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Recycled Products Evaluation Report

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Recycled Products Evaluation Report

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 5.4.2 – Recycled Products Evaluation Report. The comment and discussion provided in this report relates to the assessments undertaken of the graphite and carbonaceous pilot scale artefacts produced under Task 5.2. Detailed information relating to the production of these artefacts in covered by a suite of reports (T5.2.1 to T5.2.5). This report provides a summary of the assessments of these artefacts, as well as providing direction for further R&D in the area of graphite reuse/recycle, which could build upon, and optimise the work undertaken to date.

At the inception of the project, it was assumed that the products evaluation would be best undertaken by industrial partners not involved in the pilot scale artefact production. However, as the project progressed it was clear that this approach would not be viable, in large part because of proprietary issues surrounding the manufacturing processes involved in their production. The evaluations are therefore provided by the organisations responsible for their artefact production.

The products evaluated within this report include:

- Nuclear Grade Moderator Graphite (SGL Carbon)
- Graphite for use in Electrodes for nuclear waste vitrification (GrafTech)
- Silicon Carbide for use as a waste packing medium for use in a repository setting (NRG)
- Graphite reuse as a crucible material to dissolve spent fuel (NECSA)

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	31/01/13	Final report	Jon Goodwin	D Bradbury	D Bradbury	D Bradbury
2						

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1 Introduction

This report is in response to the Task 5.4.2, 'Recycled Products Evaluation Report', under the Task 5.4 - Products Evaluation of Work Package 5 (Recycling & New Products) of the Carbowaste Project [1].

This report provides an overview of the evaluation of various pilot scale graphitic and carbonaceous artefacts produced by participants of Work Package 5, under Task 5.2 – Identification and Making of New Products. The properties and characterisation of the pilot scale artefacts is covered in full by Technical Report 5.4.1 'Properties and Characterisation of Recycled Materials' [2], and detailed information relating to the production of the various artifacts in covered by a suite of WP5 reports (T5.2.1 to T5.2.5) [3,4,5,6,7].

At the inception of the project, it was assumed that the products evaluation would be best undertaken by industrial partners not involved in the pilot scale artefact production. However, as the project progressed it was clear that this approach would not be viable, in large part because of proprietary issues surrounding the manufacturing processes involved in their production. The evaluations are therefore provided by the organisations responsible for the artefact production, SGL, GrafTech, NECSA and NRG.

The products evaluated within this report include:

- Nuclear Grade Moderator Graphite (SGL Carbon)
- Graphite for use in Electrodes for nuclear waste vitrification (GrafTech)
- Silicon Carbide for use as a waste packing medium for use in a repository setting (NRG)
- Graphite reuse as a crucible material to dissolve spent fuel (NECSA)

2 SGL Carbon – Nuclear Grade Moderator Graphite

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 [3]. A detailed overview of this work is provided in Report 5.2.3 'Graphite for New Reactors' [4].

2.1 Summary of Work

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 (shown in Figure 2.1) 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 [8].

Figure 2.1 - Samples after graphitization (from left to right: Reference, Trial 1 with 7.5% carbon black, Trial 2 with 15% carbon black) [8]

2.2 Evaluation

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 [8].

3 GrafTech – Graphite Electrodes for Waste Vitrification

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]. A detailed overview of this work is provided in Report 5.2.4 'Other Graphite and Carbon Based Products' [6].

3.1 Summary of Work

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 [9].

3.2 Evaluation

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 [9].

4 NRG – Silicon Carbide

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’ [10]. A detailed overview of this work is provided in Report 5.2.4 ‘Other Graphite and Carbon Based Products’ [6].

4.1 Summary of Work

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 [10].

4.2 Evaluation

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 6.2 was undertaken. A sufficient amount of silicon carbide was produced and characterized; for use in these experiments, a detailed review of this work is reported under WP6 [10].

The leaching experiments were performed in three types of leachants: Q-brine, clay and pore water, at the room temperature and at 90ºC. The formed SiC and irradiated graphite (from the RRT test in WP3) were leached during a period of 160 days with sampling each 40 days. After sampling, the ^{14}C activity was determined by LSC.

For SiC at the room temperature after 40 days, the highest activity of ^{14}C was measured in Q-Brine, 20 Bq/g sample against 12 Bq/g sample for granite water and 5 Bq/g sample for clay water. During the other sampling periods, the activity measured in Q-

Brine decreased to approx. 12 Bq/g sample and remained constant. The measured activity in granite water decreased slightly and remained constant during the leaching period. In clay water, the measured activity remained about constant during the whole leaching period.

