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Other Graphite and Carbon Based Products

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Other Graphite and Carbon Based Products

Executive summary

The purpose of this report is to provide a summary of the work undertaken to demonstrate the potential for the direct reuse of graphite, as well as utilising recycled material as part of the formulation for new graphite and carbon based products, excluding new nuclear grade graphite for reactor or fuel purposes, as these are reported separately within report D.5.2.3.

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

- NECSA's work which is focused on the direct reuse of irradiated graphite without decontamination or chemical transformation. The areas investigated by NECSA are the direct reuse of graphite for:
  - Electrodes to Dissolve Spent Fuel
  - Crucible Material to Dissolve Spent Fuel
  - Disposal Containers for Solidified Matrixes
  - Manufacture of Nanotubes
- NRG's work on the recycle of irradiated graphite into new Silicon Carbide products which includes the products potential use as a packing medium for use in a repository setting. Subsequent work is reported under Work Package 6, which investigated the benefits of irradiated graphite's conversion to silicon carbides as a means of improving the materials resistance to leaching.
- GrafTech's work on the incorporation of carbon black (representing decontaminated graphite intermediate) into new products (graphite electrodes) manufactured via their proprietary 'fast processing' technique.

Revisions

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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 [1].

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 un-irradiated 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 [2].

The purpose of this report is to provide a summary of the work undertaken to demonstrate the potential for the direct reuse of graphite, as well as utilising recycled material as part of the formulation for new graphite and carbon based products, excluding new nuclear grade graphite for reactor or fuel purposes, as these are reported separately within report D.5.2.3.

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

- NECSA's work [3,4,5] which is focused on the direct reuse of irradiated graphite without decontamination or chemical transformation. The areas investigated by NECSA are the direct reuse of graphite for:
  - Electrodes to Dissolve Spent Fuel
  - Crucible Material to Dissolve Spent Fuel
  - Disposal Containers for Solidified Matrixes
  - Manufacture of Nanotubes
- NRG's work [6,7,8,9,10] on the recycle of irradiated graphite into new Silicon Carbide products which includes the products potential use as a packing medium for use in a repository setting. Subsequent work is reported under Work Package 6, which investigated the benefits of irradiated graphite's conversion to silicon carbides as a means of improving the materials resistance to leaching.
- GrafTech's work [11,12,13,14] on the incorporation of carbon black (representing decontaminated graphite intermediate) into new products (graphite electrodes) manufactured via their proprietary 'fast processing' technique.

2 Graphite Reuse (NECSA)

NECSA's contributions to Work Package 5 covered two distinct aspects of graphite recycle and reuse. The first relates to i-graphite use for the decontamination of waste streams (this work is reported in Deliverable 5.2.5), the second is the direct reuse of graphite for various applications; each of these are covered within this section.

2.1 Graphite Reuse as Electrodes to Dissolve Spent Fuel

NECSA undertook work to determine the potential for the direct reuse of graphite as electrodes for use in dissolving spent fuel. An initial electrochemical cell was constructed, using three electrodes: working, auxiliary and reference. The reference electrode used was silver/silver chloride (Ag/AgCl), while platinum was used for the auxiliary electrode. For the working electrode, a piece of non–irradiated graphite was used (Figure 2.1). The electrolyte used was an alkaline lead nitrate solution. The pH of the electrolyte was 9.8 and the voltage scan began at -1.5V to 1.5V, with a potential of 1.0V.

Figure 2.1: Electrolytic cell, where a graphite piece is the working electrode.

The resulting voltammogram (shown in Figure 2.2), indicated that the current peak due to reduction is very small. This result indicated that the graphite piece can be used as the working electrode, since the current is nearly the same as when using the glassy carbon electrode.

The voltammogram can be explained as follows: During the first part of the sweep, no current flows until the decomposition potential of the specie to be analysed is reached. Once this potential is passed, the current rises rapidly as the analyte is consumed at the electrode surface. Since the solution is unstirred, the concentration of lead at the electrode surface is soon depleted and the current begins to drop. The height of the peak is proportional to the concentration of the specie present in the sample and can be used to determine the amount remaining in the solution.

