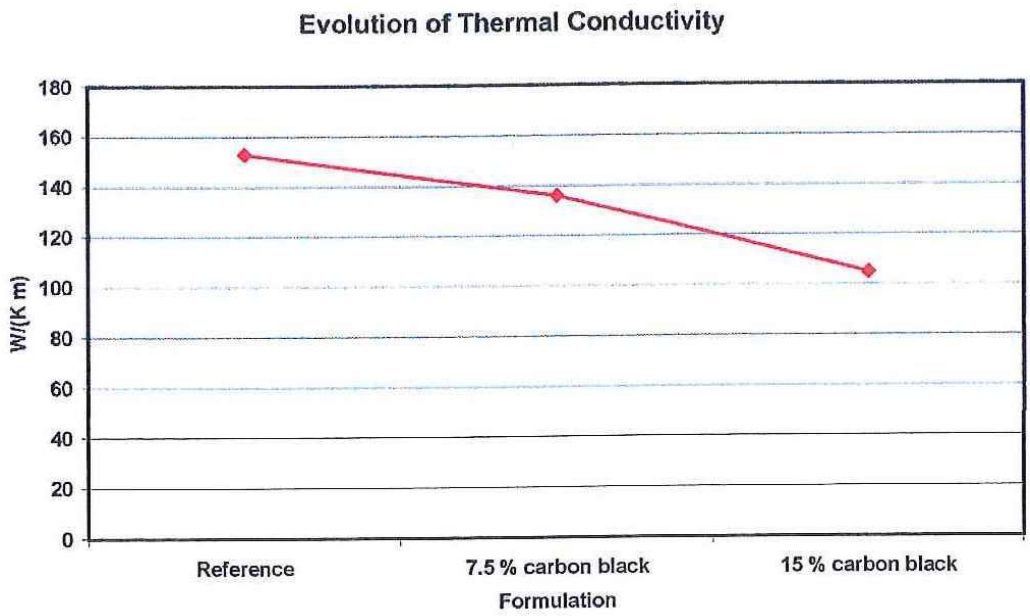


Figure 3.6 - Evolution of thermal conductivity with amount of carbon black addition [2]

3.3 Conclusions and Recommendations

The trials with addition of carbon black as surrogate for decontaminated i-graphite revealed several aspects with regard to potential application in industrial scale. The addition of carbon black as raw material had a significant impact on the binder demand.

Due to its finer particle size vs. coke flour and therefore higher surface area binder demand increases. While this is less critical for pilot plant scale trials, one can envisage a bigger impact for industrial-scale blocks with dimensions of 500 x 500 x 2000 mm or bigger. Then, a higher binder content can create a higher porosity due to escape of more volatiles during baking (binder pitch carbonization). In worst case, cracks and structural defects occur in the material. To the same extent this can be counteracted with additives or modified baking curves, but one can assume that 15 % of carbon black will exceed this limit.

Regarding material properties, a significant and increasing deterioration of mechanical and thermal characteristics is observed with increasing amounts of carbon black in the formulation. Especially the flexural strength suffers from the presence of carbon black. This can cause safety concerns when moderator or reflector blocks will be under thermo-mechanical stress during reactor start-up and operation including shrinkage/swelling under irradiation. A high thermal conductivity for good heat flux to transfer thermal energy to the cooling gas is another aspect to be considered. Also here, the addition of carbon black deteriorates the material properties as the response to heat treatment temperature is much less than coke. This cannot be healed as further increase of graphitization temperature would lead to further reduction of mechanical strength vs. reference material.

Overall, one can conclude from the results of the trials that maximum only 5-10 % of carbon black can be tolerated from process requirements 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. This, however, was outside the scope of this Task and Work Package 5 in CARBOWASTE [2].

4 NRG – Silicon Carbide

NRG under WP5, produced SiC (Silicon Carbide) under laboratory conditions using both un-irradiated and irradiated graphite. Following a detailed literature review into the potential methods for use in SiC formation, a voltage-assisted self –heat sustained method was chosen as the most suitable method to form SiC from graphite. This work led to the formation of crystalline pure SiC from virgin graphite. The same procedure was used to form SiC from irradiated graphite. A sufficient amount of SiC was prepared to be used for the leaching experiments in WP6.

The purpose of this work is to provide a basis for the use of using irradiated graphite through its conversion into SiC, to form recycled products which could include products specially manufactured to stabilise carbon in a radioactive waste disposal site, or to act as confinement or packing material for other wastes and thermal management, in the repository site. It addition, the use recycled graphite in the form of SiC could provide substantial opportunities to minimise waste volumes through its reuse in the coated-particle fuel for new HTR reactor designs [3].

Table 4.1 - The typical properties of Silicon Carbide (SiC) [3]

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

Because of its high hardness, 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 metal's and slag's), 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) [3].

4.1 Experimental Procedure

Based on the literature research, a method similar to the Morancais SHS method was used to form SiC from graphite and silicon. First, the method was tested with virgin graphite. When the procedure was modified and established, the formation of SiC from irradiated graphite could start [3].

4.1.1 Raw materials

The raw materials used for the laboratory scale production of Silicon Carbide were:

- Silicon powder (Alpha Aesar) – crystalline, 325 mesh, 99.5 % metal basis D50 – 4.29 µm
- Graphite powder (Alpha Aesar) – natural, universal grade, 200 mesh, 99.9995% metal basis
- Irradiated graphite – irradiated graphite from Carbowaste WP3 – RRT test was used, this graphite originates from UNGG, EdF. (The elemental analysis of blank graphite is presented in Table 4.2 below)
- Ethanol/methanol

Table 4.2 – Elemental Data for the irradiated graphite used for SiC formation (UNGG, EdF graphite sleeves)

Element	Conc. (ppm)	SD	SD/C
Mg	432	94	0.218
Al	963	369	0.383
Ti	225	89	0.395
Sr	93	15	0.156
Ag	69	4	0.065
Cd	25	8	0.307
Sn	**4563**	**3246**	**0.711**
Sb	21	3	0.168
Ca	9180	347	0.038
Fe	410	89	0.218
H	900	60	0.067
N	400	58	0.144

Element	Conc. (ppm)
Li	<12
Be	<12
V	<50
Mn	<10
Co	<5
Ni	<50
Nb	<10
Mo	<5
Cs	<5
Ba	<5
Eu	<5
Pb	<5
Si	<1000
O	<50
S	<50

NB: The Sn concentration is a cross contamination from the tool for taking samples.

4.1.2 Experimental Setup

A new setup for the experiment was built, as shown in Figure 4-1. 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 [3].

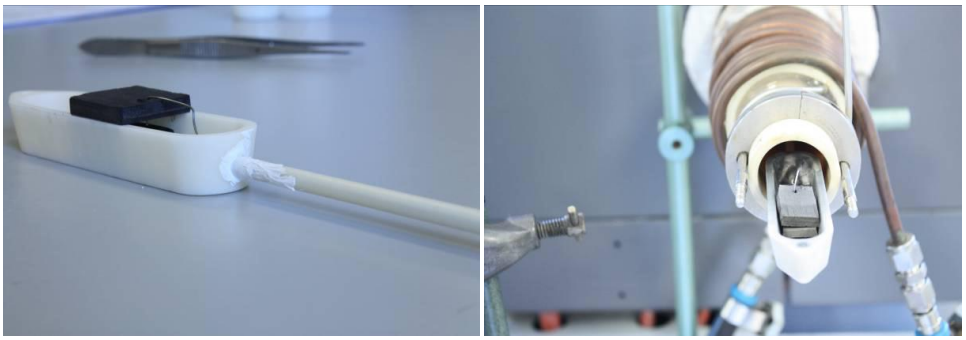


Figure 4.1 - Fixed dish to tube (left) and setup placed in the HTTF oven (right) [3]

4.1.3 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 60 min. in a ball mill IKA mixer. When the mixing was finished, the ethanol/methanol was evaporated and the powder mixture was pressed (low pressure) into a pellet suitable for the reaction setup. The sample was placed between two graphite discs, where molybdenum wires were placed for the voltage application at the desired temperature. This setup was put into the oven, the temperature program was applied, and then the voltage.

The following temperature program, slower than described by Morancais, et al. in reference [7] was used as the starting basis but was modified as experiments proceeded:

- 100°C/h to 200°C
- 200°C for 10 h
- 200°C/h to 1430°C
- 1430°C for 2h
- [voltage application]
- 200°C/h to RT.

When finished (see Figure 4.2, overleaf), the sample was taken from the setup and analyzed by XRD and SEM [3].

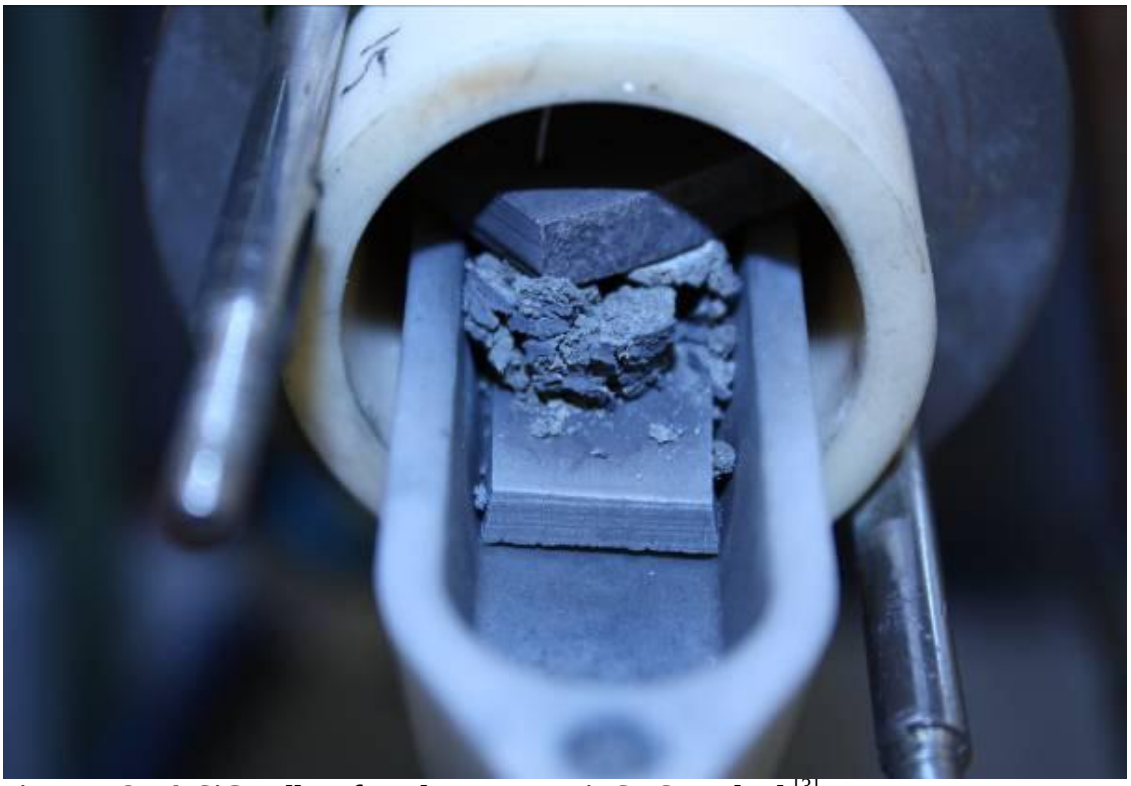


Figure 4.2 - A SiC pellet after the Morancais SHS method [3]

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.

4.2 SiC formation from virgin graphite

4.2.1 SEM analysis of raw materials and formed SiC

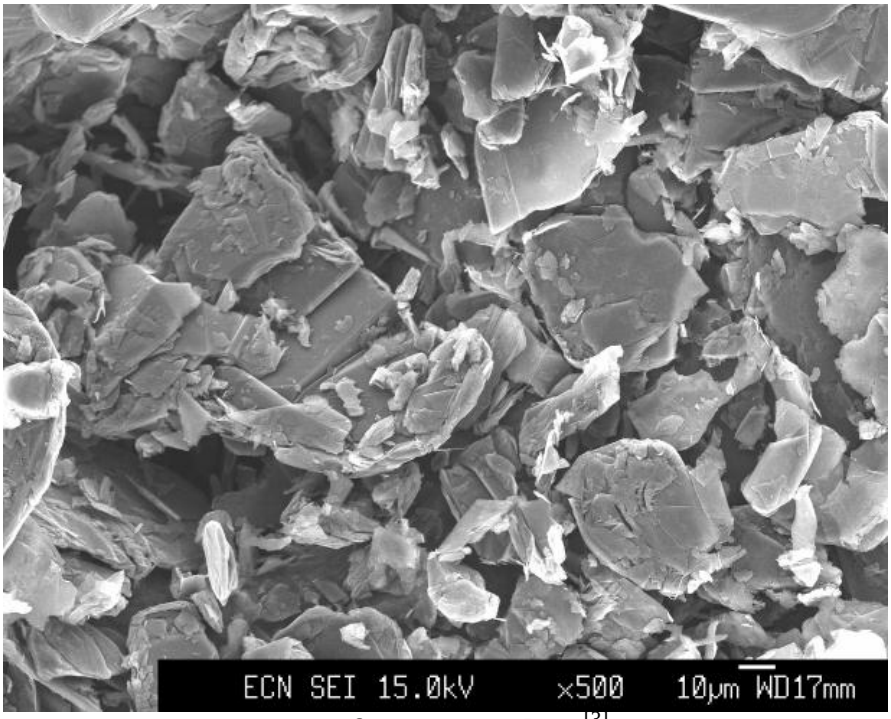


Figure 4.3 - SEM Image of virgin graphite [3]

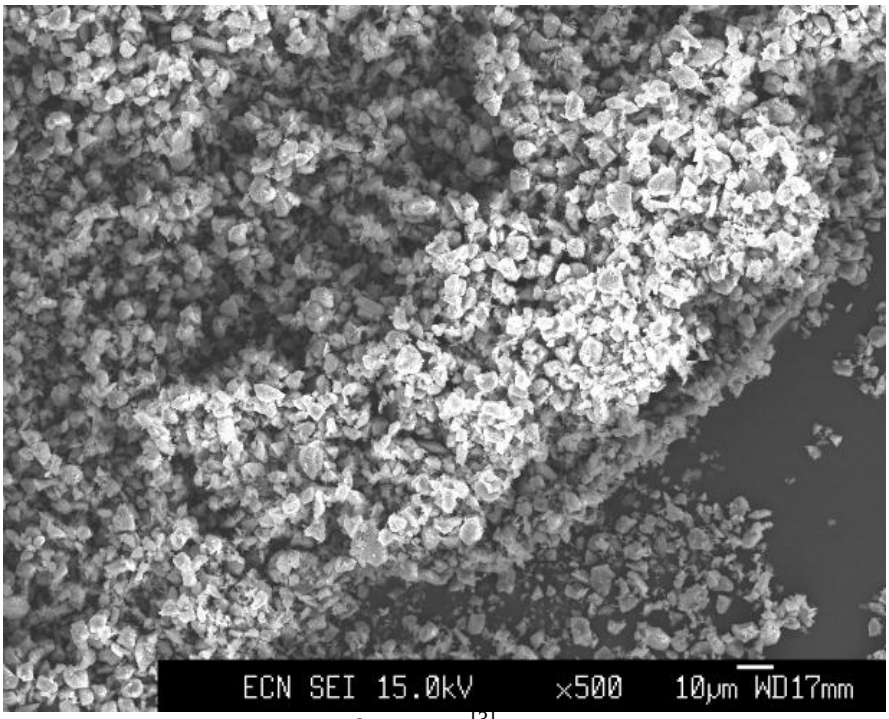


Figure 4.4 - SEM Image of Silicon [3]

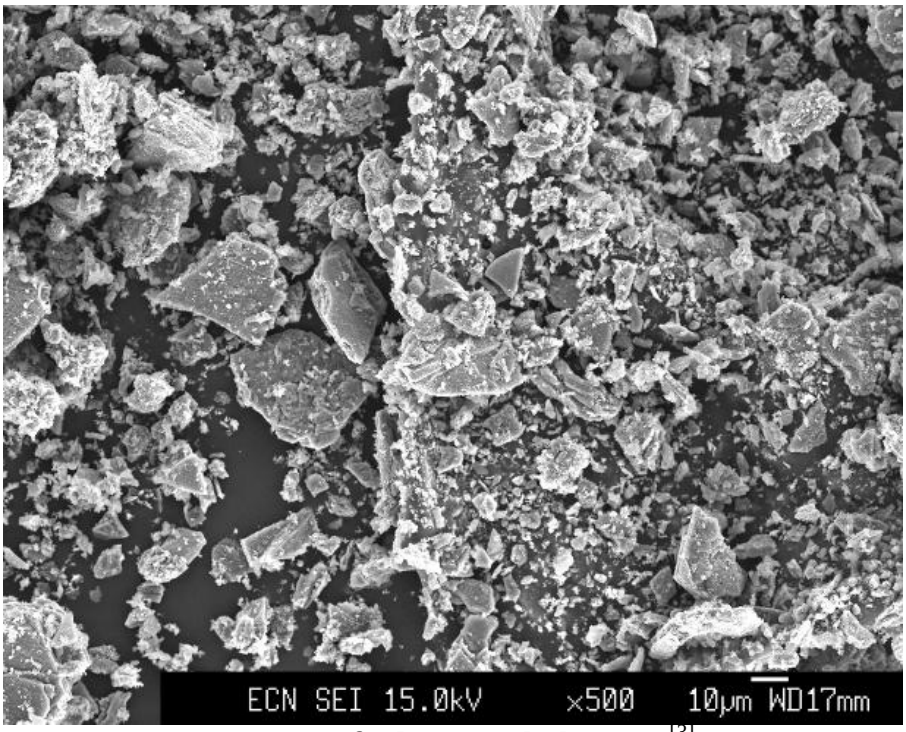


Figure 4.5 - SEM Image of Silicon Carbide (SiC) [3]

4.2.2 XRD analyses of formed SiC

X-ray powder diffraction (XRD, Bruker Advance D8) was used to evaluate the SiC formation by the Morancais SHS method, as well as SHS without voltage. All measurements were done at the ambient temperature, with angle of 20- 80 2θ.

All tested combinations of reaction conditions (see above Experiment Procedure) were measured by XRD, and results are presented in the following diffractograms, Figure 4.6 through to Figure 4.10.

In the diffractograms, colour patterns are used as follows: β - SiC, α- SiC, graphite and silicon.

Diffractogram 1
Original mixture (mengsel) of Si and graphite
SiC-02-002: after Morancais SHS (20 s, 0.8 V) reaction - Argon
SiC-02-004: after Morancais SHS (40 s, 0.8 V) reaction - noxal

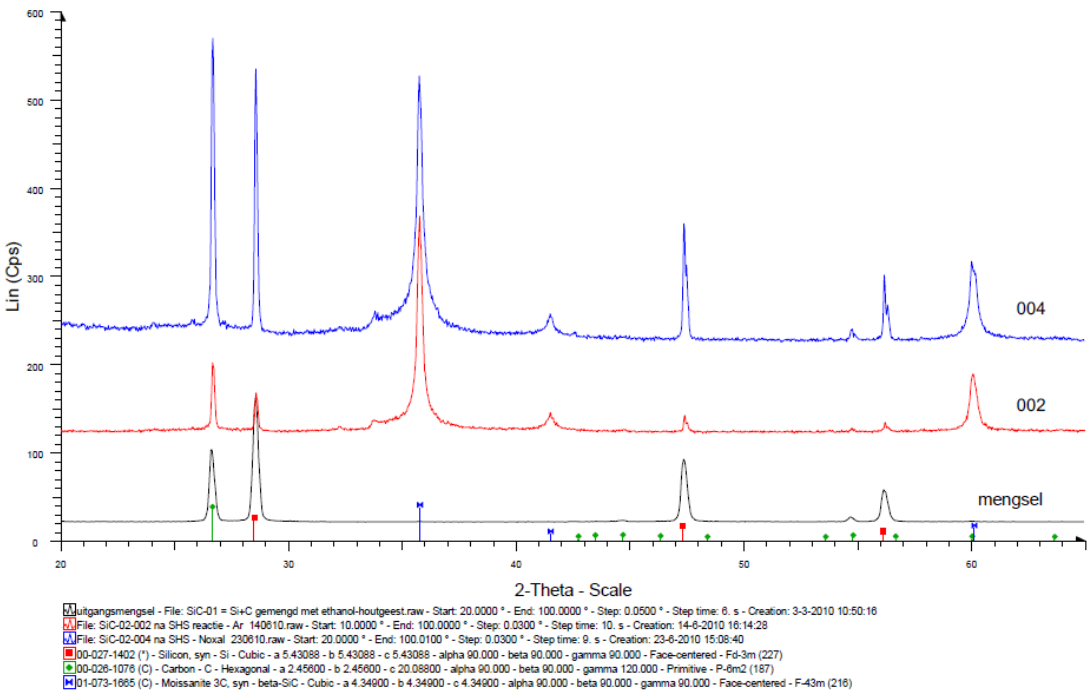


Figure 4.6 Diffractogram 1[3]

The first trial led to formation of SiC, but there are still original carbon and silicon present in the mixture.