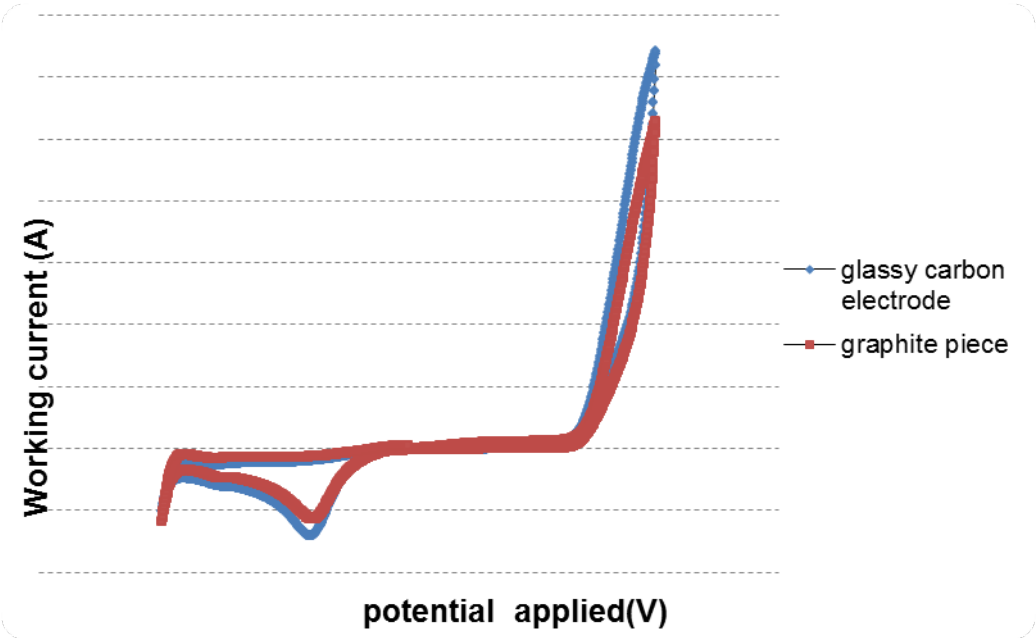

Figure 2.2: Voltammogram showing reactions using different working electrodes

The results obtained prove the basic ability of a natural graphite piece to be used as the working electrode. As nuclear graphite does not have a significant amount of nanoporosity and the surface areas are small (<1m2.g-1), most physically adsorbed species will have to be those of greatest molar mass (larger van der Waal's interactions, dispersive forces). The main areas to be studied when considering the use of irradiated

graphite as electrode are: the structure of graphite as related to electrode usage, types of possible compound formation, electrolytic behaviour of graphite electrodes, and formation of carbon-oxygen and related organic surface compounds with the resulting influence on adsorption and other phenomena.

So as not to contaminate the electrochemical system with radioactivity, it was decided not to continue with radioactive reactor graphite.

2.2 Graphite Reuse as a Crucible Material to Dissolve Spent Fuel

The re-use of irradiated graphite blocks as crucible material for radioactive waste treatment and/or using graphite blocks as waste disposal will enhance the use of irradiated graphite.

In order to manufacture a crucible from contaminated graphite and to prevent any dust formation (contamination), the use of chemical etching technology was studied for the manufacturing of waste or molten salt containers.

The result shown in Figure 2.3 indicates that with a combination of mineral acids it was possible to create a smooth cavity inside a graphite structure without damaging the surface area (no cracks). Upon receiving irradiated graphite research samples from CARBOWASTE partners, crucibles will be manufactures with chemicals etching technology and will be tested as molten salt containers. (Determine any radionuclides transfer between graphite into molten salt).

Figure 2.3: Manufacturing of graphite crucibles for molten salt applications using chemical etching technology

2.3 Graphite Reuse as Disposal Containers for Solidified Matrixes

The work undertaken by NECSA, and reported in section 2.2 above, was considered to have an additional application that being the use of graphite blocks as disposal containers for solidified matrixes.

2.4 Graphite Reuse for the Manufacture of Nanotubes

The manufacture of nanotubes with a DC plasma will be optimised and extended to irradiated graphite, once licensing has been approved. The preparation of a mould from irradiated graphite for manufacturing nanotubes with a laser is currently underway.

A different type of processed multi-walled nanotube was received from the University of Johannesburg for testing. Iodine absorption tests were done in order to compare the

different technologies for manufacture of nano tubes. The experiments were extended using a bipolar solvent in order to increase the solubility of the nanotubes in order to increase the possibility if iodine absorption. The results in Table 2.1 indicate that the new nanotubes from University of Johannesburg (UoJ) that was fabricated with a different technology is not suitable for radionuclide absorption. However, the addition of the bipolar solvent increased the aborption dramatically (from 51 ml/g to 394 ml/g).

Table 2.1: Absorption of Iodine on nanotube fabricated with different technologies.

Sample	K_d (ml/g)	pH	Bipolar Solvent
SWNT(commercial)	43178	3	-
SWNT(commercial)	4543	3	Y
SWNT(commercial)	3351	10	-
SWNT(commercial)	282	10	Y
MWNT(UoJ)	51	3	-
MWNT(UoJ)	394	3	Y
MWNT(UoJ)	3	10	-
MWNT(UoJ)	19	10	Y
MWNT(WA)	685	3	-
MWNT(WA)	707	3	Y
MWNT(WA)	88	10	-
MWNT(WA)	121	10	Y

The results in Table 2.1 also confirmed that a high absorption of iodine occurs on commercially available single-walled nano-tubes without any surface modification in a low pH. However with the addition of the bipolar solvent the absorption of the iodine decreases significantly (from 43178 ml/g to 4543 ml/g).

As ^{36}Cl is a troublesome nuclide in the nuclear graphite industry, it was decided to investigate the adsorption of chlorine onto carbon nanotubes (CNTs). Two solutions,

pH 3 (adjusted pH to 3 with 0.01 M nitric acid) and pH 7 (adjusted pH to 10 with 0.01 M NaOH) of Cl-36 were prepared from the stock solution. The CNTs used were commercial MWCNTs (Bayertubes), MWCNTs from UoJ and commercial SWNTs (Sigma-Aldrich). The results in Table 2.2 indicate that there is slight adsorption on the Bayertubes and SWNTs in acidic medium. Measurements are currently underway at pH 7.

Table 2.2: Absorption of ^{36}Cl onto different nanotubes.

CNT	K_d (pH 3) ml/g	K_d (pH 10) ml/g
Bayertubes	66.1	16.2
UJ MWNTs	16.0	0
SWNTs Sigma	53.9	11.0

Further work is underway to determine the influence of CMPO (Octyl(phenyl)-N,N-disobutylcarbamoylmethyl-phosphine-oxide) absorbed onto the surface of nanotubes for actinide extraction, the results from which were not available at the time of producing this report.

3 Graphite Recycle into Silicon Carbide (NRG)

Under Work Package 5, NRG participated in sub-task 5.2.3 “Carbonaceous ceramics for waste management” and concentrated on SiC formation from graphite for use in disposal sites as backfill, encapsulants, etc., without oxidation of the carbon and providing safety during processing.

3.1 Introduction

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

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

Table 3.1: Typical properties of SiC

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

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

3.2 SiC Formation

Literature research on SiC formation from graphite was done, several suitable methods were found and finally a technique published by A. Morancais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956 [2], was chosen as method to be tested. In the paper, the method is called "a process involving an SHS stage."

The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite has been studied. Products with very high pore contents (≈80%) were obtained using a process, shown in Figure 3.1 overleaf, which consisted of heating the reactive pellets in purified argon, at 15 °C min−1, up to 1430 °C and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of a SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the formation of silicon carbide, during heating from about 1325 up to 1430 °C, is

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

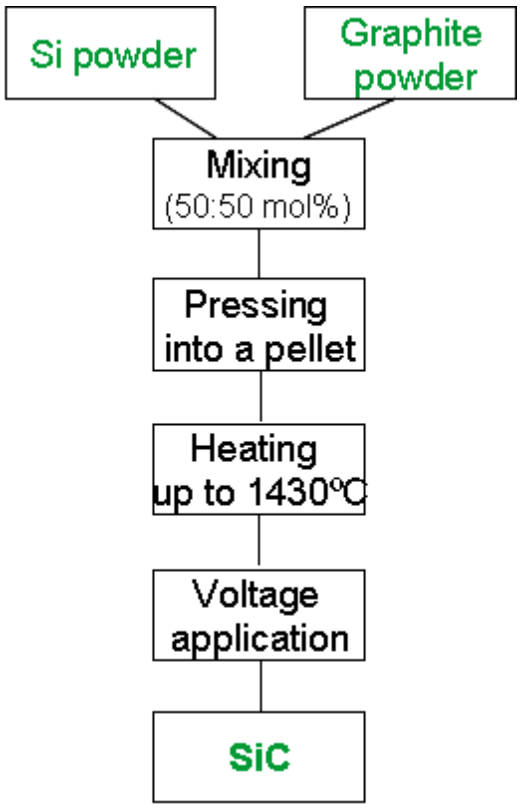

Figure 3.1: Flowchart showing the SiC formation method

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

3.3 Raw Materials

The raw materials used for the production of SiC were:

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

3.4 Experimental Set-up

A new setup for the experiment was built, as shown in Figure 3.2. This setup was designed to avoid pressure on the molybdenum wires during movement of the pellet to the middle of the ceramic tube in the high temperature oven (HTTF) – because during testing of the original setup wires were often broken. This setup consists of a ceramic tube with a length of 1 meter with 2 bores (an internal diameter of 1 mm). A ceramic dish was fixed to the ceramic tube using an aluminium oxide mixture (ceramic paste), which was slowly sintered to 1000°C to harden. Afterwards the two molybdenum wires were placed through the bores and cut to length. After forming the ends of the molybdenum wire so that the two graphite plates could move freely, the space between the bore and the molybdenum wire was filled up with ceramic paste. This ensured that there would be no gas leakage through this end.

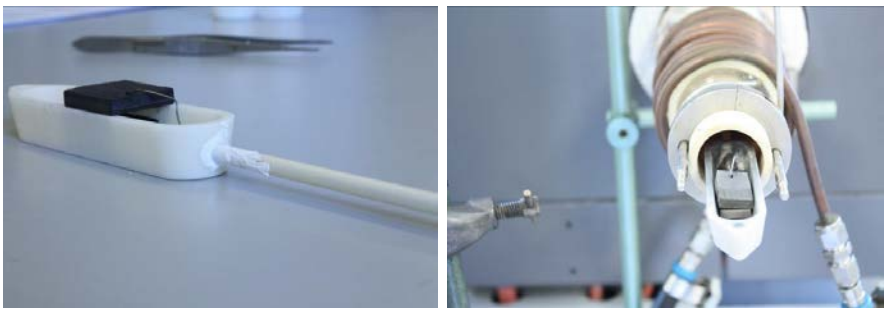

Figure 3.2: Fixed dish to tube (left) and setup placed in the HTTF oven (right)

3.5 Experimental Procedure

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

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

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

When finished, the sample was taken from the setup and analyzed by XRD and SEM.