Diffractogram 2
SiC-02-004: after Morancais SHS reaction - noxal
SiC-02-005: 5 hours 1430°C after Morancais SHS reaction - noxal
SiC-02-006: 5 hours 1430°C after SHS (with no voltage) - noxal
SiC-02-007: 5 hours 1430°C after SHS (with no graphite spray – no voltage) – noxal

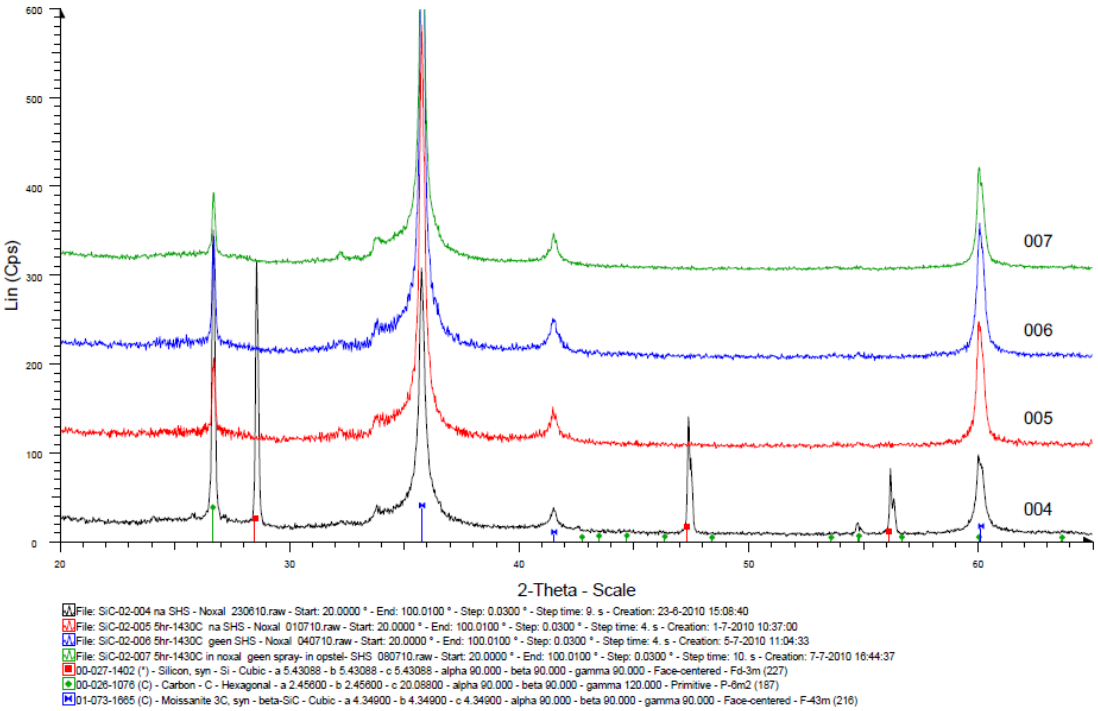


Figure 4.7 - Diffractogram 2[3]

In this diffractogram, the time at 1430ºC was prolonged to 5 hours, which had positive influence on the formation of SiC – all Si had reacted and it is no longer visible by XRD, although there is still a part of original graphite in the mixture. It was also tested without the voltage application during the SHS reaction and it seemed that the reaction can occur even without the voltage application, i.e. different time and value of voltage had no influence on the SiC formation [3].

Diffractogram 3
SiC-02-005: 5 hours 1430°C after SHS reaction - noxal
SiC-02-009: 40 sec SHS with voltage application + 5 hr 1430°C noxal + 1 hr 1430°C argon
SiC-02-010: 40 sec SHS with voltage application + 4 hr 1430°C noxal + 2 hr 1430°C argon

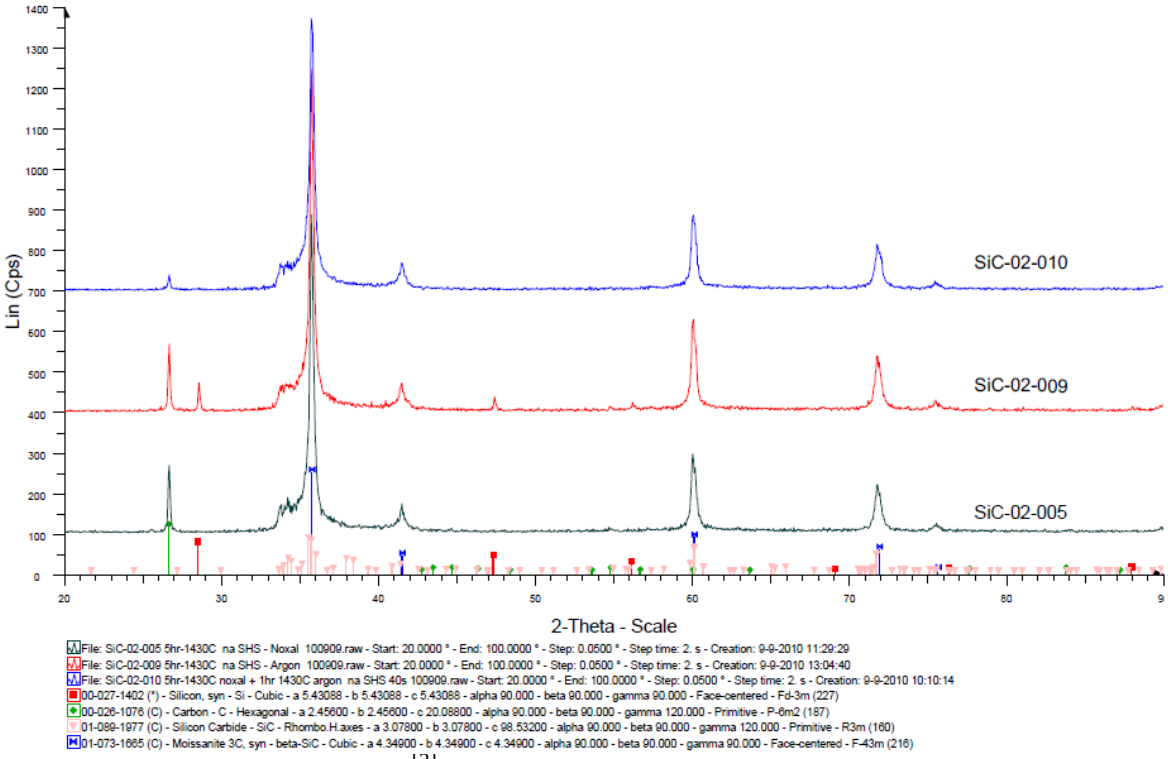


Figure 4.8 - Diffractogram 3[3]

As shown in diffractogram 2, there was still some free graphite present in the mixture. There were several tests done to try to remove the free carbon by thermal treatment. The reaction mixture was, after the normal heating in noxal, then additionally heated in argon for a period of one or two hours, which led to less amount of carbon in the mixture [3].

Diffractogram 4
SiC-02-012: 4 hr 1430°C noxal + 2 hr 1430°C argon
SiC-02-012b = SiC-02-012 + 3 hr 1430°C noxal + 3 hr 1430°C argon
SiC-02-012c = SiC-02-012b + 5 hr 1600°C argon
SiC-02-012d = SiC-02-012c + 5 hr 1350°C argon
SiC-02-012e = SiC-02-012d + 5 hr 1500°C argon
SiC-02-012f = SiC-02-012e + 50 hr 1600°C argon

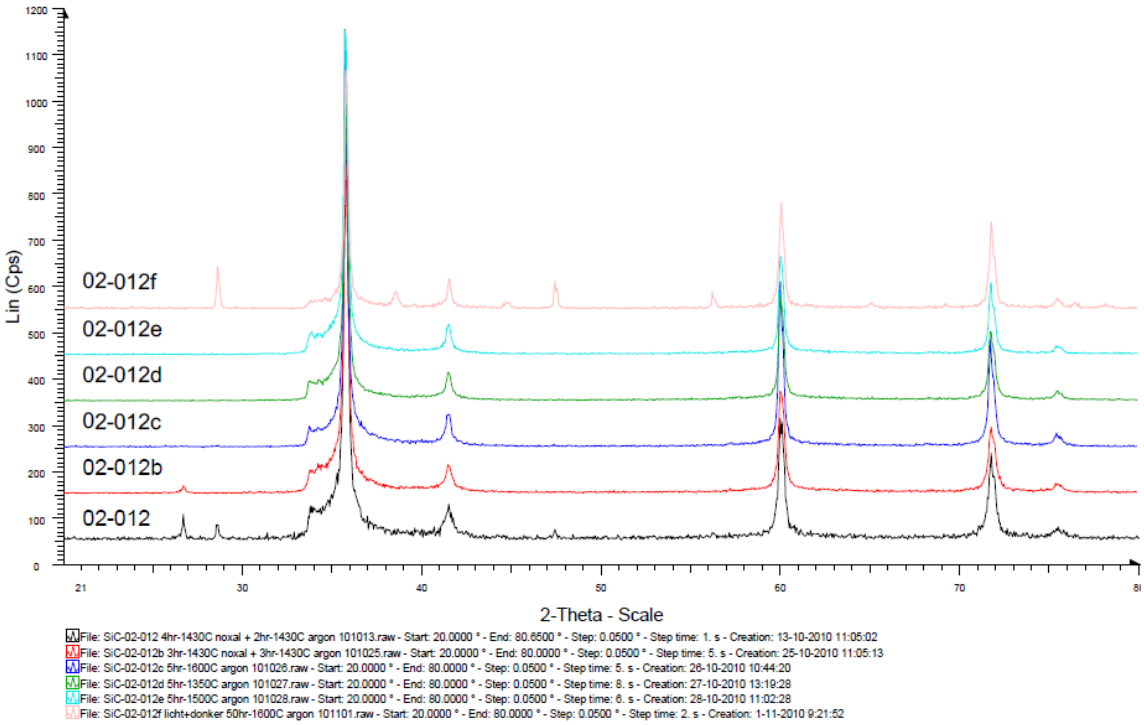


Figure 4.9 - Diffractogram 4[3]

Other tests were done with different time periods at the two atmospheres and even with higher temperatures. The higher temperature – 1600 ºC – during a long period (50 h) led to decomposition of the formed SiC to Si and C [3].

Diffractogram 5
SiC-02-012f = SiC-02-012e + 50 hr 1600°C argon

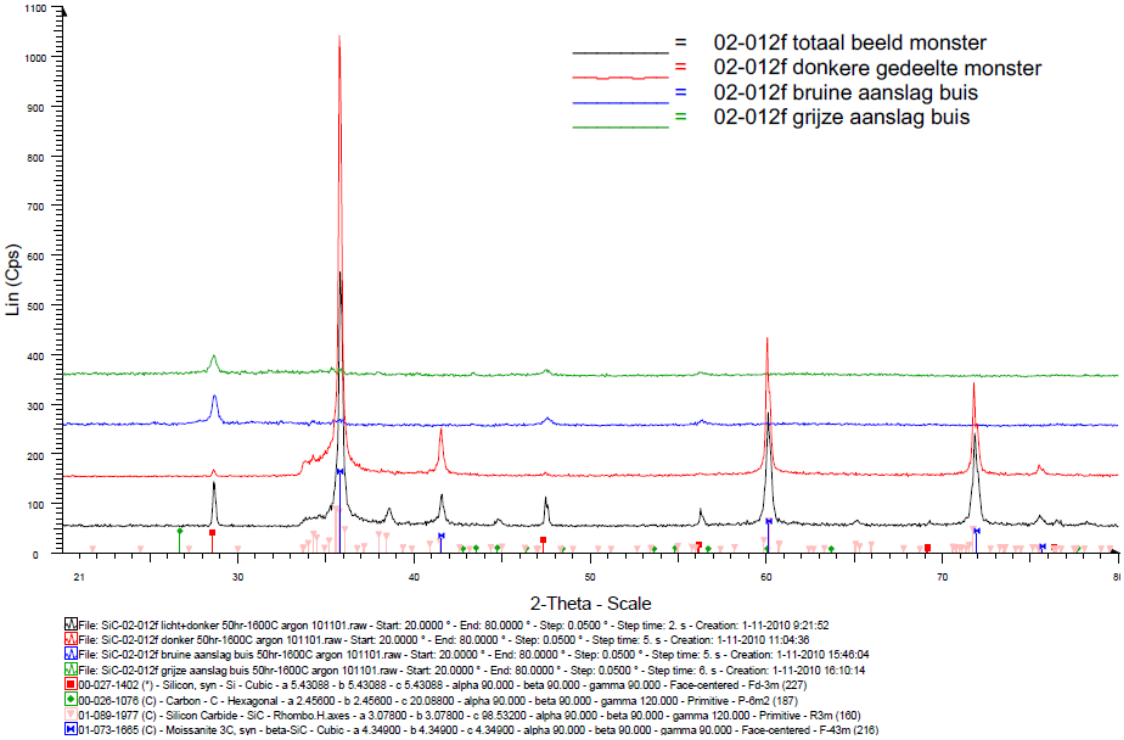


Figure 4.10 - Diffractogram 5 [3]

In the diffractogram above, measurements of different parts of the sample SiC-02-012f are depicted. It shows that mainly on the outside of the sample, free Si appears at the temperature 1600 ºC.

Based on the presented results, it was concluded that the best way to form SiC is:

A mixture of Si and C powders (50mol %: 50mol %), is mixed by IKA mixer for 60 min. in ethanol. After mixing, ethanol is evaporated in the box atmosphere. Pellets are pressed at low pressure and then heated to 1430ºC for 7 hours in noxal and 10 hours in argon.

This procedure was then applied for SiC formation from irradiated graphite [3].

4.3 SiC formation from irradiated graphite

The SiC formation from irradiated graphite was done according to the procedure established for virgin graphite.

4.3.1 SEM analysis on silicon carbide formed from irradiated graphite

The irradiated graphite and the formed silicon carbide powders were analyzed by SEM (JEOL 6490 LV SEM).

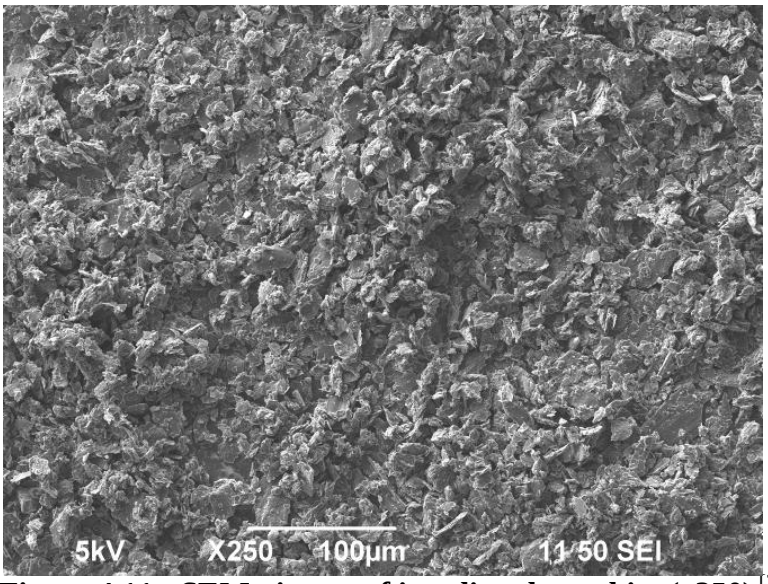


Figure 4.11 - SEM picture of irradiated graphite (x250) [3]

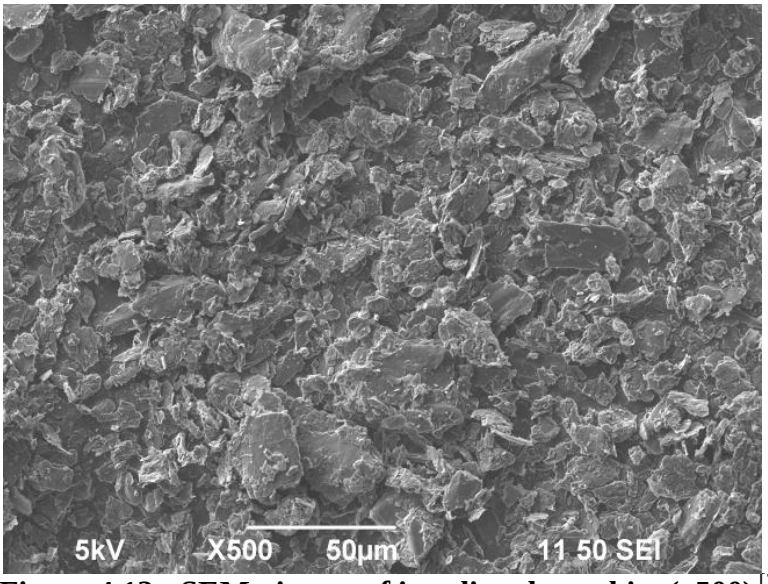


Figure 4.12 - SEM picture of irradiated graphite (x500) [3]

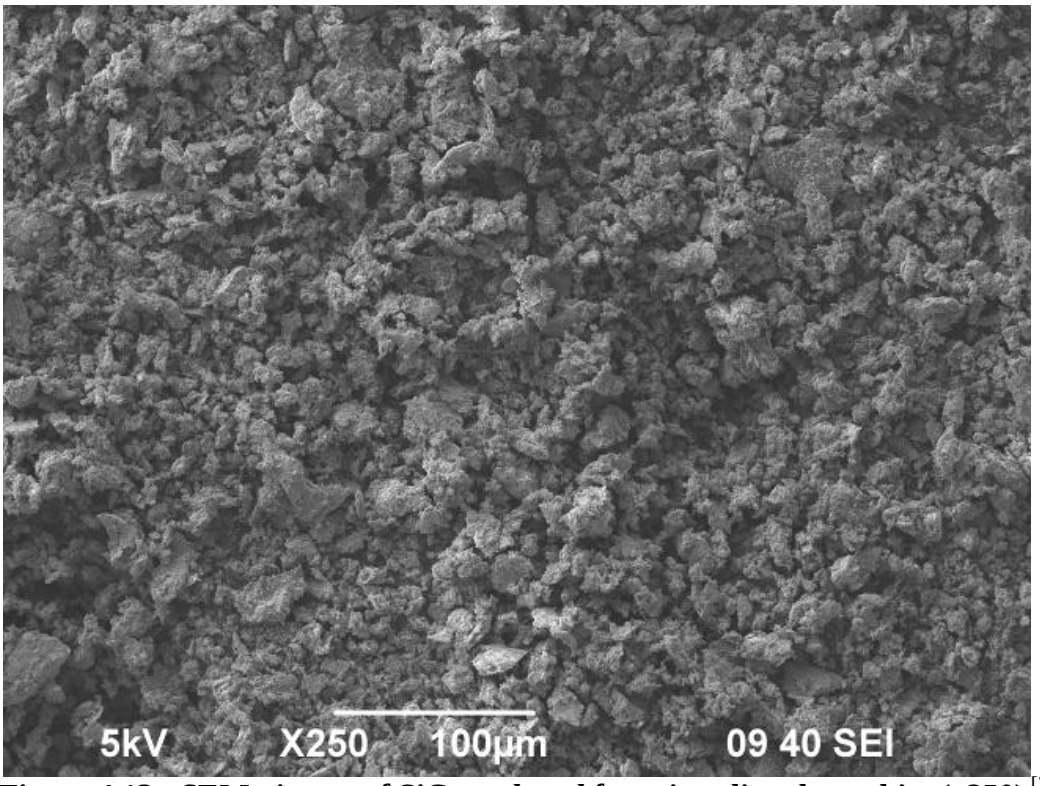


Figure 4.13 - SEM picture of SiC produced from irradiated graphite (x250) [3]

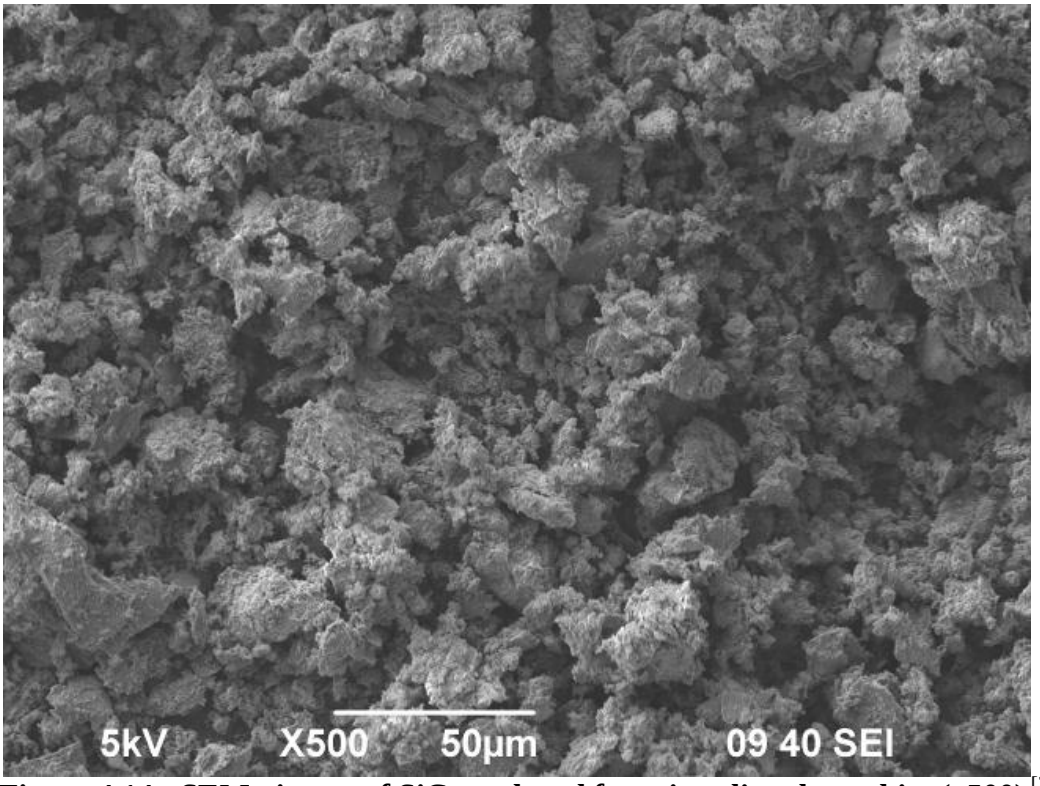


Figure 4.14 - SEM picture of SiC produced from irradiated graphite (x500) [3]

4.3.2 XRD analysis on silicon carbide formed from irradiated graphite

First, an XRD analysis of both graphite types was done.

Diffractogram A + detail
C onbestraald – C virgin, powder – in black
C bestraald – C irradiated, powder - in red

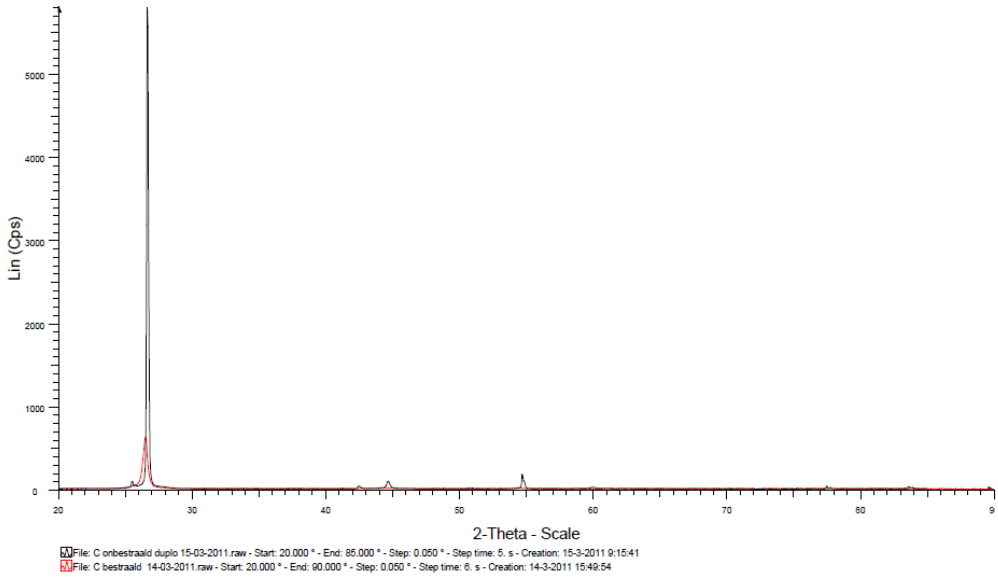


Figure 4.15 - Diffractogram A[3]

In the following diffractogram (Figure 4.16, below), a detail of diffractogram A is depicted, and the height of the main peaks is changed to allow direct comparison of the two measurements. The position of the two main peaks differs negligibly; it is the same crystalline structure, although the virgin graphite is better crystalline. No other crystalline structures were found [3].

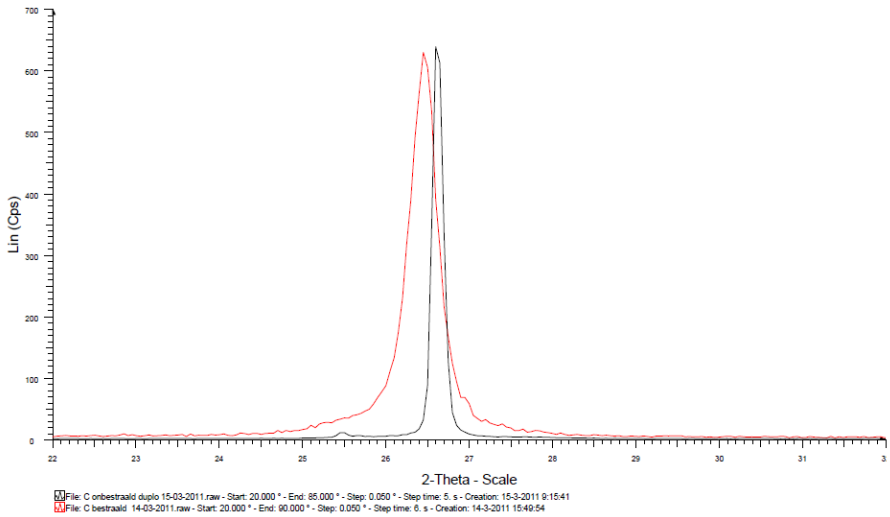


Figure 4.16 - Detail of diffractogram A[3]

Diffractogram B

SiCirr-01-002 powder: 6 hr 1430°C noxal + 6 hr 1430°C argon
SiCirr-01-002b powder: 6 hr 1430°C noxal
SiCirr-01-002c powder: 4 hr 1430°C noxal + 6 hr 1430°C argon
SiCirr-01-002d powder: 6 hr 1600°C argon
SiCirr-01-002e powder: 2 hr 1600°C argon
SiCirr-01-002f powder: SiCirr-01-002c + 2 hr 815°C air
SiCirr-01-002g powder: SiCirr-01-002c + 16 hr 815°C air

An overview of different measurements is presented. Details and differences are explored in subsequent diffractograms [3].

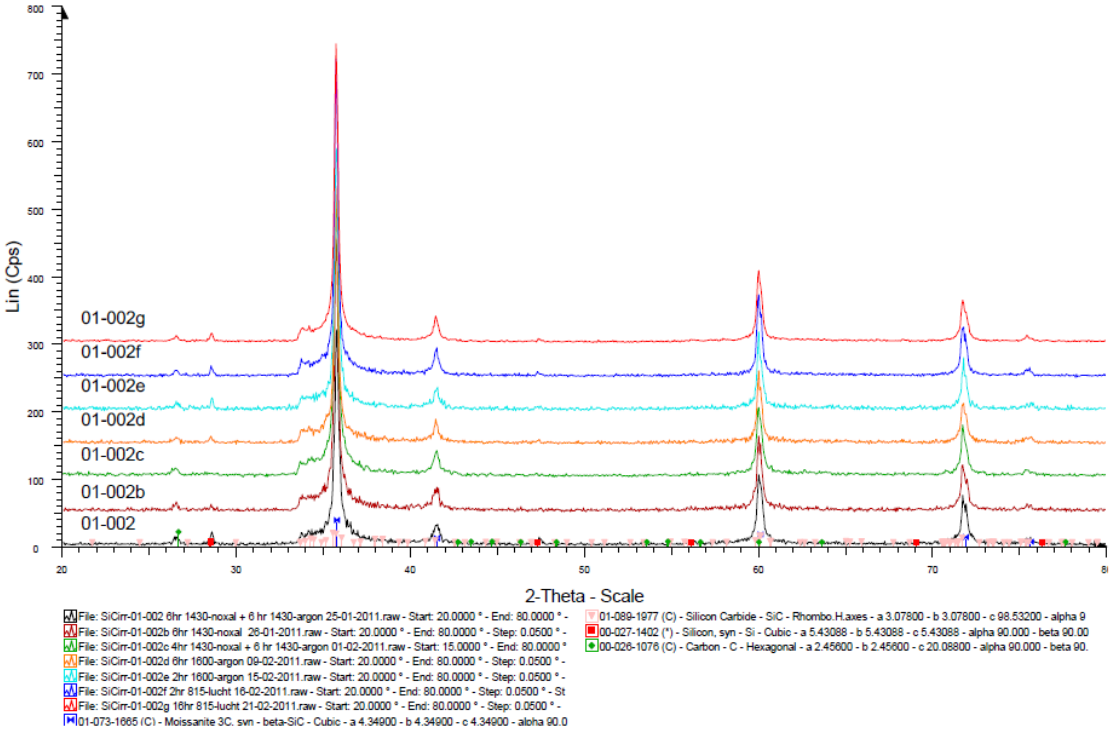


Figure 4.17 - Diffractogram B[3]

Diffractogram C – all 3 samples heated to 1430ºC
SiCirr-01-002 powder: 6 hr 1430°C noxal + 6 hr 1430°C argon
SiCirr-01-002b powder: SiCirr-01-002 + 6 hr 1430°C noxal
SiCirr-01-002c powder: SiCirr-01-002b + 4 hr 1430°C noxal + 6 hr 1430°C argon

In this diffractogram, it can be seen that heating in the noxal atmosphere only is not sufficient; also the time of the heating in the reaction atmosphere can influence the reaction results. The best result is achieved by 4 hr 1430°C noxal + 6 hr 1430°C argon, but even in this reaction mixture, some free C is still present [3].

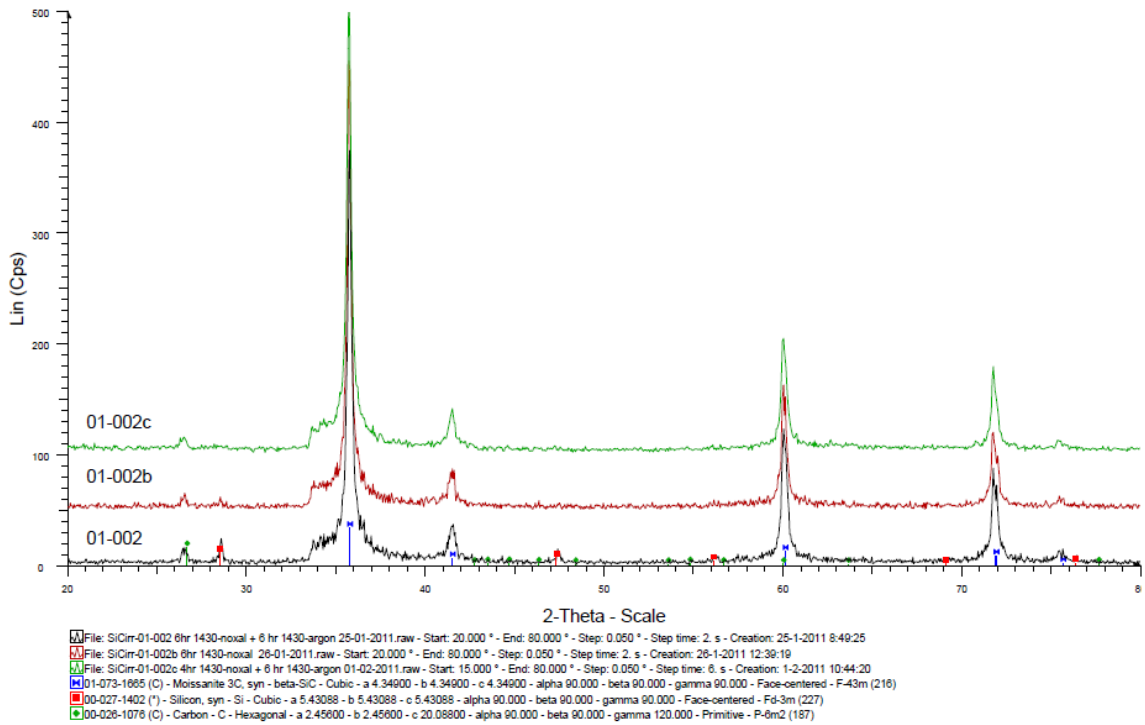


Figure 4.18 - Diffractogram C[3]

Diffractogram D – 2 samples heated to 1600ºC
SiCirr-01-002d powder: SiCirr-01-002c + 6 hr 1600°C argon
SiCirr-01-002e powder: SiCirr-01-002c + 2 hr 1600°C argon

In this diffractogram, the mixtures were heated to 1600 ºC to try to remove the free C from the mixture. Unfortunately, this reaction led to the decomposition of the formed SiC, even when heated to 1600 ºC for 2 hours only (different from results with SiC formed from virgin graphite, where heating at 1600 ºC for a period of 5 hours did not lead to its decomposition) [3] .

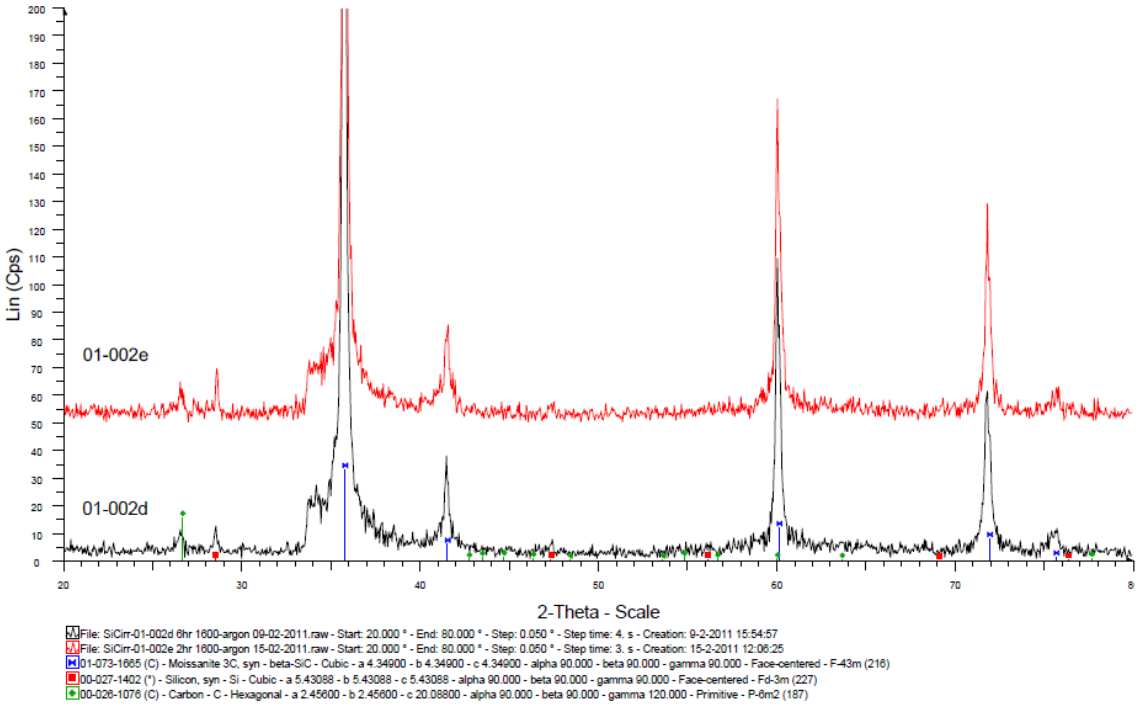


Figure 4.19 - Diffractogram D[3]

As mentioned above, many tests were performed to establish the right reaction conditions for the SiC formation from irradiated graphite. Unfortunately, it has to be concluded that the reaction between irradiated graphite and silicon did not lead to the formation of pure SiC; a small amount of free C is always present as well [3].

4.4 SiC formation from irradiated graphite for leaching experiments

This Carbowaste project WP5 is followed by WP6 - Task 6.2: Disposal behaviour of carbonaceous waste. In this task, chemical properties of the formed SiC will be studied. A set (at different temperature and in various leaching liquids) of leaching experiments will be performed. To allow the leaching experiments, an amount of about 8 g of SiC had to be produced using the irradiated graphite. The same procedure was followed to form this silicon carbide, only bigger amounts of the reaction mixtures were used (about 1 g). To allow the reaction to occur properly, the period of thermal treatment was prolonged to 40 hours. Several batches were made and reacted. Their composition was checked by XRD [3].

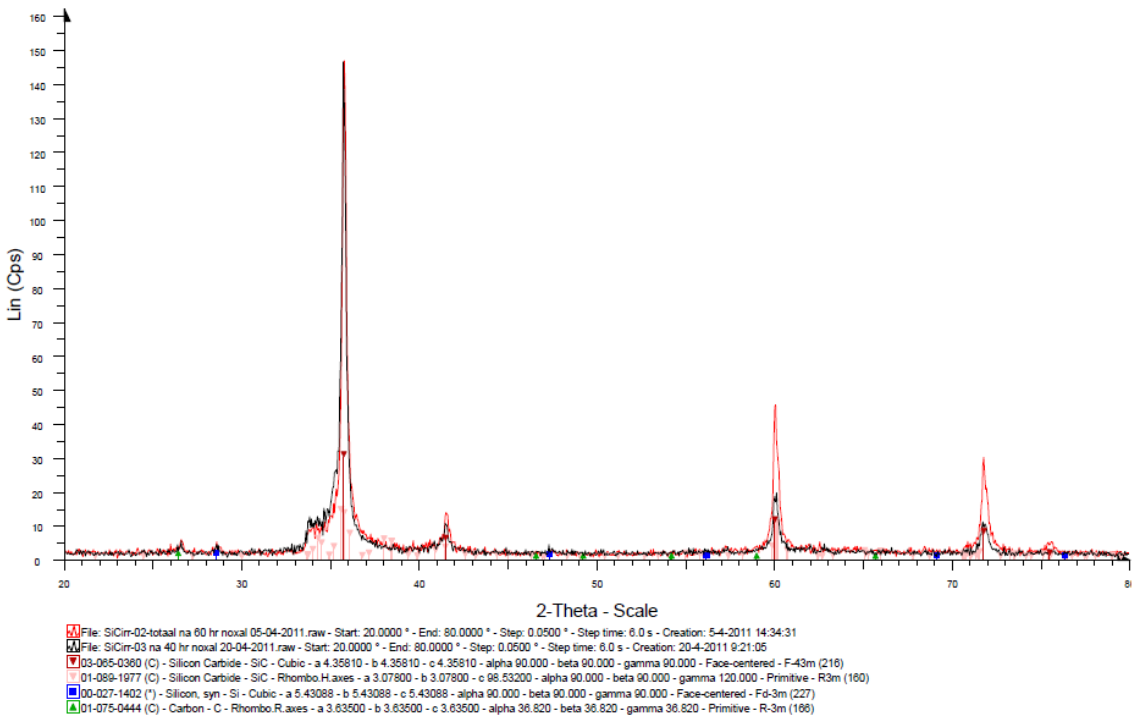


Figure 4.20 - XRD of SiC for the leaching experiments – batch 2 and 3[3]

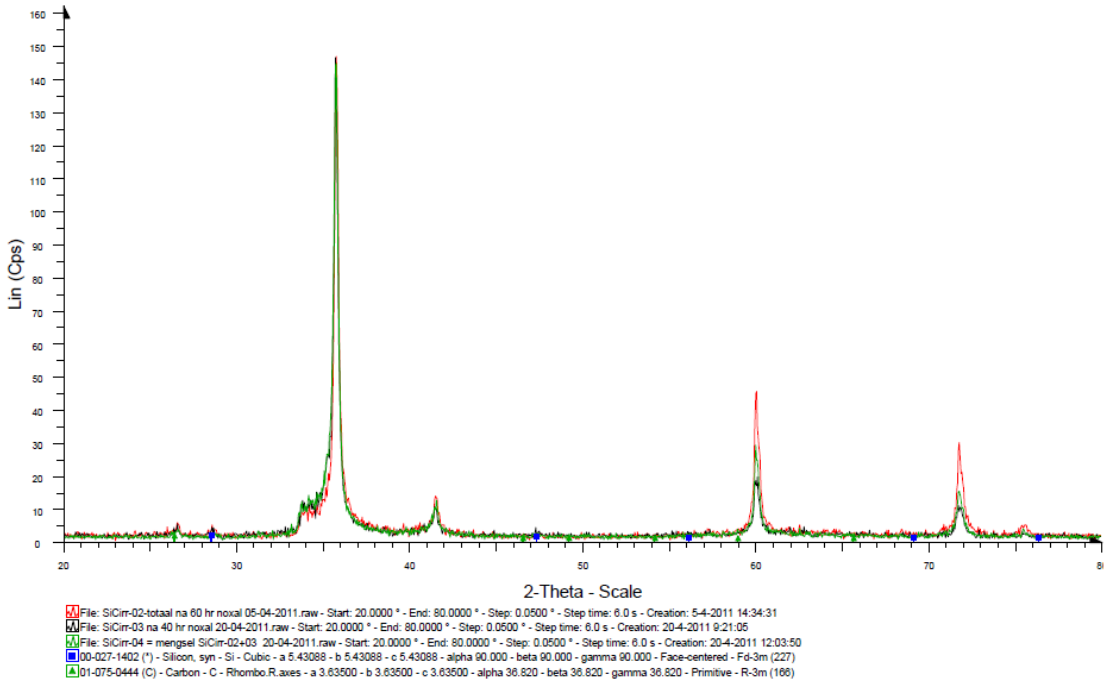


Figure 4.21 - XRD of SiC for the leaching experiments – batch 2 and 3 and their mixture – batch 4[3]

Sufficient amount (8 g) of SiC for the leaching experiments was prepared and this material will be used in the following work within the WP6 [3].