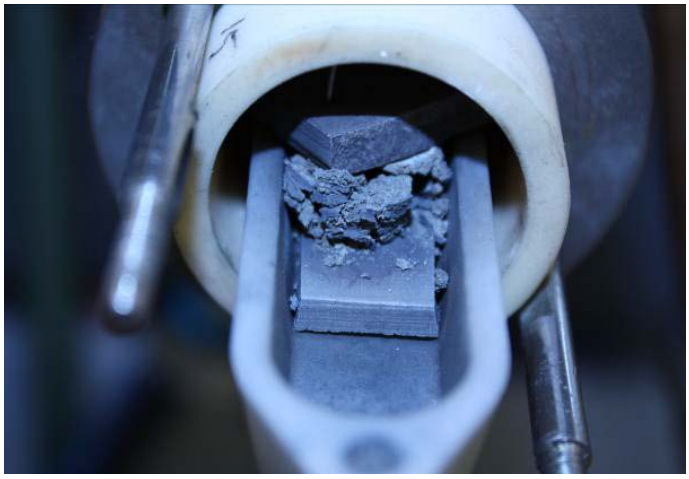

Figure 3.2: A SiC pellet after the Morancais SHS method

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

3.6 Conclusions

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

The synthesis and characterization of SiC was completed, with the material then being used for leaching experiments within the WP6 – task 6.2.

The key conclusions drawn from the leaching experiments are that:

- The measured activities of ^{14}C leached from irradiated graphite are much higher comparing to the ones leached from the SiC made from this graphite. Based on that, it seems that the transformation of irradiated graphite into silicon carbide could be a way of decreasing of the ^{14}C release from the material.

- To confirm that silicon carbide could be a suitable product formed from irradiated graphite concerning the lower ^{14}C release, more tests must be performed. Long-term tests should be done, better comparable amount of materials to be leached should be studied and material in the form of pellets should be leached as well (if SiC is used as e.g. container material).

- Since the trace amount of free carbon in the synthetized SiC could be responsible for the observed ^{14}C leaching, it is also important to further optimize the synthesis procedure.

4 Graphite Recycle into Graphite Electrodes (GrafTech)

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.

Specifically, this work included:

- Defining the maximum fraction of carbon black or other recycled material that can be utilized in a “new” graphite artifact without compromising the strength and other physical and mechanical characteristics of the said graphite artifact.
- Defining the ideal processing conditions to produce such a graphite artifact that will include a fraction of carbon black and/or other recycled material. This includes the investigation of a “fast” process to manufacture graphite artifacts as a possible means to produce samples for evaluation.

4.1 Introduction

GrafTech fabricated 5 different varieties of graphite material that were 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 drastically 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.

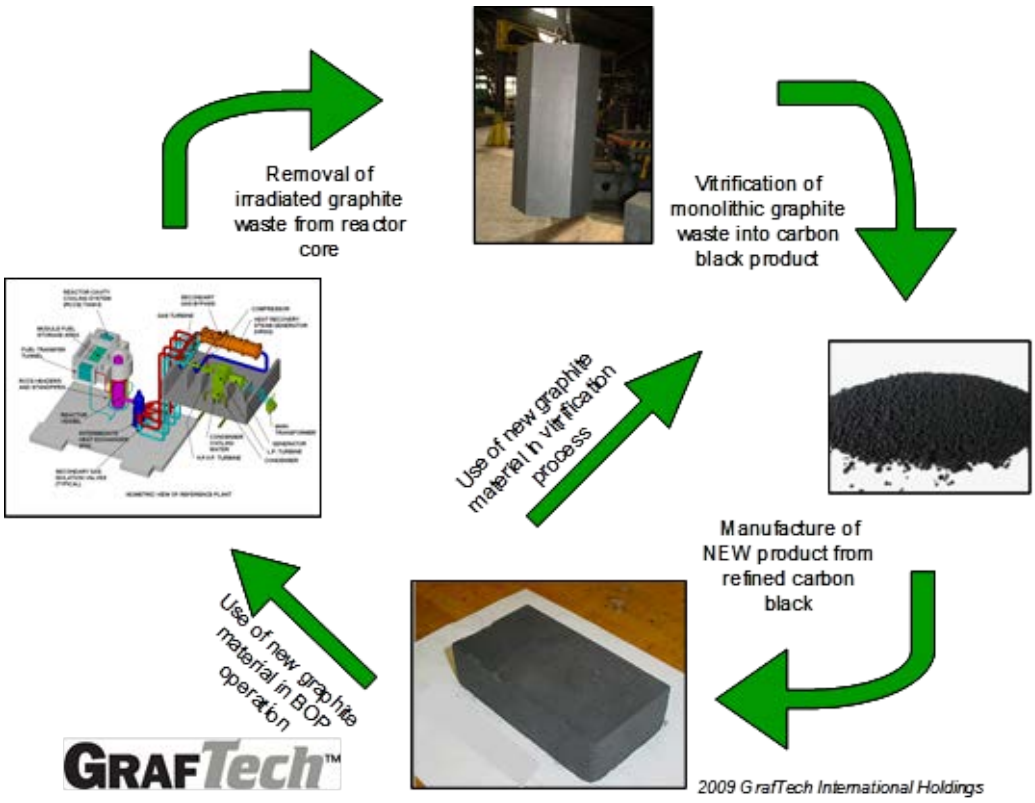

Figure 4.1: Schematic diagram depicting the cycle of the irradiated graphite graphite, vitrification, and new electrode.

4.2 Experimental Overview

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 the Table 4.1 below:

Table 4.1: Formulations for Recycle Intermediate

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 drastically 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.

4.2 Results and Discussion

Optical microscopy images taken of representative areas of the final graphitic artifacts produced for this work are shown in Figure 4.2 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 4.3 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.

Other analysis performed on the graphite artifacts included density, flexural strength (Figure 4.4), coefficient of thermal expansion (Figure 4.5), thermal conductivity (Figure 4.6), Young’s modulus and specific resistance (Figure 4.7). All figures show two samples tested for each value of carbon black loading.

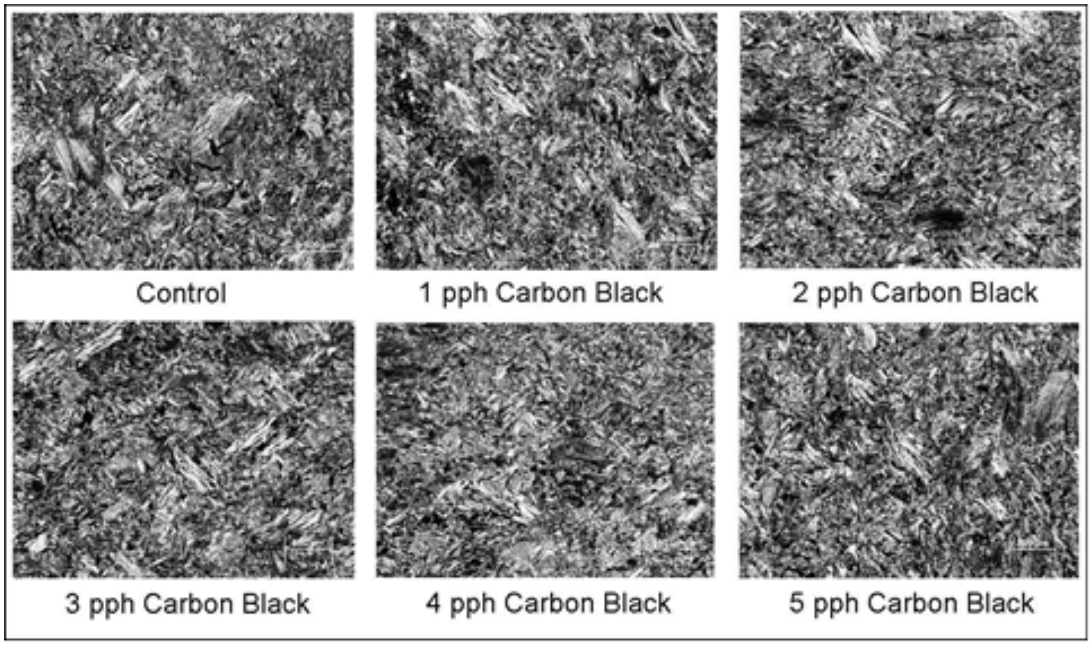

Figure 4.2: Comparison of graphite artifacts made with varying concentrations of carbon black. Images show uniform areas of graphitized material

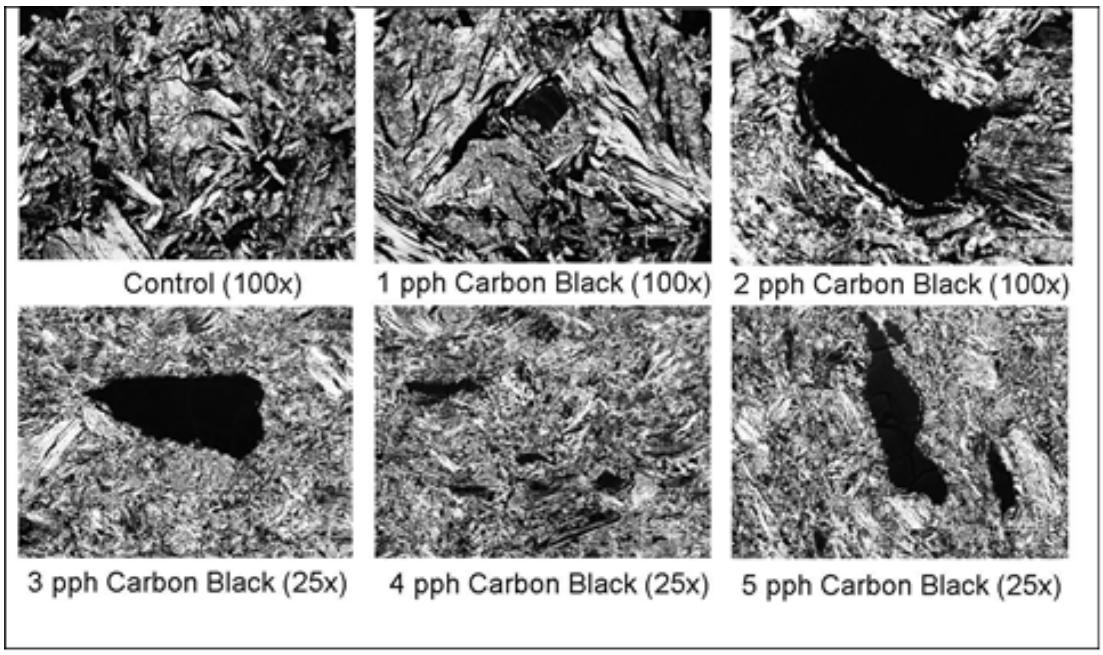

Figure 4.3: Optical microscopy images showing aggregation of carbon black due to lack of sustained mixing. Carbon black aggregates show as dark areas in polarized light