4.5 Conclusions

The SiC formation from graphite was studied. Based on the literature research, a slower version of the Morancais self-heat-sustained (SHS) method was used to form SiC. This method was applied first to virgin graphite; when the method was modified and established, irradiated graphite was used.

Many tests at different reaction conditions were tested to form pure SiC; all tests were followed by XRD. The optimal combination of reaction conditions was identified to yield the best SiC. It was determined that different time and value of voltage had no influence on the SiC formation, and in fact voltage is not needed for this application. Based on results, it can be concluded that pure SiC from graphite and silicon can be formed directly.

The same procedure was applied to the irradiated graphite; unfortunately these two graphite types seem not to react in the same way. Reaction conditions were changed to find out the way 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.

The synthesis of SiC for the leaching experiments within the WP6 – task 6.2was undertaken. A sufficient amount of silicon carbide SiC was produced and characterized; it can be used for the experiments [3].

5 DOE Deep Burn Program

External to the current Carbowaste Programme, work has been undertaken by Oak Ridge National Laboratory and GrafTech, under contract to the US DOE as part of their Deep Burn Program, which has relevance to the work being undertaken within Work Package 5. As this report represents the collation of data defining the properties and characteristics of recycled graphitic products; this could not be deemed comprehensive without summarising the sterling work undertaken under the Deep Burn Program [4].

5.1 Introduction

The R&D activities relating to the technology of nuclear fuel "Deep-Burn" are aimed at establishing the technological foundations that will support the role of the Very-High-Temperature, gas-cooled Reactor (VHTR) in the nuclear fuel cycle, one of the prototype reactors being researched under the DOE's Generation IV Nuclear power program.

Part of the Deep Burn Program, in which plutonium and higher transuranics recycled from spent nuclear fuel are destroyed while generating energy, is focused on the potential recycle of large portions of the graphite in order to mitigate the impact of this potentially enormous volume of activated waste.

The ultimate scope of commercial graphite recycle is challenging as it will require the large scale processing (crushing, pressing, chemical purification and machining) of large blocks of irradiated graphite. The current Deep Burn effort related to graphite recycle is limited to whether the reformation of graphite is technically viable. To address this, three areas of work have been undertaken:

1. Investigating the viability of recycling non-irradiated graphite .
2. Investigating the annealing kinetics of irradiated graphite in the annealing range appropriate to the recycle process.
3. Investigating the potential to recycle nuclear graphite. Recycled graphite was made with increasing percentages of ground (un-irradiated) graphite, and properties were

measured for each specimen. The process was then carried out on the irradiated, radioactive graphite.

Nuclear grade graphite used as a moderator should preferably exhibit certain key properties in order to minimize structural damage during irradiation. The process of nuclear grade graphite manufacture is shown in the process flow diagram in Figure 5.1, overleaf. The recycle graphite process, on an industrial scale, would be identical to this except that the coke filler would be replaced with particles of ground irradiated graphite [4].

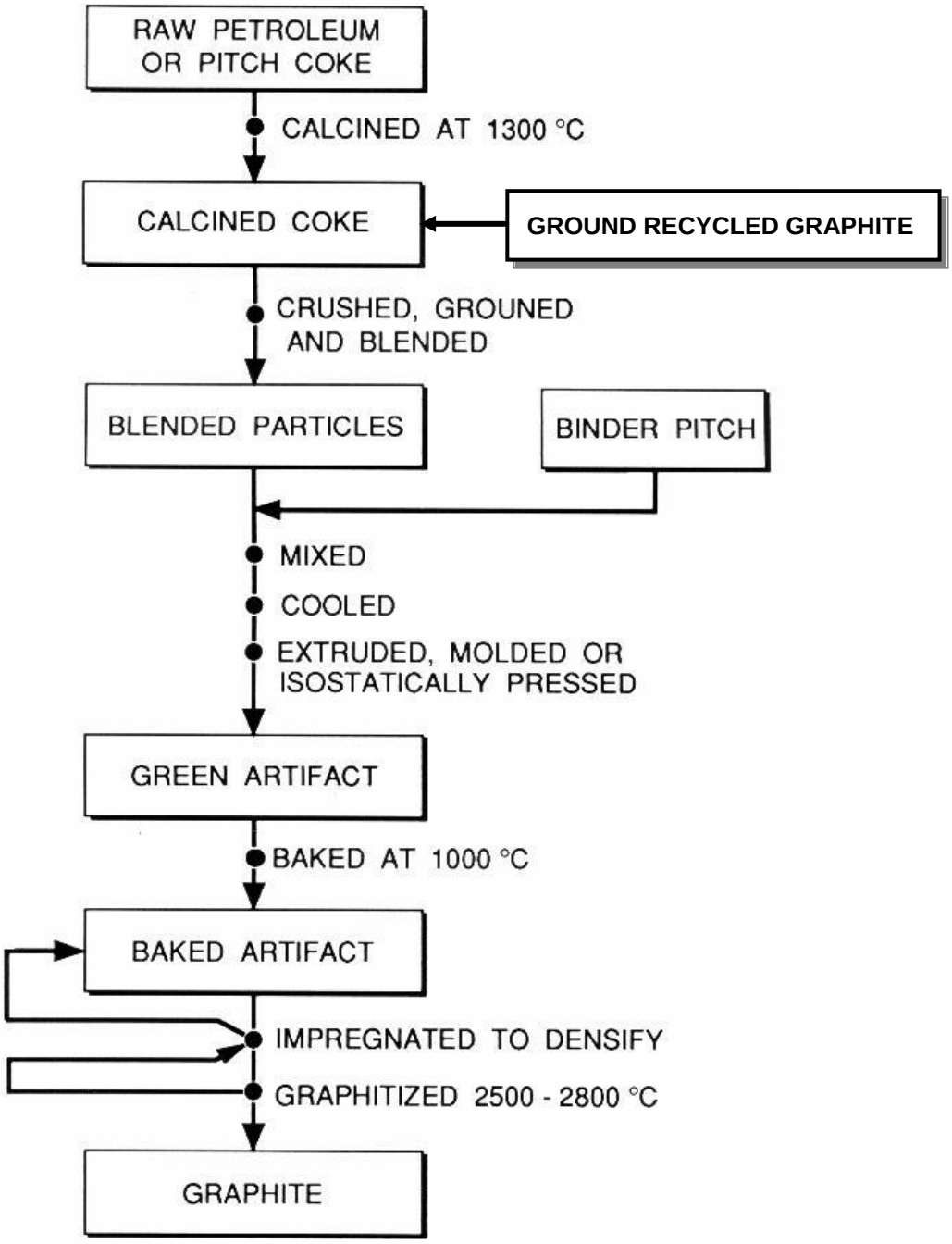


Figure 5.1 - Process flow diagram for production of graphite [4]

The pilot scale billets were processed with increasing amounts of (unirradiated) graphite (from 20% to 100%) introduced to the formulation with the goal of determining if large fractions of recycle graphite have deleterious effect on properties. Ultimately, selected specimens will provide irradiated raw stock for the study of irradiated graphite recycle.

5.2 Experimental

5.2.1 Materials

A block of PCEA graphite (nuclear grade, extruded grade, pitch impregnated three times) was obtained and ground into a set (non-disclosed) particle size. The ground PCEA graphite particles were designated as "RG" particles for tracking purposes. In total, 27 graphite billets were fabricated for the initial phase of this study. Nine (9) mix formulations containing different percentages of RG were used and three (3) billets were made per mix formulation. Figure 2 shows an image of nine (9) billets, one from each mix formulation.

Figure 5.2 - Image of recycle PCEA billets formed by GTI under Subcontract to the Deep Burn program; one is shown from each mix formulation [4]

In addition to the "virgin" nature of the recycled graphite starting material, and the scale of the graphite products being formed, the other significant difference in the GTI work as compared the ORNL effort previously reported [8] is the fact that it is a 3 PI material. Thus, the GTI materials are appreciably denser due to the second and third impregnation.

The density of the recycled graphite (as reported by GTI) was relatively unaffected by the percentage of RG particles. The densities of all of the billets (except the second in Mix #1) are all over 1.8 g/cc, which is typical of nuclear graphite. The lowest density (1.789 g/cc) was actually found in the set of billets with the least amount of recycle material, which was 20%. The density of the final recycle graphite does not appear to be negatively impacted by having 100% recycle material. No virgin material, such as coke or synthetic graphite, appears necessary when making the recycled graphite from non-irradiated stock.

5.3 Results and Discussion

5.3.1 Bulk Density

The recycle graphite fraction was introduced into the green mix in two forms, particles or a particle/flour mix. The billets were sampled to provide 15 specimens (6x6x50 mm) in the with-grain (WG) and 15 specimens in the against-grain (AG) orientation. The density in the WG orientated specimens appear to be consistently greater than in the AG , and reflects the preferred orientation of the extruded billet texture. The range of densities is similar for both graphite's (flour/particles and particles) although the graphite with flour/particles in its mix appears to exhibit a maximum density at ~60% recycle fraction. A maximum is not seen in the density of the graphite with particles only, rather, the density increases when the recycle fraction increases above ~25% reaching ~1.84 g/cm^3 at 50% recycle fraction. It should be noted that the overall variation in density of the graphite billets were relatively small, ranging from 1.812 to1.846 g/cm^3, a variation of less than 2%, in agreement with the GTI whole billet data.

5.3.2 Elastic Modulus

The mean Dynamic Young's Modulus values obtained from the specimen sets demonstrates that property anisotropy is observed, the WG value being consistently greater than the AG value, although the observed differences were generally less than 10% (typical for near-isotropic graphite). There appears to be no systematic variation of modulus with recycle fraction.

5.3.3 Electrical Resistivity

There appears to be no systematic variation of electrical resistivity with recycle fraction. The observed variations were small, being less than ±1 standard deviation. Typically for an extruded product the WG resistivity is less that the AG resistivity. This was not uniformly observed in our data sets. However, grade PCEA is an isotropic grade and thus the variation with grain orientation would be expected to be small and may be less than the experimental error (standard deviation).

5.3.4 Coefficient of Thermal Expansion

All of the specimens tested have exhibited the expected thermal expansion behaviour with an increasing expansion coefficient with increasing temperature. The ASTM specification [9] for nuclear graphite required the average CTE (RT to 500°C) in the WG direction to be between 3.5 and 5.5 °C-1, a requirement which all specimens tested have met. The AG CTE is larger than the WG CTE as expected. The ASTM Specification [9] requires the CTE (RT-500°C) ratio (AG/WG) to be between 1.0 and 1.10 for isotropic extruded nuclear graphite. The data for billet 03-4 gives the CTE (RT-500°C) as 1.09 indicating the recycle PCEA graphite would qualify as an "isotropic" grade. A limited data set for CTE in the WG direction suggests that increasing the recycle fraction causes a slight reduction in CTE. Further work is needed to confirm this.

5.4 Conclusions

A series of recycle PCEA graphite pilot scale billets were manufactured. Thirty specimens were machined from each billet (15 with grain and 15 against-grain specimens). The characterization performed here suggests that increasing the recycle fraction of graphite has no deleterious effect on the properties of the graphite. There is some evidence of CTE being reduced by increasing recycle fractions, but the reduction is small. Thus it appears as if the coke filler could be completely replaced with ground recycle graphite. However, further work is needed to complete this study.

For a further, more detailed account of the work reported here, please refer to the following reference:

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

For the tabulated data and graphical plots associated with the properties and characterisation of the recycled graphite produced under Deep Burn, please refer to Appendix A.

6 Discussion

The use of carbon black as an intermediate for recycling irradiated graphite has been achieved, although there are significant limitations on the proportion which can be included within 'new graphite' which if exceeded would have significant consequences on the products properties (strength etc..).

Further work should be undertaken to optimise the proportion of carbon black which can be incorporated, primarily in respect to its addition to the recipe, as it has been shown that without significant mixing prior to the forming of the 'green artifact' the carbon black with form aggregations which affect the strength of the final product.

The work undertaken by Oak Ridge National Laboratory and GrafTech as part of the US DOE Deep Burn project, has shown that candidate products produced directly from irradiated graphite are considerably more robust, and retain nuclear graphite grade properties even with very high additions of recycled graphite. This is not a surprising conclusion, since the recycle of a certain proportion of graphite has been a routine part of manufacturing processes.

The uptake of graphite recycle on an industrial scale requires the consideration of other factors besides those discussed above, and this was recognised at the outset in the design of the Work Package 5 programme. In particular the requirement for fully radiologically qualified manufacturing facilities (including gamma shielding) was considered an almost insurmountable barrier to industrial uptake of graphite recycle. Accordingly the carbon black route was selected because it allowed for efficient decontamination of the graphite prior to recycle, most particularly the removal of gamma emitting isotopes. Accordingly the use of simple containment techniques would provide sufficient radiological protection during the manufacturing processes. Furthermore, the selection by the manufacturers of simple manufacturing routes for products meant that just a part of their facilities (and not the whole factory) could be radiologically qualified for recycle activities.

Since the original design of the WP5 programme there has been significant developments in the decontamination of graphite, and the concerns expressed in the

previous paragraph might not be so serious in the light of these developments. If graphite can be effectively decontaminated by gas phase or liquid phase methods, the radiological constraints on its recycle might be eased.

The worked undertaken in Work Package 5, coupled with that in the Deep Burn Programme summarised here and the more recent decontamination developments (e.g. as reported in Work Package 4 of CARBOWASTE) will provide a good basis for the manufacturers to consider future commercial opportunities for graphite recycle. They will have the options of using 1) carbon black as a substrate, which permits a limited uptake of recycled graphite in the final product but would only require minimal radiological protection costs for manufacturing, 2) using graphite which has been extensively decontaminated using the new techniques or 3) using undecontaminated graphite and bearing the full cost of radiological protection of the manufacturing facilities.

.

Glossary

AG	Against Grain
ASTM	American Society for Testing and Materials
CTE	Coefficient of Thermal Expansion
DBP	Dibutyl Phthalate
EdF	Électricité de France
GTI	GrafTech International
HTR	High Temperature Reactor
IKA	Mixer
NBG	Nuclear Block Graphite
ORNL	Oak Ridge National Laboratory
pph	Parts per hundred
R&D	Research & Development
RG	Recycled Graphite
RRT	Round Robin Test
SEM	Scanning Electron Microscopy
SHS	Self Heat Sustained
SiC	Silicon Carbide
SR	Specific Resistance
UNGG	Uranium Naturel Graphite Gaz
USDOE	United States Department Of Energy
VHTR	Very High Temperature Reactor
WG	With Grain
XRD	Powder X-ray Diffraction

References

[1] Albers, T. 'Carbowaste Technical Report for WP5 – Utilization of a Fast Processing Technique to form Graphite Electrodes for Waste Vitrification'. Report prepared by GrafTech, July 2011.

[2] Hiltmann, F. 'Carbowaste Technical Report T5.2.1 SGL-02 – Recycling of Carbon Black as Surrogate for Decontaminated i-Graphite into Nuclear Graphite Formulations'. Report prepared by SGL Carbon, May 2011.

[3] Visser-Tynova, E de. Cobussen, H.L. 'Carbowaste Technical Report – SiC Formation from Graphite'. Report prepared by NRG, September 2011.

[4] Burchell, T., Pappano, P. 'The Characterization of Grade PCEA Recycle Graphite Pilot Scale Billets', prepared for the US DOE Deep Burn Program, and the Office of Nuclear Energy Science and Technology, prepared by Oak Ridge National Laboratory (Rep No. ORNL/TM-2010/00169). August 27th 2010.

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

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

[7] A. Morancais et al. in J. of Eur. Ceram. Soc. 23 (2003) 1949-1956.

[8] P.J. Pappano and T.D. Burchell, An Interim Report on Recycle of Irradiated Graphite Specimens, ORNL/TM-2009/177, September 2009.

[9] ASTM D7219, Standard Specification for Isotropic and Near-isotropic Nuclear Graphite's, American Society for Testing and Materials, West Conshohocken, PA 19428.

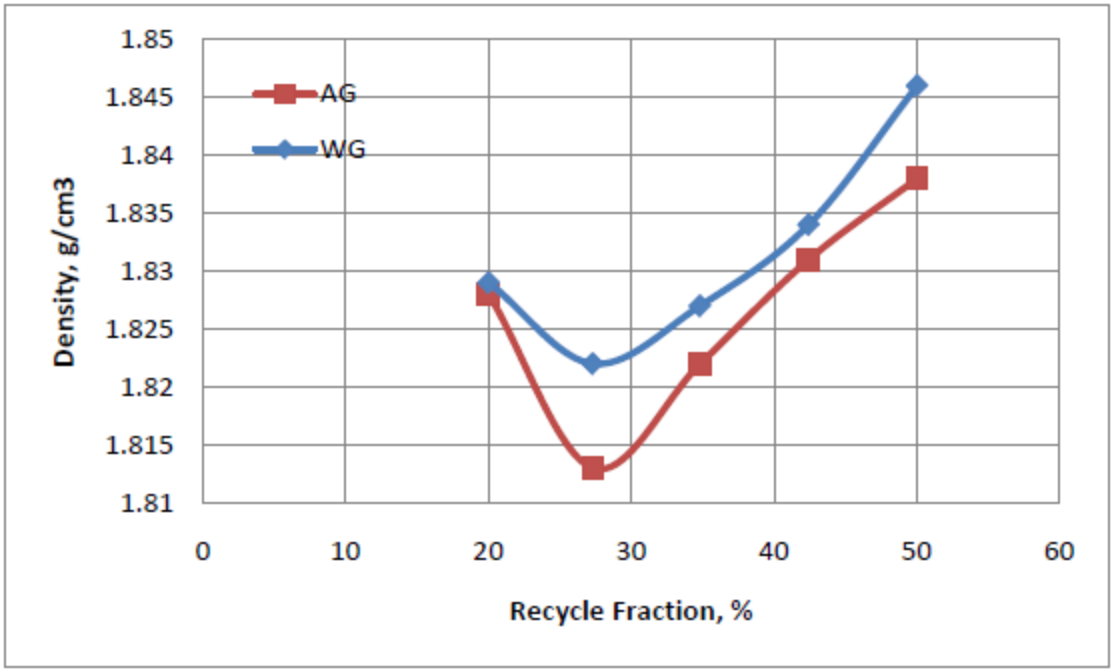
Appendix A: Properties and characteristics of the graphite materials

A1 - Mass, volume, and densities for GTI recycle PCEA graphite

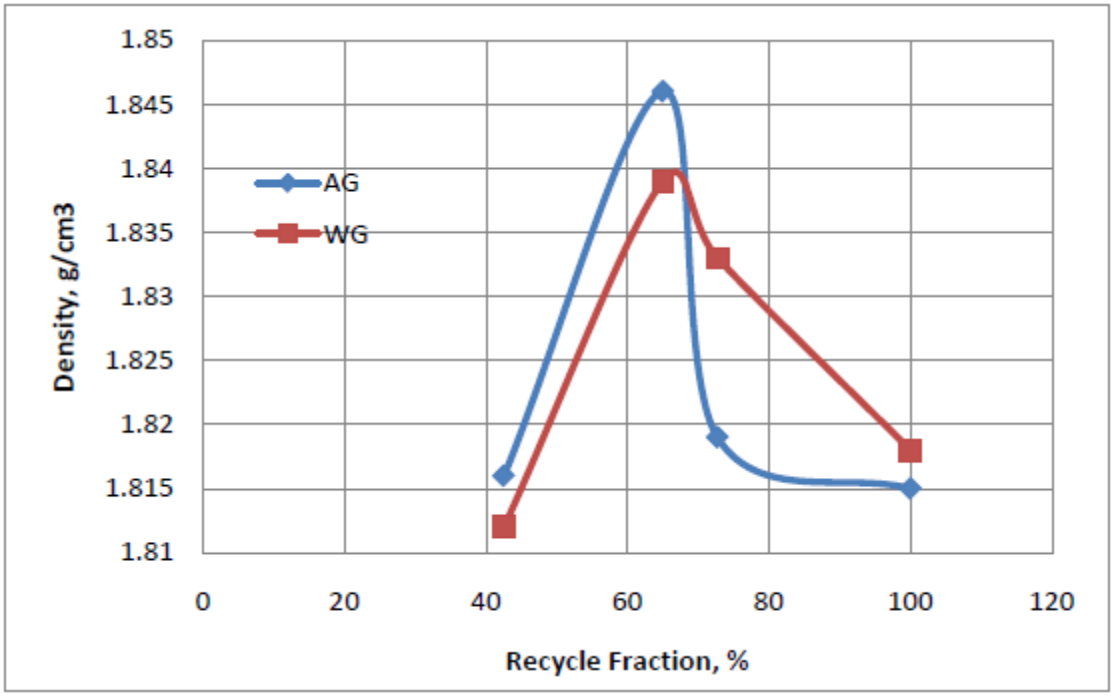
	Billet Identification No.	Wt. (gm)	Avg.Diam. (in)	Avg.Lgth. (in)	Density (g/cc)	Vol. (cc)
	092001-2	10013.6	5.845	12.448	1.829	5474
Mix 1 (20% RG as particles)	092003-1	9048.6	5.681	12.179	1.789	5058
Mix 1 (20% RG as particles)	092003-2	9044.9	5.721	11.909	1.803	5017
Mix 1 (20% RG as particles)	092003-3	9269.3	5.708	12.249	1.805	5137
Mix 1 (20% RG as particles)	092003-4	9338.5	5.727	12.209	1.812	5153
Mix 1 (20% RG as particles)	092003-5	9356.8	5.715	12.274	1.814	5159
Mix 2 (27.3% RG as particles)	092004-2	9502.6	5.794	12.190	1.804	5267
Mix 2 (27.3% RG as particles)	092004-3	9467.7	5.783	12.142	1.812	5226
Mix 2 (27.3% RG as particles)	092004-4	9592.9	5.780	12.294	1.815	5287
Mix 2 (27.3% RG as particles)	092004-5	9548.3	5.796	12.203	1.810	5276
Mix 3 (34.8% RG as particles)	092005-3	10638.1	5.827	13.491	1.804	5896
Mix 3 (34.8% RG as particles)	092005-4	10498.8	5.804	13.334	1.816	5781
Mix 3 (34.8% RG as particles)	092005-5	9812.3	5.807	12.467	1.814	5410
Mix 4 (42.4% RG as particles)	092006-1	10720.7	5.789	13.755	1.807	5933
Mix 4 (42.4% RG as particles)	092006-2	10594.1	5.828	13.241	1.830	5788
Mix 4 (42.4% RG as particles)	092006-3	10411.3	5.792	13.170	1.831	5685
Mix 4 (42.4% RG as particles)	092006-4	10675.4	5.801	13.407	1.839	5806
Mix 4 (42.4% RG as particles)	092006-5	10431.8	5.798	13.092	1.842	5664
Mix 5 (50% RG as particles)	092007-1	9803.4	5.803	12.339	1.833	5347
Mix 5 (50% RG as particles)	092007-2	9800.3	5.825	12.175	1.843	5317
Mix 5 (50% RG as particles)	092007-3	9884.7	5.814	12.325	1.843	5363
Mix 5 (50% RG as particles)	092007-4	9900.1	5.831	12.270	1.844	5369
Mix 5 (50% RG as particles)	092007-5	9716.6	5.775	12.371	1.830	5309
Mix 6 (42.4% RG part and flour)	092008-2	9805.5	5.846	12.271	1.817	5397
Mix 6 (42.4% RG part and flour)	092008-3	9634.3	5.818	12.172	1.817	5302
Mix 6 (42.4% RG part and flour)	092008-4	9903.2	5.870	12.310	1.814	5460
Mix 6 (42.4% RG part and flour)	092008-5	9844.9	5.828	12.373	1.820	5408
Mix 7 (65%RG part and flour)	092009-1	9592.4	5.759	12.295	1.828	5248
Mix 7 (65%RG part and flour)	092009-2	9633.1	5.776	12.176	1.843	5228
Mix 7 (65%RG part and flour)	092009-4	9586.0	5.747	12.226	1.844	5198
Mix 7 (65%RG part and flour)	092009-5	9529.1	5.727	12.226	1.846	5161
Mix 8 (72.7% RG part and flour)	092010-1	9735.9	5.813	12.222	1.832	5316
Mix 8 (72.7% RG part and flour)	092010-3	10111.6	5.896	12.363	1.828	5530
Mix 8 (72.7% RG part and flour)	092010-4	10047.4	5.874	12.367	1.830	5491
Mix 8 (72.7% RG part and flour)	092010-5	9734.0	5.855	12.060	1.829	5321
Mix 9 (100% RG part and flour)	092011-1	9902.2	5.832	12.397	1.825	5427
Mix 9 (100% RG part and flour)	092011-2	10356.4	5.948	12.507	1.819	5695
Mix 9 (100% RG part and flour)	092011-3	10356.1	5.986	12.349	1.818	5695
Mix 9 (100% RG part and flour)	092011-4	10101.7	5.902	12.380	1.820	5551
Mix 9 (100% RG part and flour)	092011-5	10257.7	5.930	12.461	1.819	5638

A2 - GrafTech pilot scale billets being characterized at ORNL

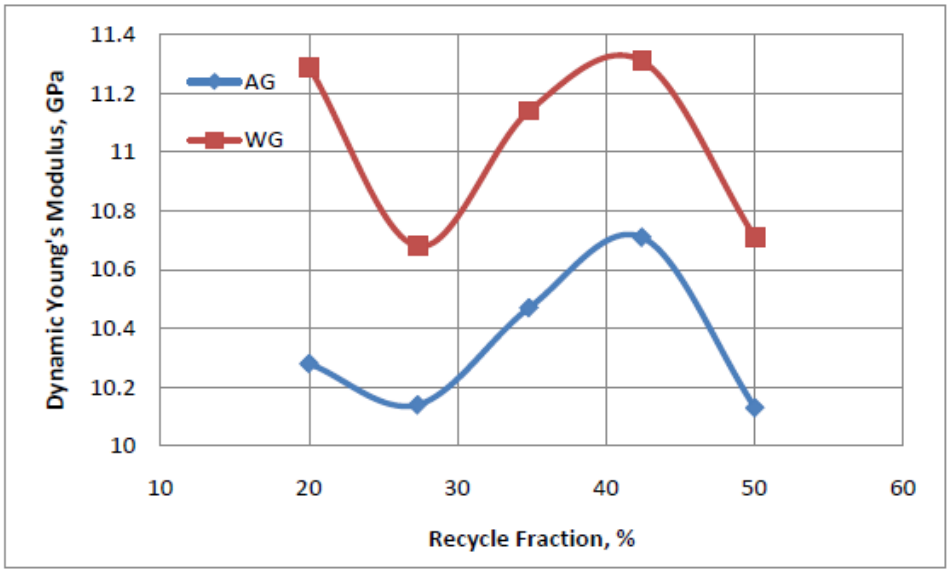
Billet Code	Specimen Orientation	Number of specimens	Recycle Fraction %	Mean Density g/cc	GrafTech Billet Density g/cc	Recycle Fraction Condition
03-4	AG	15	20	1.828	1.812	particles
03-4	WG	15	20	1.829	1.812	particles
04-3	AG	15	27.3	1.813	1.812	particles
04-3	WG	15	27.3	1.822	1.812	particles
05-4	AG	15	34.8	1.822	1.816	particles
05-4	WG	15	34.8	1.827	1.816	particles
06-3	AG	15	42.4	1.831	1.831	particles
06-3	WG	15	42.4	1.834	1.831	particles
07-3	AG	15	50	1.838	1.843	particles
07-3	WG	15	50	1.846	1.843	particles
08-3	AG	15	42.5	1.816	1.817	particles &
08-3	WG	15	42.5	1.812	1.817	particles &
09-2	AG	15	65	1.846	1.843	particles &
09-2	WG	15	65	1.839	1.843	particles &
10-5	AG	15	72.7	1.819	1.829	particles &
10-5	WG	15	72.7	1.833	1.829	particles &
11-4	AG	15	100	1.815	1.82	particles &
11-4	WG	15	100	1.818	1.82	particles &



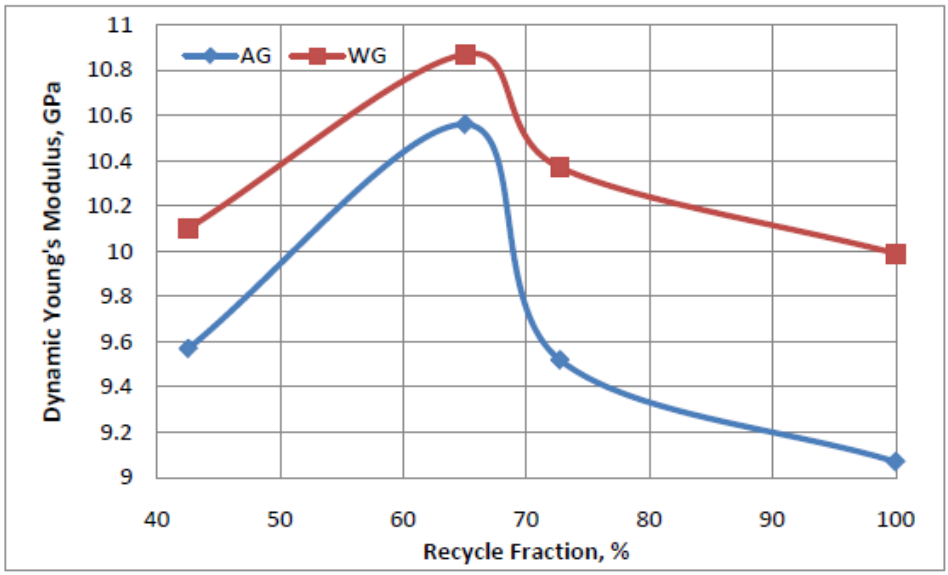
A3 - The variation of bulk density with recycle fraction for the GrafTech billets made with recycle graphite as particles in the green mix



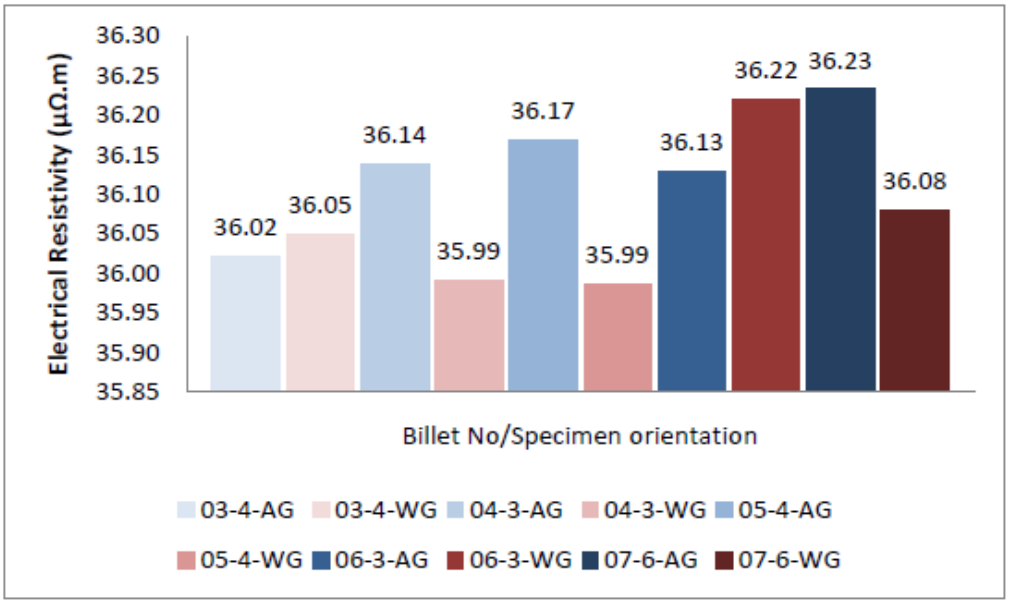
A4 - The variation of bulk density with recycle fraction for the GrafTech billets made with recycle graphite as a particle/flour mix in the green mix



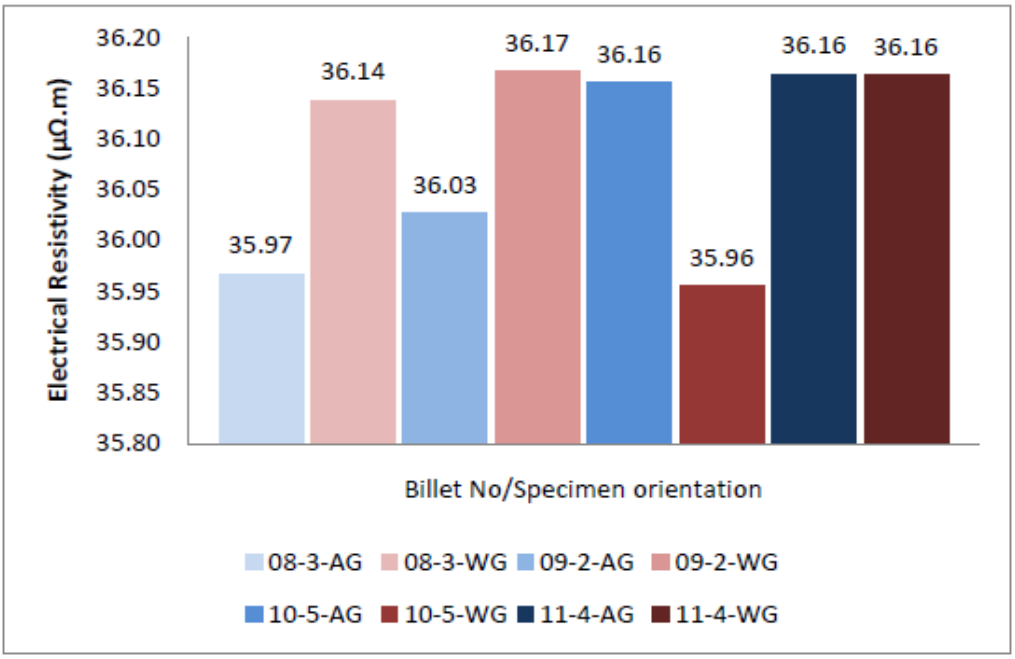
A5 - Variation of Mean dynamic Young's modulus with recycle fraction for the GrafTech billets made with recycle graphite as particles in the green mix



A6 - Variation of Mean dynamic Young's modulus with recycle fraction for the GrafTech billets made with recycle graphite as a particles/flour mix in the green mix



A7 - Summary of mean Electrical Resistivity data organized by % of recycle particles and specimen orientation



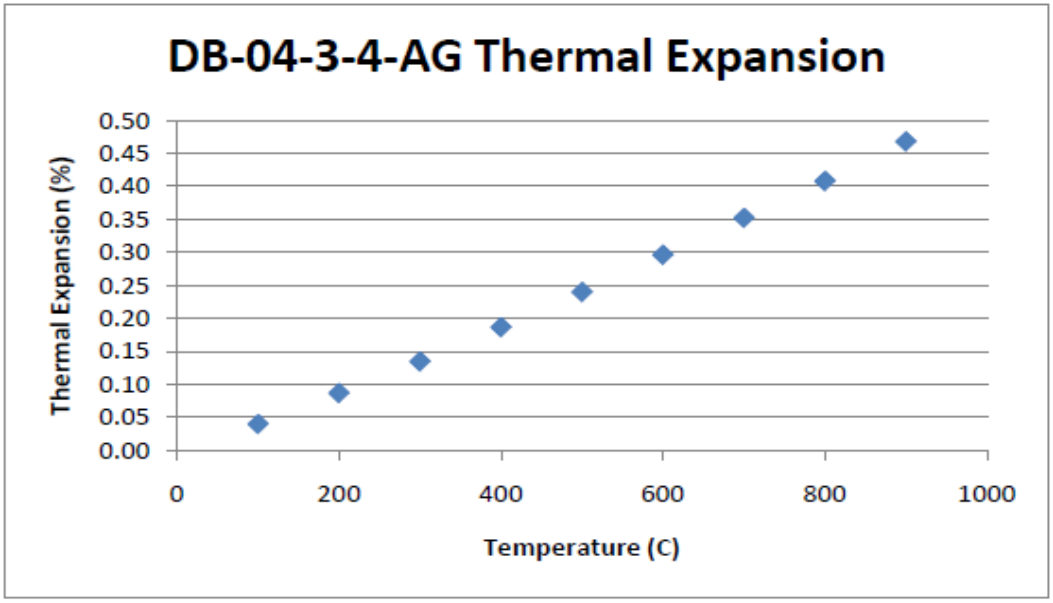
A8 - Summary of mean Electrical Resistivity data organized by % of recycle particles/flour and specimen orientation

A9 - Electrical resistivity for each specimen, and the mean and standard deviation of the billet/orientation group (particles only)