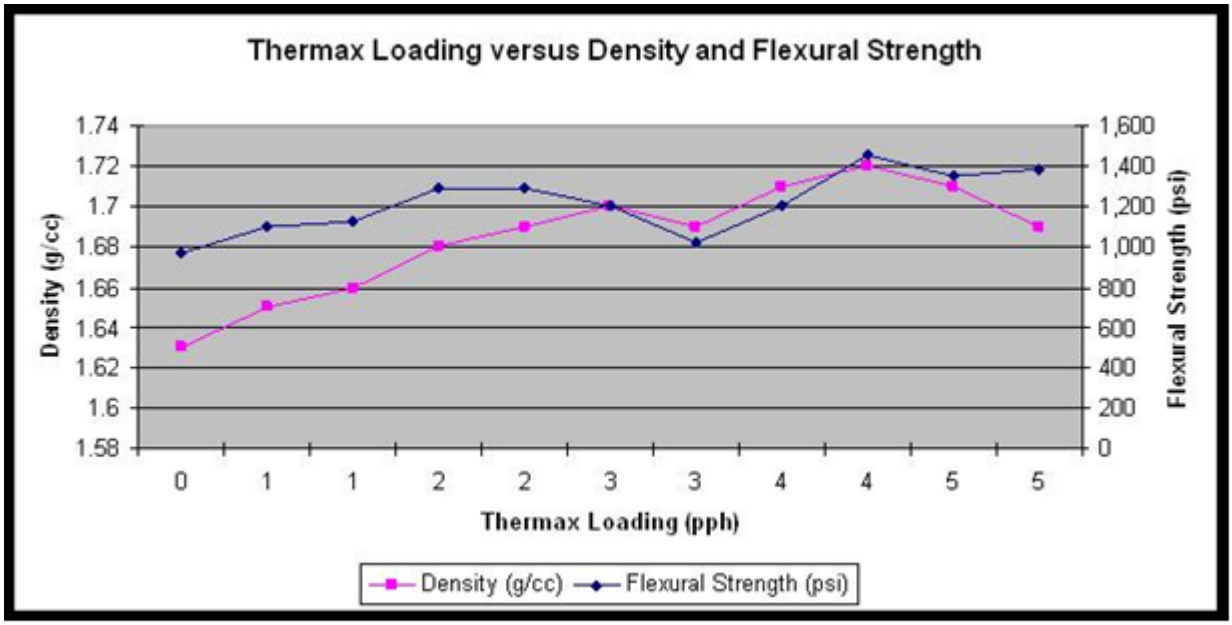

Figure 1.4: Results of measured density and flexural strength at various levels of carbon black loading.

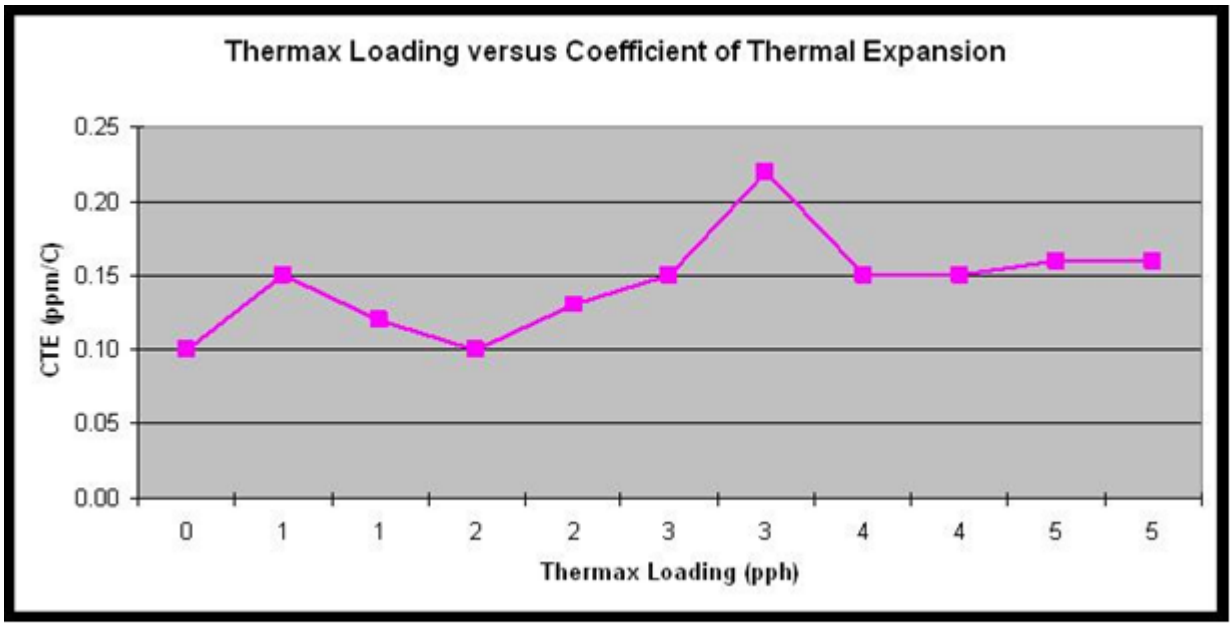

Figure 4.2: Measurement of the slight change in CTE as a function of carbon black loading.