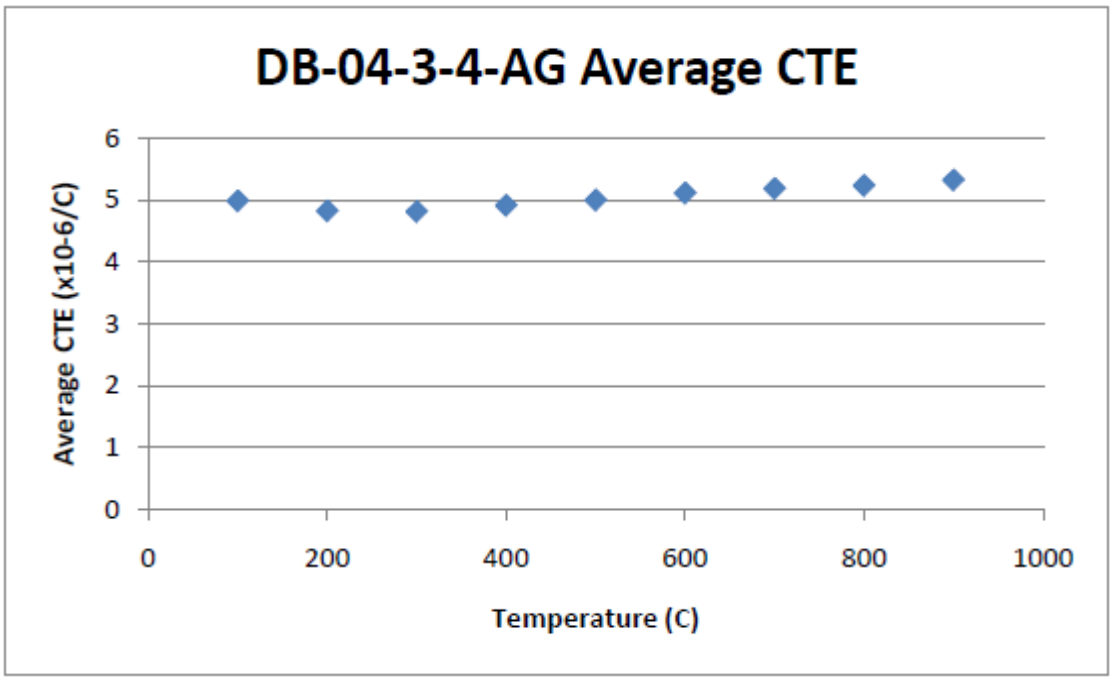
Deep Burrn PCEA Recycle Graphite(Particles only)																			
Billet 03-4-AG		Billet 03-4-WG		Billet 04-3-AG		Billet 04-3-WG		Billet 05-4-AG		Billet 05-4-WG		Billet 06-3-AG		Billet 06-3-WG		Billet 07-6-AG		Billet 07-3-WG	
Specimen Number	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)	**Specimen Number**	Resistivity (μΩ.m)
03-4-AG-1	35.96	03-4-WG-1	35.99	04-3-AG-1	36.19	04-3-WG-1	35.97	05-4-AG-1	36.13	05-4-WG-1	36.09	06-3-AG-1	36.08	06-3-WG-1	36.09	07-3-AG-1	36.27	07-3-WG-1	36.18
03-4-AG-2	36.15	03-4-WG-2	36.05	04-3-AG-2	36.17	04-3-WG-2	35.94	05-4-AG-2	36.19	05-4-WG-2	36.00	06-3-AG-2	36.13	06-3-WG-2	36.32	07-3-AG-2	36.30	07-3-WG-2	35.96
03-4-AG-3	36.00	03-4-WG-3	35.99	04-3-AG-3	36.06	04-3-WG-3	36.06	05-4-AG-3	36.10	05-4-WG-3	36.00	06-3-AG-3	36.15	06-3-WG-3	36.10	07-3-AG-3	36.20	07-3-WG-3	36.01
03-4-AG-4	36.03	03-4-WG-4	36.08	04-3-AG-4	36.12	04-3-WG-4	35.96	05-4-AG-4	36.21	05-4-WG-4	35.97	06-3-AG-4	36.12	06-3-WG-4	36.29	07-3-AG-4	36.27	07-3-WG-4	36.17
03-4-AG-5	36.09	03-4-WG-5	36.17	04-3-AG-5	36.09	04-3-WG-5	36.05	05-4-AG-5	36.27	05-4-WG-5	35.97	06-3-AG-5	36.16	06-3-WG-5	36.25	07-3-AG-5	36.26	07-3-WG-5	36.12
03-4-AG-6	36.06	03-4-WG-6	36.08	04-3-AG-6	36.07	04-3-WG-6	35.88	05-4-AG-6	36.11	05-4-WG-6	36.05	06-3-AG-6	36.26	06-3-WG-6	36.21	07-3-AG-6	36.34	07-3-WG-6	36.14
03-4-AG-7	36.00	03-4-WG-7	35.97	04-3-AG-7	36.06	04-3-WG-7	36.06	05-4-AG-7	36.06	05-4-WG-7	35.94	06-3-AG-7	36.07	06-3-WG-7	36.22	07-3-AG-7	36.30	07-3-WG-7	36.10
03-4-AG-8	35.97	03-4-WG-8	36.11	04-3-AG-8	36.22	04-3-WG-8	35.82	05-4-AG-8	36.22	05-4-WG-8	35.94	06-3-AG-8	36.33	06-3-WG-8	36.23	07-3-AG-8	36.21	07-3-WG-8	36.14
03-4-AG-9	36.02	03-4-WG-9	35.94	04-3-AG-9	36.14	04-3-WG-9	36.00	05-4-AG-9	36.13	05-4-WG-9	36.08	06-3-AG-9	36.11	06-3-WG-9	36.29	07-3-AG-9	36.11	07-3-WG-9	36.09
03-4-AG-10	36.03	03-4-WG-10	36.03	04-3-AG-10	36.24	04-3-WG-10	36.12	05-4-AG-10	36.08	05-4-WG-10	36.00	06-3-AG-10	36.11	06-3-WG-10	36.28	07-3-AG-10	36.23	07-3-WG-10	36.04
03-4-AG-11	35.97	03-4-WG-11	36.05	04-3-AG-11	36.14	04-3-WG-11	35.98	05-4-AG-11	36.16	05-4-WG-11	36.03	06-3-AG-11	36.08	06-3-WG-11	36.23	07-3-AG-11	36.23	07-3-WG-11	36.01
03-4-AG-12	36.09	03-4-WG-12	36.00	04-3-AG-12	36.20	04-3-WG-12	36.04	05-4-AG-12	36.19	05-4-WG-12	35.97	06-3-AG-12	36.05	06-3-WG-12	36.11	07-3-AG-12	36.11	07-3-WG-12	36.18
03-4-AG-13	35.96	03-4-WG-13	36.17	04-3-AG-13	36.16	04-3-WG-13	36.03	05-4-AG-13	36.23	05-4-WG-13	35.90	06-3-AG-13	36.05	06-3-WG-13	36.29	07-3-AG-13	36.35	07-3-WG-13	35.97
03-4-AG-14	35.99	03-4-WG-14	36.08	04-3-AG-14	36.14	04-3-WG-14	36.00	05-4-AG-14	36.24	05-4-WG-14	35.94	06-3-AG-14	36.13	06-3-WG-14	36.16	07-3-AG-14	36.20	07-3-WG-14	36.02
03-4-AG-15	36.03	03-4-WG-15	36.09	04-3-AG-15	36.05	04-3-WG-15	35.96	05-4-AG-15	36.22	05-4-WG-15	35.94	06-3-AG-15	36.12	06-3-WG-15	36.22	07-3-AG-15	36.11	07-3-WG-15	36.08
Mean	36.02	Mean	36.05	Mean	36.14	Mean	35.99	Mean	36.17	Mean	35.99	Mean	36.13	Mean	36.22	Mean	36.23	Mean	36.08
St. Dev.	0.056	St. Dev.	0.067	St. Dev.	0.061	St. Dev.	0.076	St. Dev.	0.065	St. Dev.	0.055	St. Dev.	0.076	St. Dev.	0.074	St. Dev.	0.078	St. Dev.	0.074

A10 - Electrical resistivity for each specimen, and the mean and standard deviation of the billet/orientation group (particles & flour)

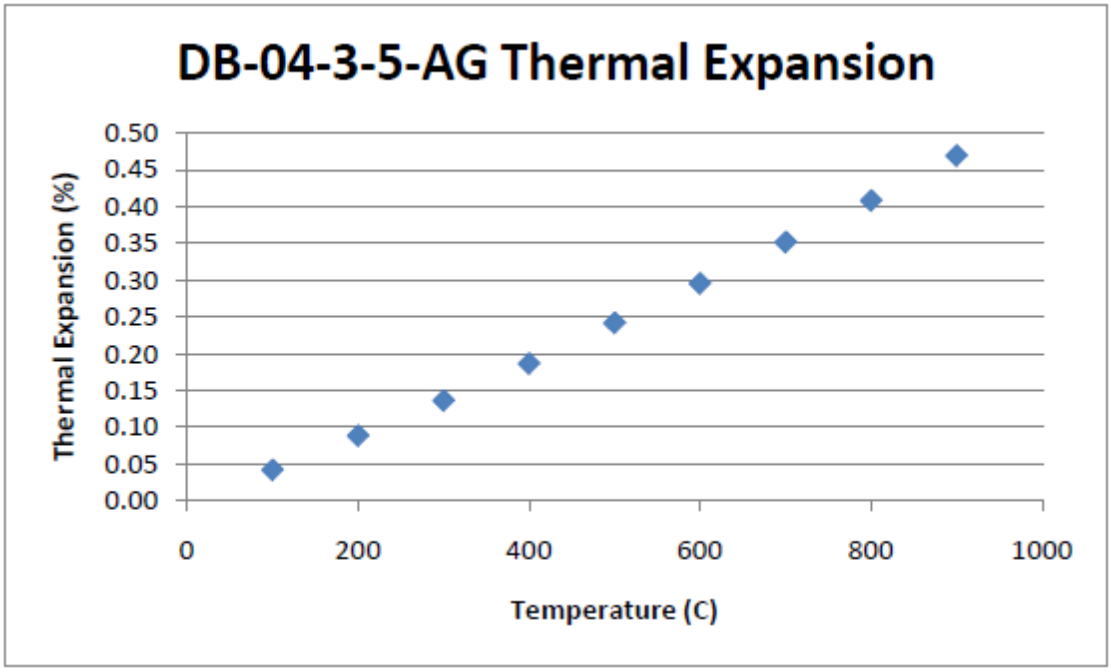
Deep Burrn PCEA Recycle Graphite (Particles & Flour)															
Billet 08-3-AG		Billet 08-3-WG		Billet 09-2-AG		Billet 09-2-WG		Billet 10-5-AG		Billet 10-5-WG		Billet 11-4-AG		Billet 11-4-WG	
Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)	Specimen Number	Resistivity (μΩ.m)
08-3-AG-1	35.84	08-3-WG-1	36.22	09-2-AG-1	36.03	09-2-WG-1	36.16	10-5-AG-1	36.10	10-5-WG-1	35.99	11-4-AG-1	36.21	11-4-WG-1	36.12
08-3-AG-2	36.00	08-3-WG-2	36.21	09-2-AG-2	36.06	09-2-WG-2	36.15	10-5-AG-2	36.19	10-5-WG-2	35.85	11-4-AG-2	36.30	11-4-WG-2	36.12
08-3-AG-3	35.93	08-3-WG-3	36.13	09-2-AG-3	36.08	09-2-WG-3	36.15	10-5-AG-3	36.27	10-5-WG-3	35.98	11-4-AG-3	36.05	11-4-WG-3	36.26
08-3-AG-4	35.90	08-3-WG-4	36.14	09-2-AG-4	36.17	09-2-WG-4	36.20	10-5-AG-4	36.03	10-5-WG-4	35.87	11-4-AG-4	36.02	11-4-WG-4	36.27
08-3-AG-5	36.09	08-3-WG-5	36.14	09-2-AG-5	36.08	09-2-WG-5	36.08	10-5-AG-5	36.22	10-5-WG-5	35.94	11-4-AG-5	36.00	11-4-WG-5	36.30
08-3-AG-6	35.99	08-3-WG-6	36.14	09-2-AG-6	35.87	09-2-WG-6	36.05	10-5-AG-6	36.20	10-5-WG-6	35.91	11-4-AG-6	36.02	11-4-WG-6	36.15
08-3-AG-7	36.08	08-3-WG-7	36.17	09-2-AG-7	35.97	09-2-WG-7	36.15	10-5-AG-7	36.08	10-5-WG-7	35.90	11-4-AG-7	36.20	11-4-WG-7	36.12
08-3-AG-8	35.97	08-3-WG-8	36.19	09-2-AG-8	36.04	09-2-WG-8	36.21	10-5-AG-8	36.07	10-5-WG-8	36.01	11-4-AG-8	36.25	11-4-WG-8	36.17
08-3-AG-9	35.87	08-3-WG-9	36.14	09-2-AG-9	36.06	09-2-WG-9	36.23	10-5-AG-9	36.20	10-5-WG-9	35.90	11-4-AG-9	36.25	11-4-WG-9	36.14
08-3-AG-10	35.89	08-3-WG-10	36.07	09-2-AG-10	36.01	09-2-WG-10	36.26	10-5-AG-10	36.25	10-5-WG-10	36.04	11-4-AG-10	36.21	11-4-WG-10	36.08
08-3-AG-11	36.03	08-3-WG-11	36.06	09-2-AG-11	36.05	09-2-WG-11	36.10	10-5-AG-11	36.07	10-5-WG-11	35.97	11-4-AG-11	36.05	11-4-WG-11	36.16
08-3-AG-12	35.92	08-3-WG-12	36.12	09-2-AG-12	36.01	09-2-WG-12	36.05	10-5-AG-12	36.16	10-5-WG-12	36.00	11-4-AG-12	36.19	11-4-WG-12	36.09
08-3-AG-13	35.91	08-3-WG-13	36.04	09-2-AG-13	35.98	09-2-WG-13	36.19	10-5-AG-13	36.21	10-5-WG-13	35.94	11-4-AG-13	36.25	11-4-WG-13	36.04
08-3-AG-14	36.07	08-3-WG-14	36.19	09-2-AG-14	36.00	09-2-WG-14	36.23	10-5-AG-14	36.15	10-5-WG-14	36.03	11-4-AG-14	36.26	11-4-WG-14	36.26
08-3-AG-15	36.03	08-3-WG-15	36.09	09-2-AG-15	35.98	09-2-WG-15	36.27	10-5-AG-15	36.13	10-5-WG-15	36.00	11-4-AG-15	36.18	11-4-WG-15	36.16
Mean	35.97	Mean	36.14	Mean	36.03	Mean	36.17	Mean	36.16	Mean	35.96	Mean	36.16	Mean	36.16
St. Dev.	0.081	St. Dev.	0.055	St. Dev.	0.066	St. Dev.	0.071	St. Dev.	0.072	St. Dev.	0.061	St. Dev.	0.102	St. Dev.	0.078



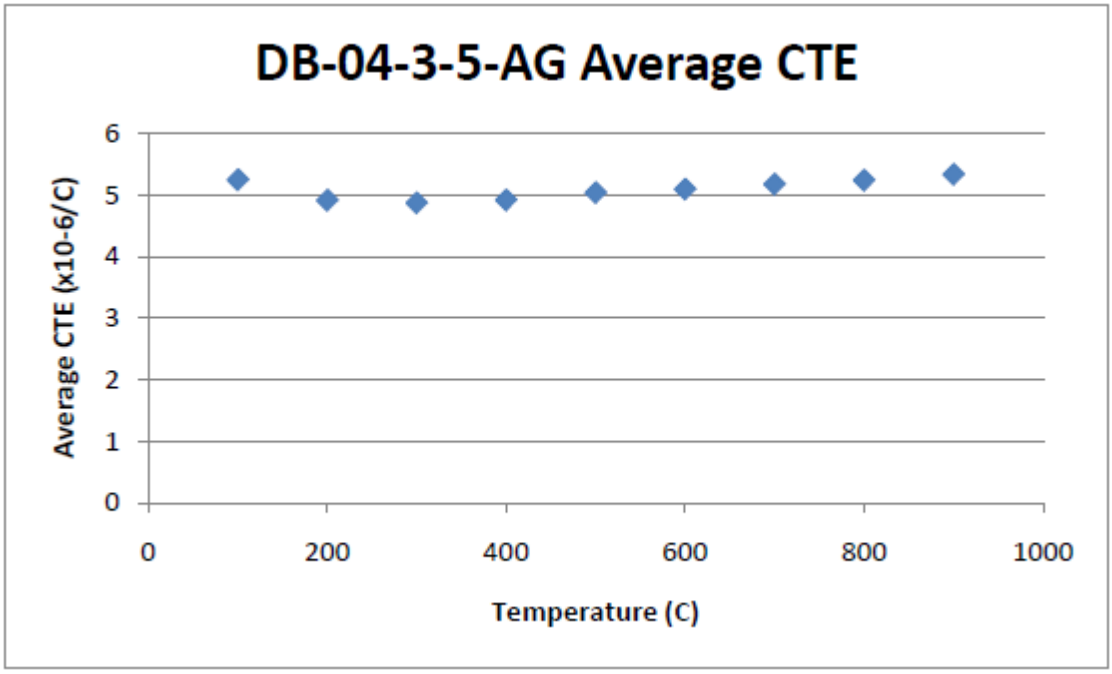
A11 - Thermal expansion behaviour of PCEA recycle graphite specimen 04 -3-4 (AG) with 27.3% of recycle particles



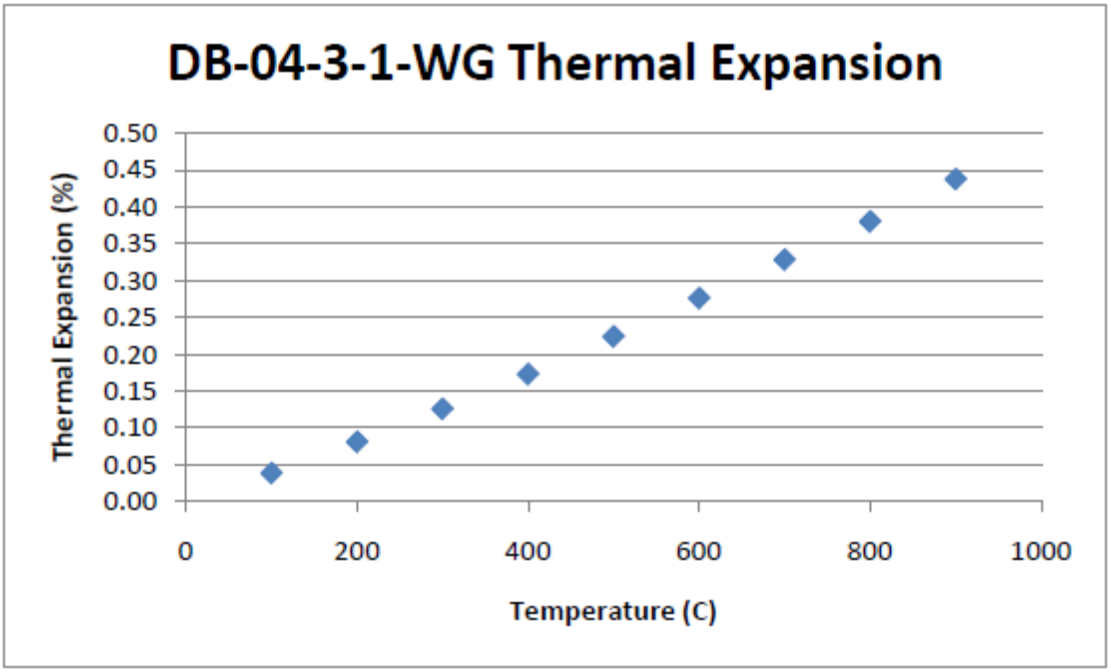
A12 - Average CTE of PCEA recycle graphite specimen 04-3-4 (AG) with 27.3% of recycle particles



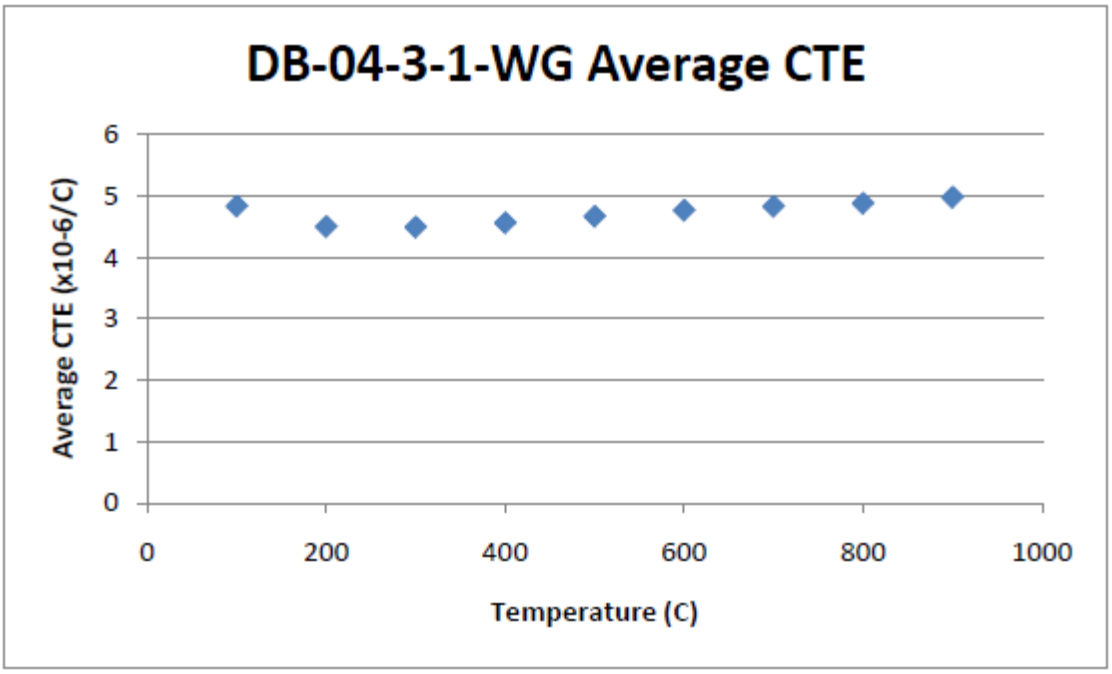
A13 - Thermal expansion behaviour of PCEA recycle graphite specimen 04-3-5 (AG) with 27.3% of recycle particles