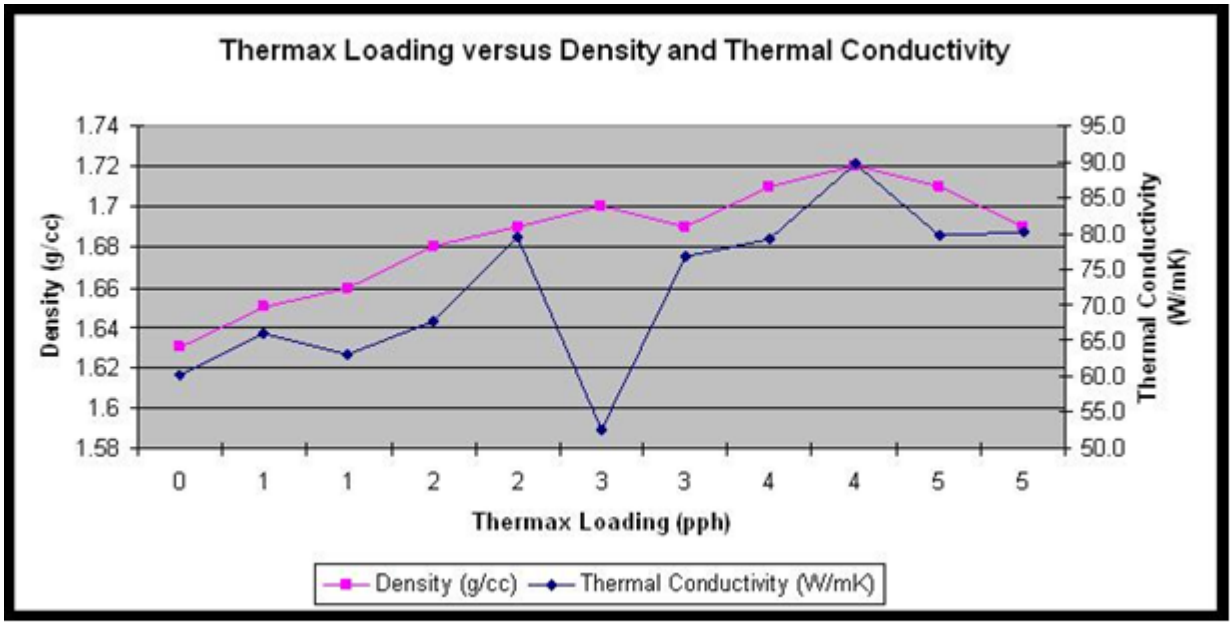

Figure 4.3: Measurement of the density and thermal conductivity of graphite made with varying levels of carbon black.

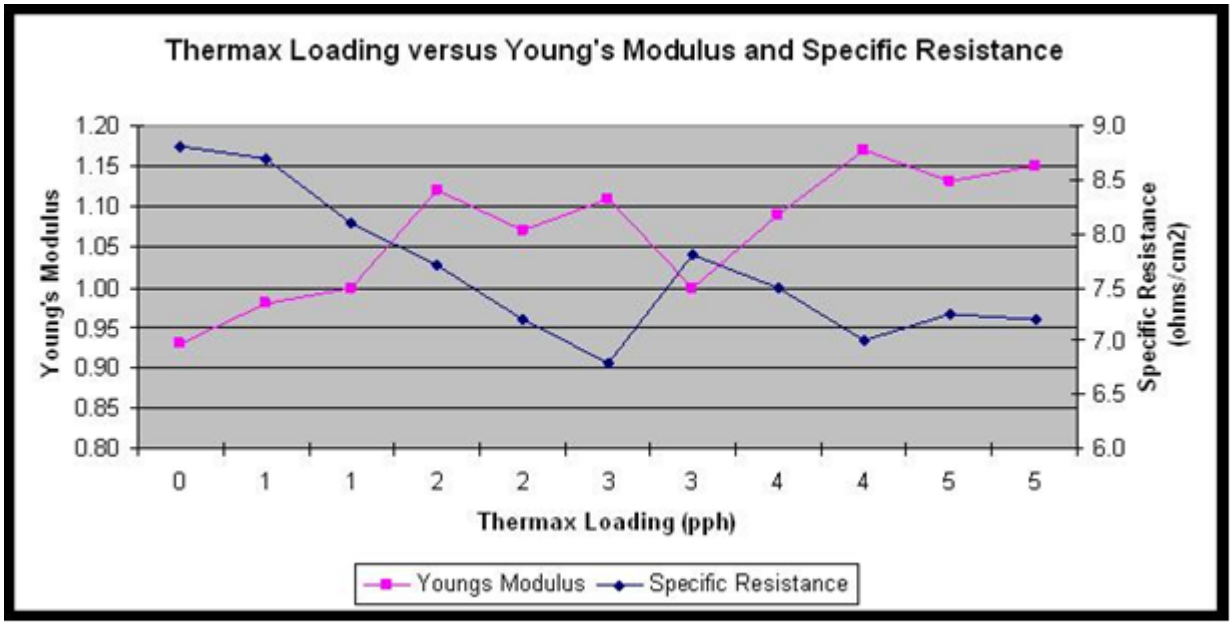

Figure 4.4: Variation in Young's modulus and SR with varying levels of carbon black loading.

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

4.4 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 drastically 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.

5 Discussion & Conclusions

All the products described within this report are based on either the direct reuse of i-graphite or its recycle through its addition to the formulation of new graphite/carbonaceous items. Other potential uses of i-graphite, either by direct reuse or through recycle to those covered may provide other significant opportunities which align with the principals of the waste hierarchy, and which if utilized could lead to significant reductions in the volumes of waste graphite which require long term management.

It should be noted that significant work has been undertaken over many years to investigate the various options and approaches other areas of graphite management, which include retrieval, characterization, processing and long term management. The area of i-graphite reuse/recycle is barley in its infancy, as prior to the start of the Carbowaste project in April 2008; very little work had been undertaken in this area. Since 2008, and largely as a result of WP5 of the Carbowaste project, interest has been raised to the opportunities afforded by reuse/recycle, as well as the potential economic savings which could be achieved through its successful implementation. One key example of this has been the direct involvement of the graphite manufacturers who initially had little interest in this area, but who, through WP5 have undertaken significant and interesting work in the initial development of this field of graphite management.

In terms of the work covered in this report, the key conclusions drawn by the participating organizations are:

- The recycle of i-graphite into components for nuclear applications, such as graphite electrodes for waste vitrification is achievable.
- The use of carbon black as the recycled intermediate is viable, but only as a low proportion of the new product recipe due to limitations in its graphitizability, binding ability and conductivity. The use of carbon black as the recycled intermediate provided the benefit of an optimal decontamination approach, and

therefore the minimization in radiological controls required in a manufacturing facility.

- Results of work both within and external to the Carbowaste project show that significantly higher proportions of i-graphite can be incorporated into new products, without a significant reduction in their performance, if the material is still graphite, and has not undergone transformation.

- The transformation of i-graphite into silicon carbide is achievable and provides a means of reducing the leaching potential of the material under repository conditions.

- Further work on silicon carbide is necessary to develop this approach, which would include further leaching tests, over longer durations and with larger samples. In addition, conversion of the lab scale process of converting graphite and silicon into SiC to an industrial scale would also need to be considered.

Glossary

CMPO	Octyl(Phenyl)-N,N-Diisobutylcarbonoylmethyl-Phosphine Oxide
CNT	Carbon Nanotube
CVD	Chemical Vapour Deposition
DC	Direct Current
EdF	Electricite de France
MWCNT	Multi-walled Carbon Nanotube
NECSA	South African Nuclear Energy Corporation Limited
NRG	Nuclear Research and Consultancy Group
Pph	Parts Per Hundred
PSA	Pressure Swing Adsorption
SEM	Scanning Electron Microscope
SHS	Self-propagating High-temperature Synthesis
SiC	Silicon Carbide
SR	Specific Resistance
SWNT	Single Walled Carbon Nanotude
UNGG	Uranium Naturel Graphite Gaz
UoJ	University of Johannesburg
VLS	Vapour-liquid solid process
XRD	X-ray Diffraction

References

[1] EURATOM Annex 1 "Description of Work" CARBOWASTE: Treatment and Disposal of Irradiated Graphite and other Carbonaceous Waste. February 2008.

[2] Carbowaste Report T.5.2.1 'Identification of Requirements for Intermediates Needed for New Products Synthesis'

[3] Meyer. W.C.M.H. Necsa report "Progress report on the Carbowaste Programme for 2008/2009

[4] Meyer. W.C.M.H. Necsa ¼ Carbowaste Project Report, Doc No: NWR-CAWGENREP-09001. Dated June 2009.

[5] Meyer. W.C.M.H. 'Necsa Work Package 5 Progress Report for 2010/2011'. Issued 01 April 2011.

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

[7] E. de Visser – Týnová and H.L. Cobussen – SiC formation from graphite NRG-22260/11.109977, I&D – report for Carbowaste project – task 5.2, September 2011

[8] E. de Visser – Týnová and H.L. Cobussen - Internal communications on SiC formation

[9] V. Smit – Groen – Internal notes on XRD on SiC and graphite samples

[10] H.L. Cobussen – Internal note on leaching experiments 2.2260.40/12.112831 I&D/JC/PvS

[11] Email correspondence from Tracy Albers, GrafTech, dated the 8th December 2009.

[12] Email correspondence from Tracy Albers, GrafTech, dated the 13th April 2010.

[13] Pappano.P, Strizak.J, Burchell.T, Albers.T "Deep Burn: A Hot New Way to Reuse Irradiated Graphite". Paper presented at the 10th International Nuclear Graphite Specialists Meeting held at Yellowstone, USA. September 27th – 30th, 2009.

[14] Albers.T. "Green Graphite: Our effort towards reduce, reuse, recycle", Paper presented at the 10th International Nuclear Graphite Specialists Meeting held at Yellowstone, USA. September 27th – 30th, 2009.