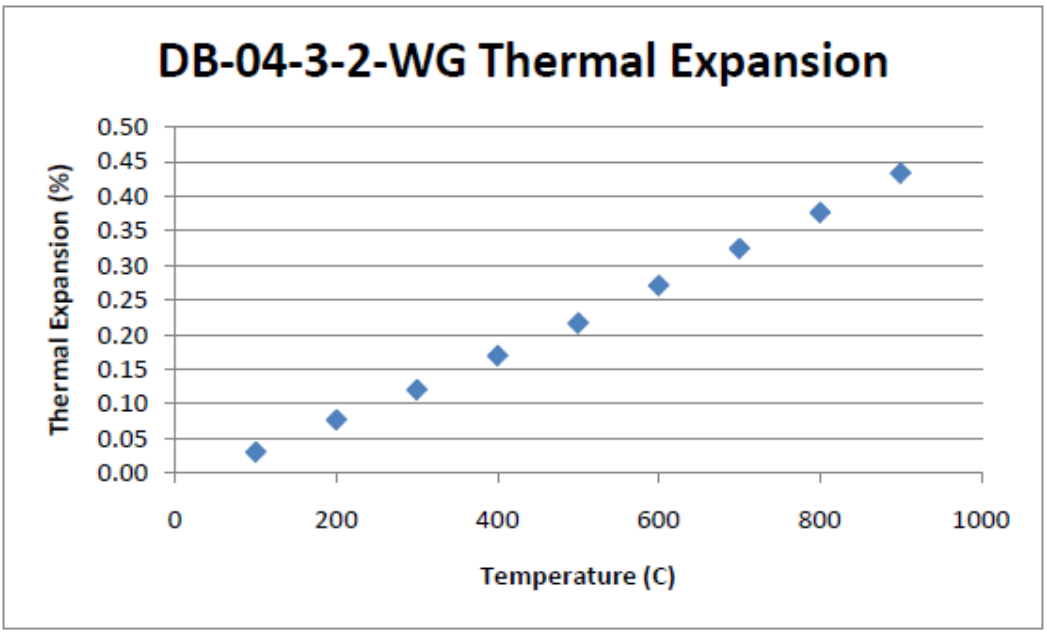
A14 - Average CTE of PCEA recycle graphite specimen 04-3-5 (AG) with 27.3% of recycle particles



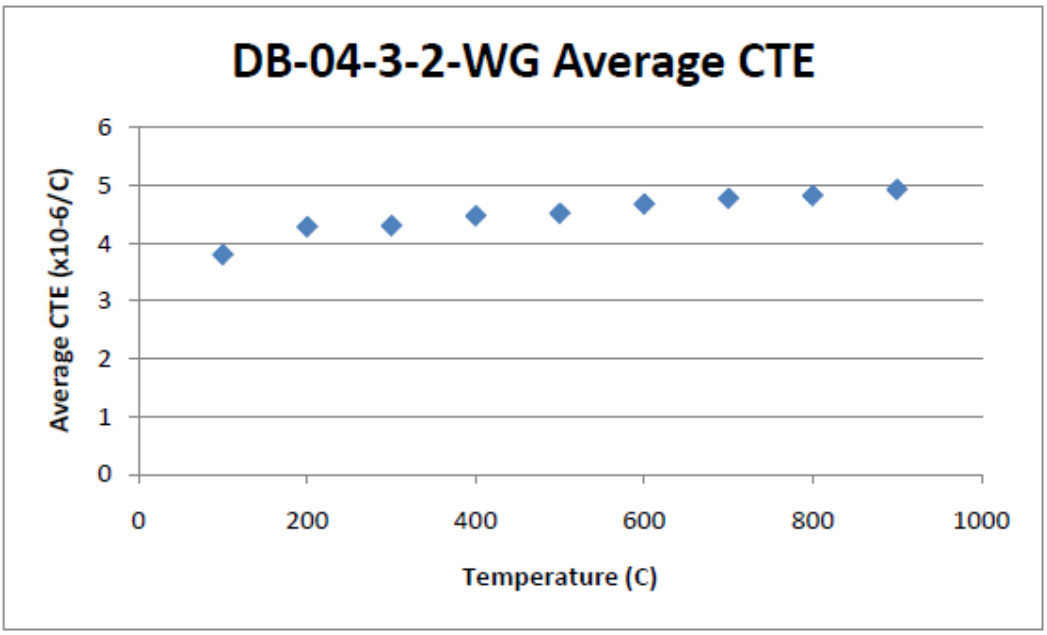
A15 - Thermal expansion behaviour of PCEA recycle graphite specimen 04-3-1 (WG) with 27.3% of recycle particles



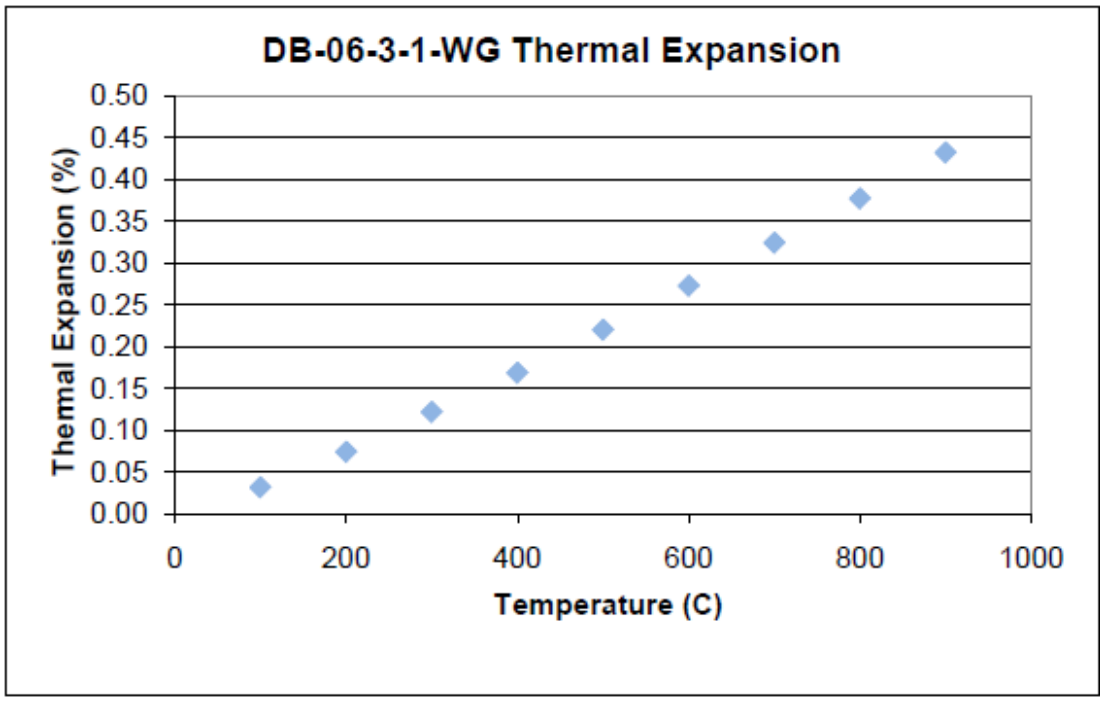
A16 - Average CTE of PCEA recycle graphite specimen 04-3-1 (AG) with 27.3% of recycle particles



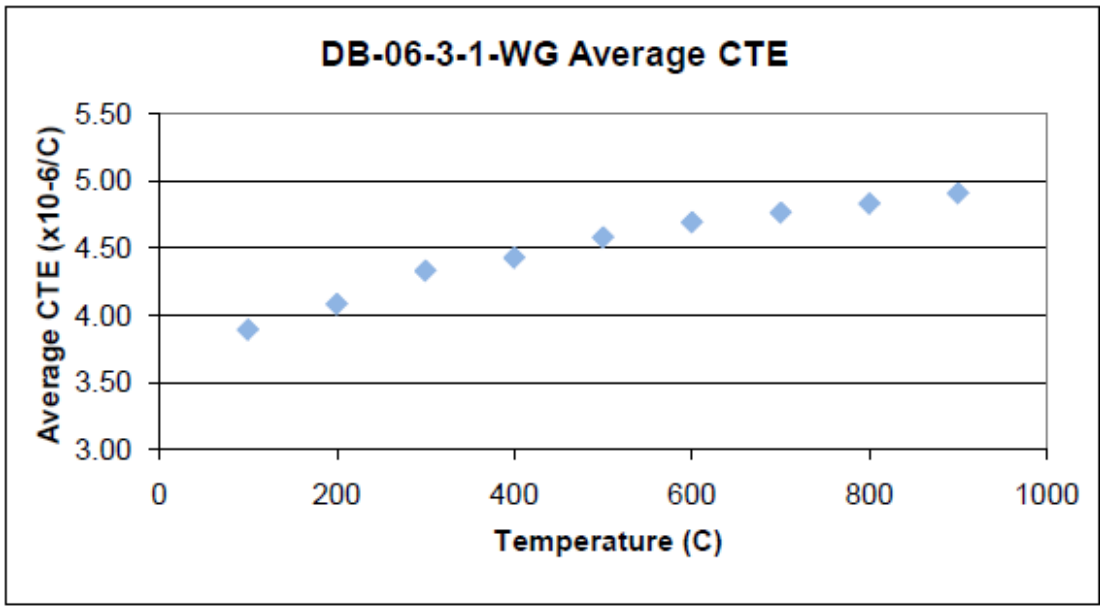
A17 - Thermal expansion behaviour of PCEA recycle graphite specimen 04-3-2 (WG) with 27.3% or recycle particles



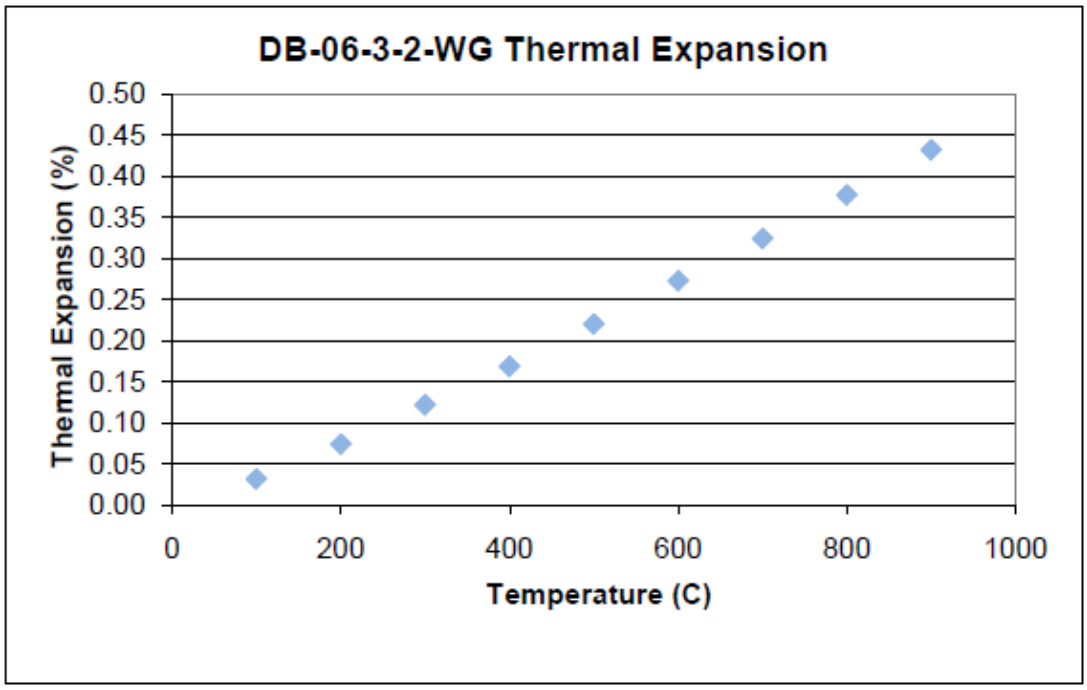
A18 - Average CTE of PCEA recycle graphite specimen 04-3-2 (WG) with 27.3% of recycle particles



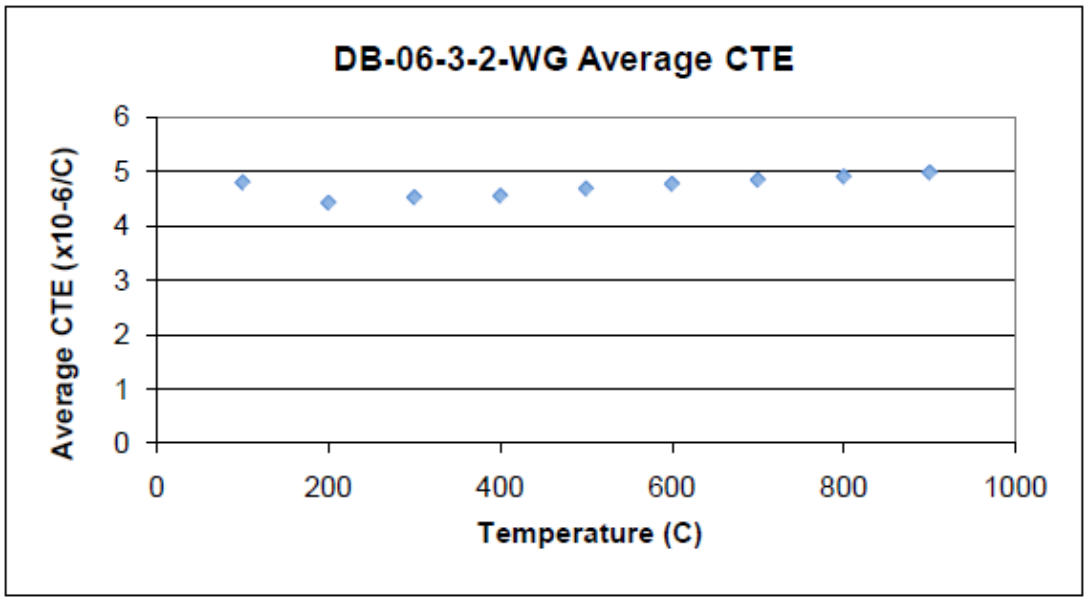
A19 - Thermal expansion behaviour of PCEA recycle graphite specimen 06-3-1 (WG) with 42.4% of recycle particles



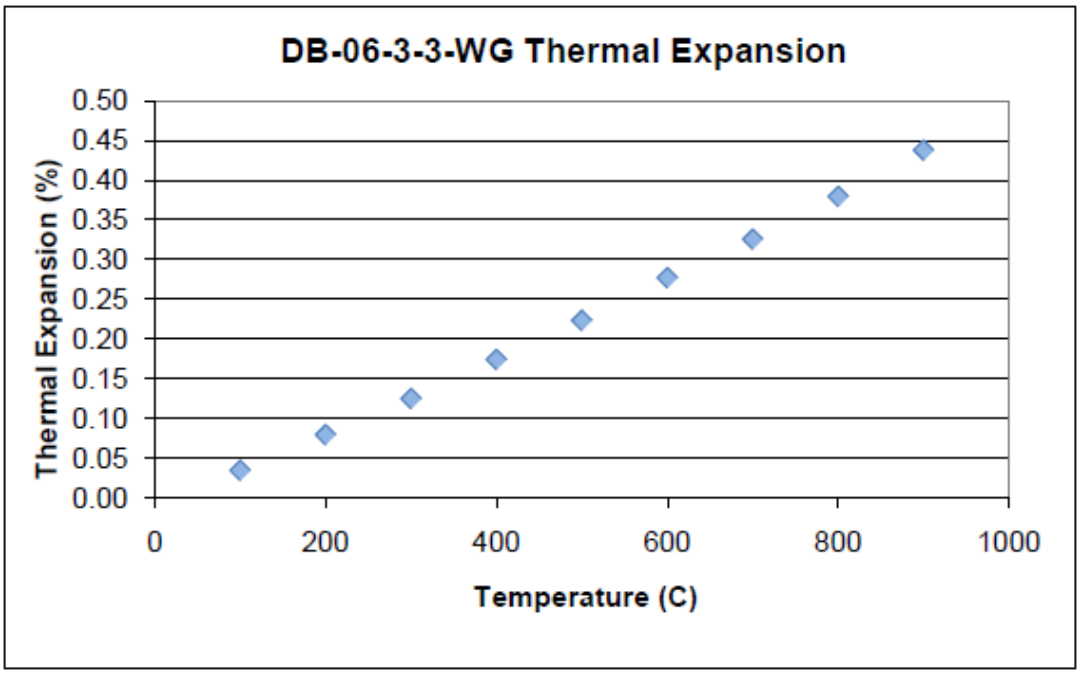
A20 - Average CTE of PCEA recycle graphite specimen 06-3-1 (WG) with 42.4% of recycle particles



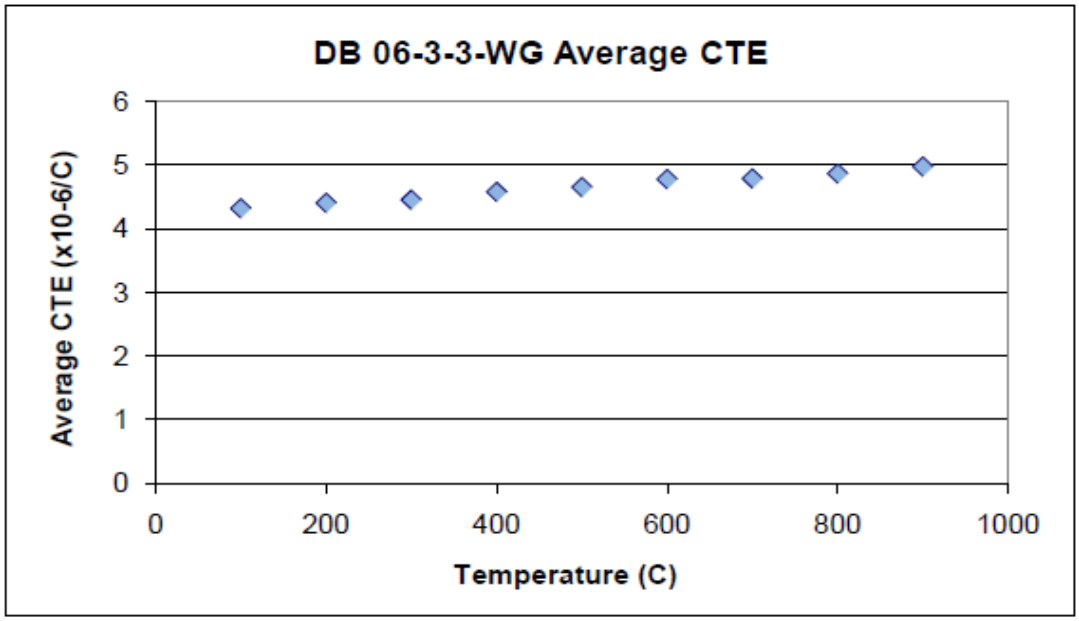
A21 - Thermal expansion behaviour of PCEA recycle graphite specimen 06-3-2 (WG) with 42.4% of recycle particles



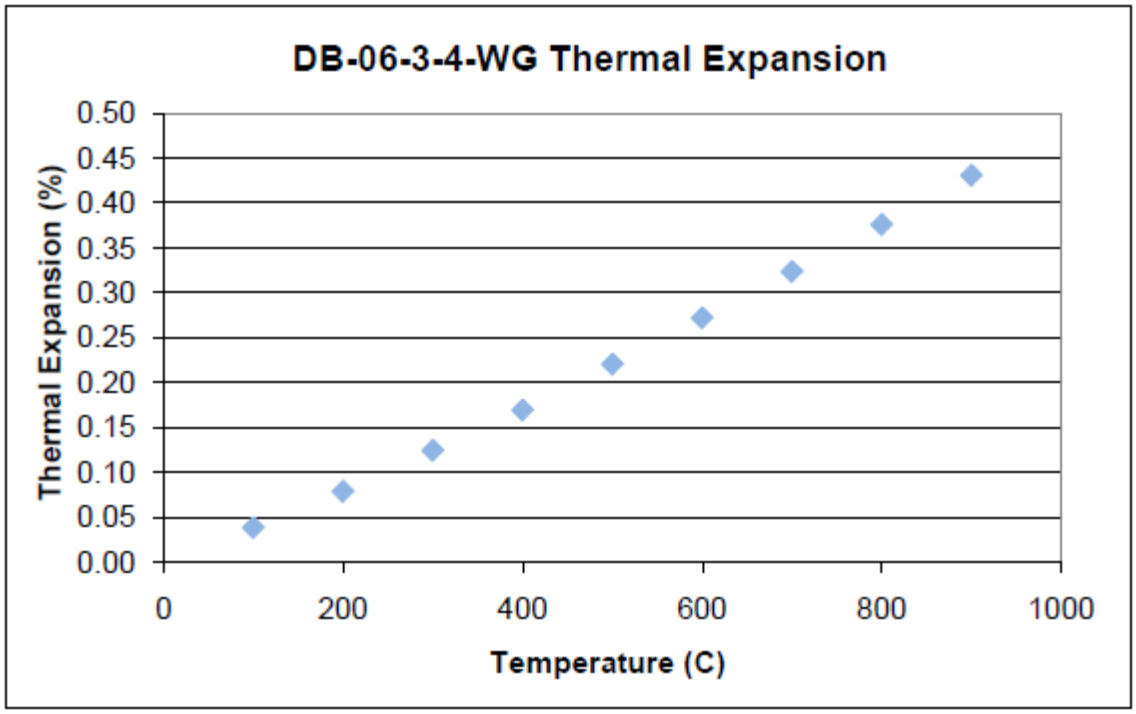
A22 - Average CTE of PCEA recycle graphite specimen 06-3-2 (WG) with 42.4% of recycle particles



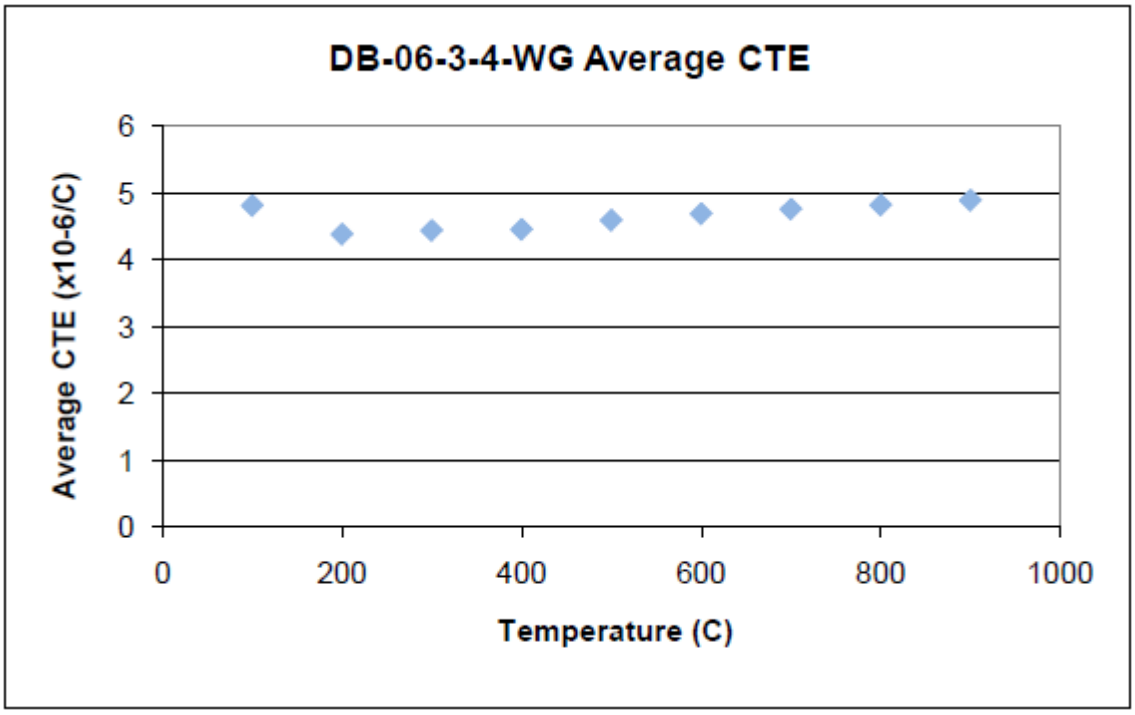
A23 - Thermal expansion behavior of PCEA recycle graphite specimen 06-3-3 (WG) with 42.4% of recycle particles



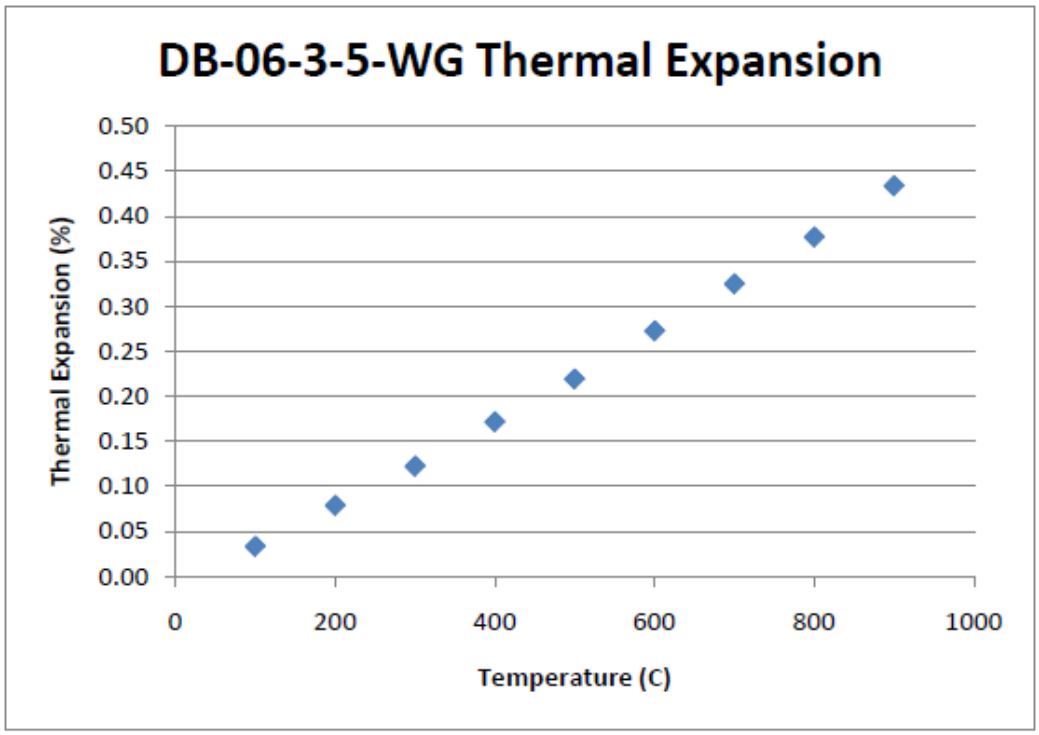
A24 - Average CTE of PCEA recycle graphite specimen 06-3-3 (WG) with 42.4% of recycle particles



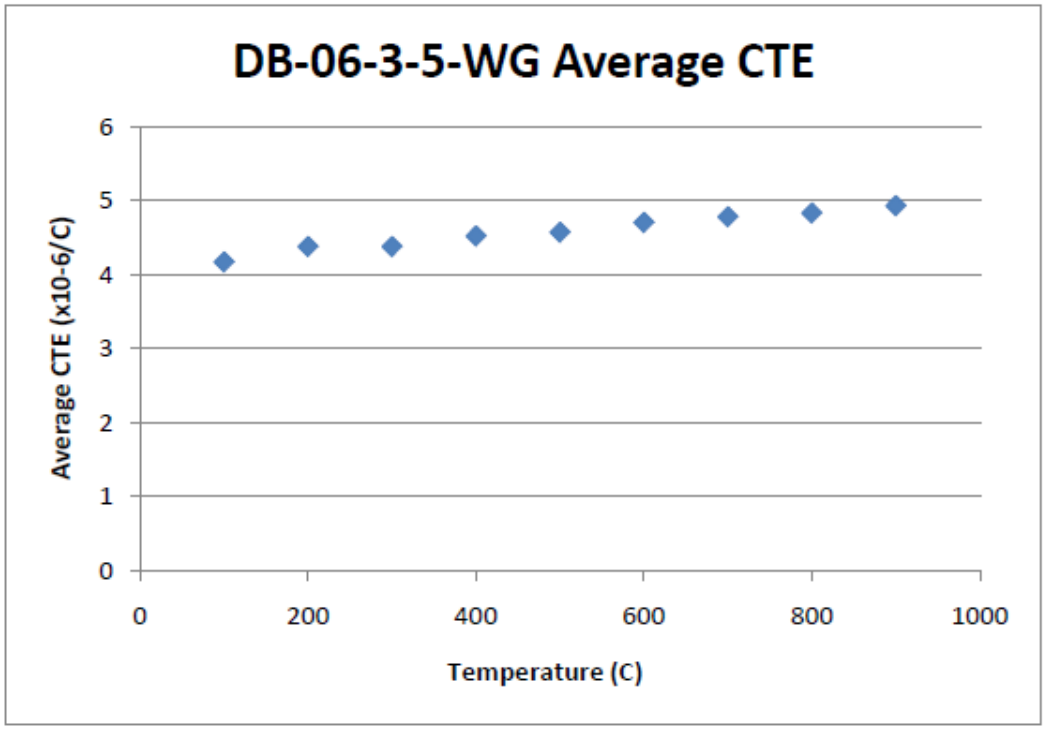
A25 - Thermal expansion behaviour of PCEA recycle graphite specimen 06-3-4 (WG) with 42.4% of recycle particles



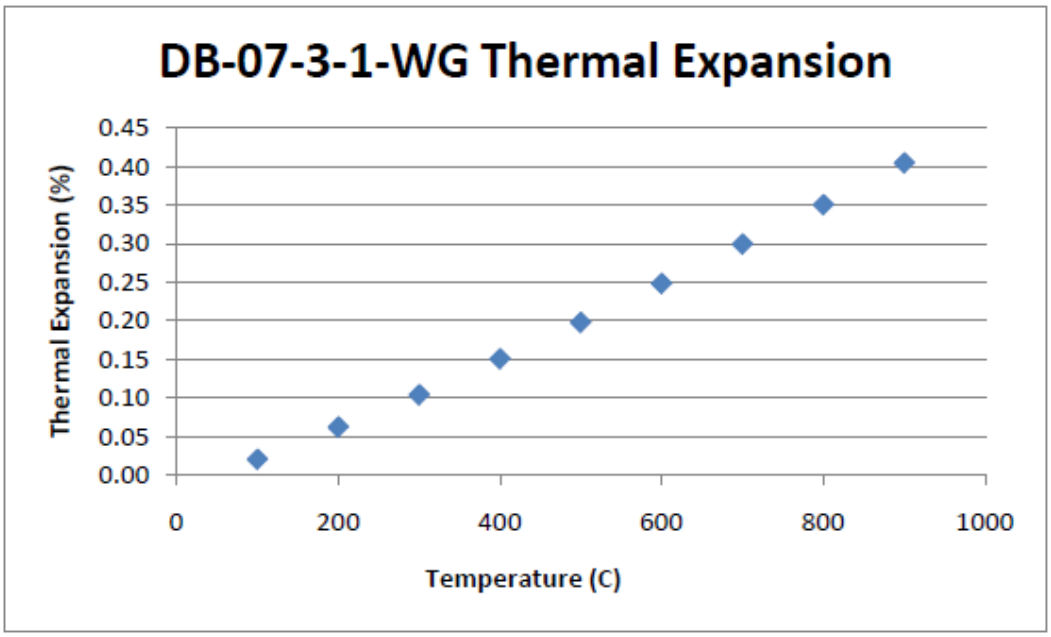
A26 - Average CTE of PCEA recycle graphite specimen 06-3-4 (WG) with 42.4% of recycle particles



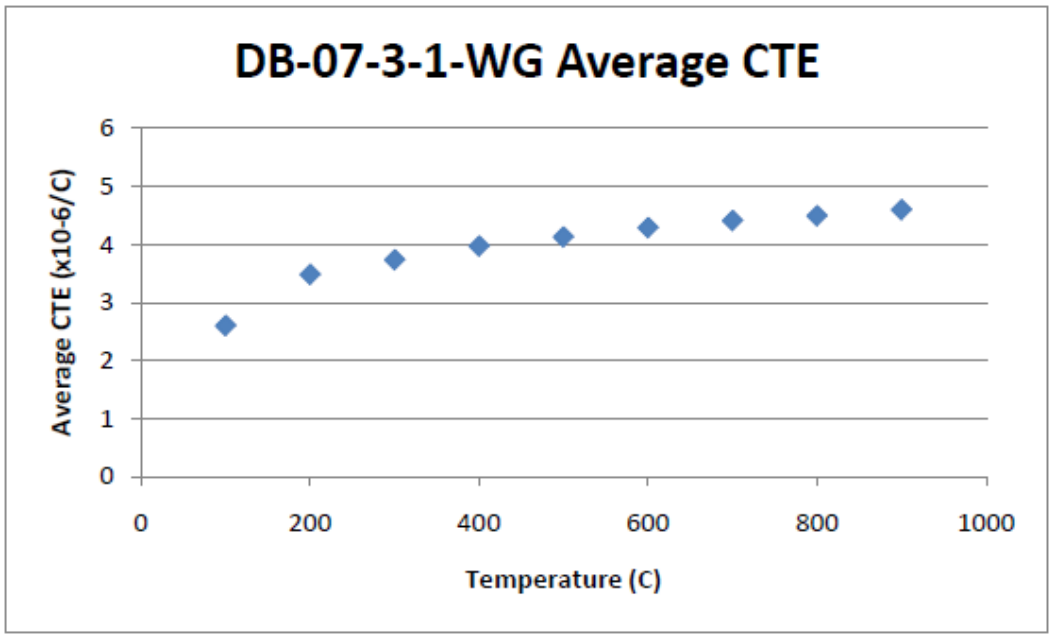
A27 - Thermal expansion behaviour of PCEA recycle graphite specimen 06-3-5 (WG) with 42.4% of recycle particles



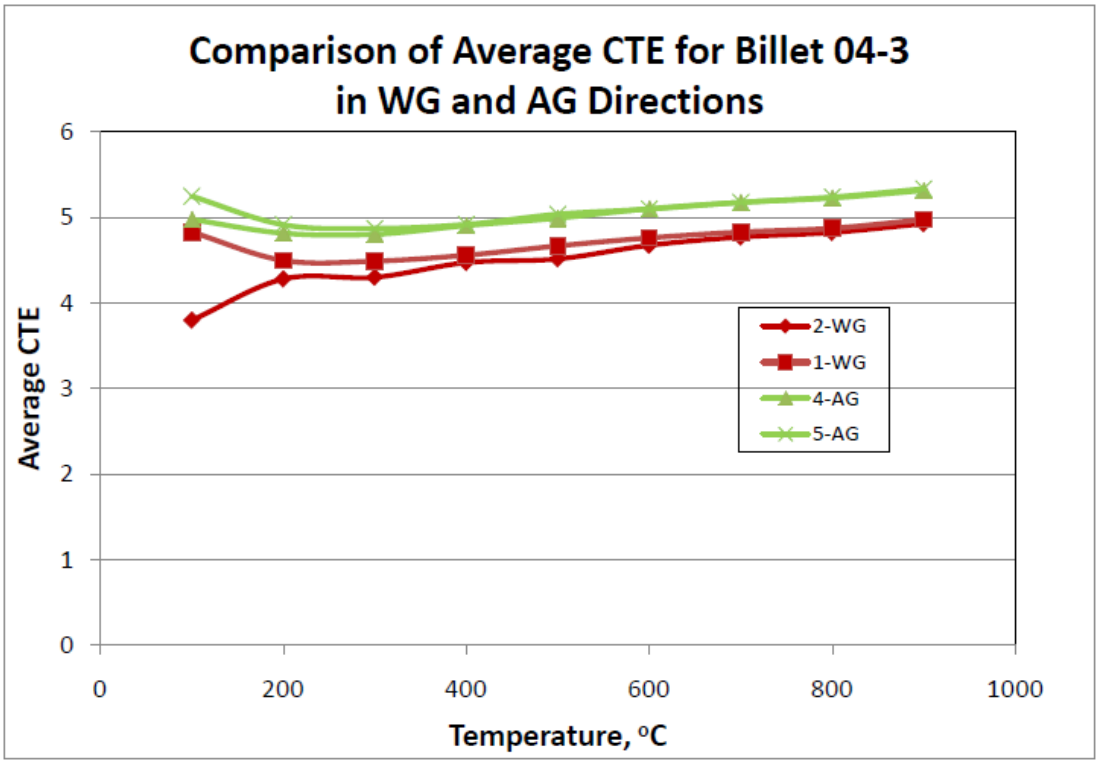
A28 - Average CTE of PCEA recycle graphite specimen 06-3-5 (WG) with 42.4% of recycle particles



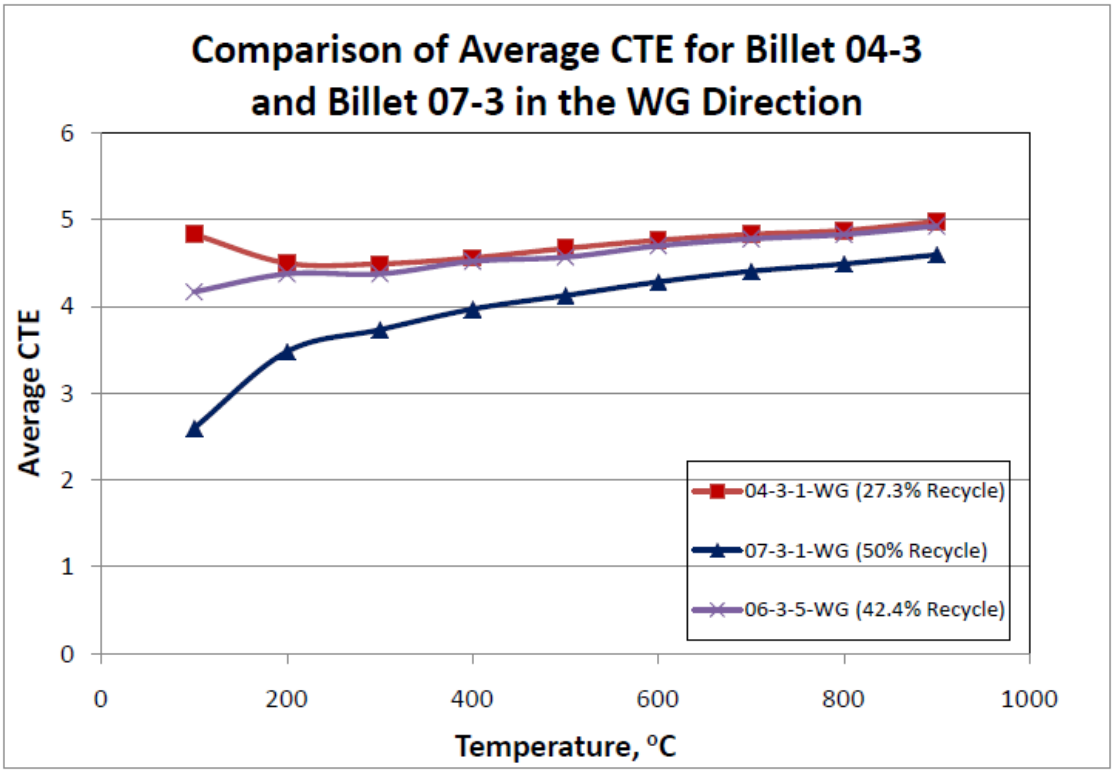
A29 - Thermal expansion behaviour of PCEA recycle graphite specimen 07-3-1 (WG) with 50% of recycle particles



A30 - Average CTE of PCEA recycle graphite specimen 07-3-1 (WG) with 50% of recycle particles



A31 - A comparison of the average CTE of PCEA recycle graphite billet 04-3 (27.3% recycle fraction) in the WG and AG directions



A32 - A comparison of the average CTE of PCEA recycle graphite billets 04-3 (27.3% recycle fraction), billet 06-3 (42.4% recycle) and billet 07-3 (50% recycle fraction) in the WG direction