The SiC powder leached at the temperature of 90ºC showed measured activity in all thre leachants remaining about constant during whole the leaching period. The measured activity in Q-Brine is 10 times higher than in the other two leachnats (40 resp. 4 Bq/g sample).

The measured activity of ^{14}C in Q-Brine is about two –three times higher at the temperature of 90ºC than at the room temperature. It seems that there is no significant influence of temperature on the leaching behaviour of the SiC powder in clay water, in the granite water the higher activities are measured at the room temperature.

For the irradiated graphite, the highest activity of ^{14}C is found in the Q-brine water, after 40 days of leaching the measured activity was about 1200 Bq/g sample, in 80 days it became about two times higher, stayed constant and decreased to about 1800 Bq/g sample after 160 days leaching.

The measured ^{14}C activity in the granite water was during the whole leaching period 750-900 Bq/g. At the first sampling it was higher, then it decreased slightly and after 160 days it increased to the initial value. For the clay water, the activity was about 650 Bq/g during the first two sampling, than it decreased to about 500 Bq/g.

The experiments performed at 90ºC showed that the highest activity of ^{14}C was measured in the Q-brine leachant. During the first three sampling it was about 2500 Bq/g and it increased to 3000 Bq/g at the 160 days sampling.

In the granite water, the activity of $^{14}C$was about 600 Bq/g, during the 160 days of the leaching period it increased to the activity of about 1200 Bq/g, i.e. the activity became two times higher.

The activity of ^{14}C in clay pore was about 450- 500 Bq/g and remained constant during the 160 days.

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. Because of limited amount of available irradiated graphite, the above mentioned tests are done with very small amount of irradiated graphite (0.02 g in 20ml leachant) comparing to the silicon carbide (0.4g in 20 ml leachant), this could have influence on the leaching rates. 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).

In addition, 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 [11].

5 NECSA – Crucible Material to Dissolve Spent Fuel

NECSA's contribution included the processing of graphite blocks for use as a crucible material to dissolve spent fuel. A more detailed overview of this work is provided in Report 5.2.4 'Other Graphite and Carbon Based Products' [6].

5.1 Summary of Work

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.

5.2 Evaluation

The result in Figure 5.1 below 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) [11].

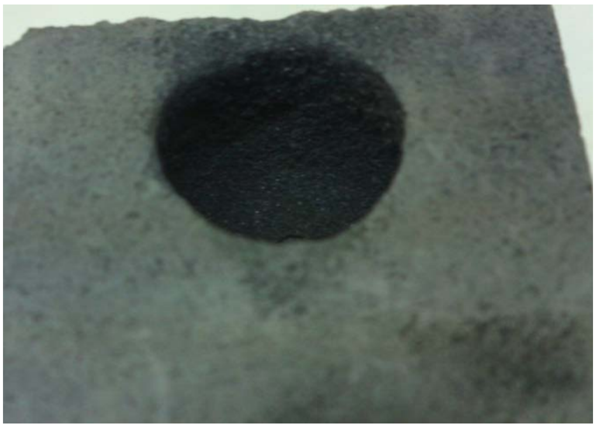

Figure 5.1: Manufacturing of graphite crucibles for molten salt applications using chemical etching technology

6 Discussion

It is clear that there are numerous opportunities which could conceivably incorporate recycled graphite as a key component of new products, thereby limiting the waste volumes requiring long term management.

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.

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 [12].

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 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

HTR	High Temperature Reactor
NBG	Nuclear Block Grade
NECSA	South African Nuclear Energy Corporation
NRG	Nuclear Research and Consultancy Group
pph	Parts Per Hundred
RRT	Round Robin Test
SHS	Self-Heat Sustaining
SiC	Silicon Carbide
XRD	X-Ray Diffraction

References

[1] Annex I – "Description of Work", CARBOWASTE

[2] Carbowaste Report T5.4.1 'Properties and Characterisation of Recycled Materials'

[3] Carbowaste Report T5.2.1 'Identification of Requirements for Intermediates Needed for New Products Synthesis'.

[4] Carbowaste Report T5.2.2 'Interim Report on Potential New Products within the Nuclear Industry'

[5] Carbowaste Report D5.2.3 'Graphite for New Reactors and Fuel Produced from Purified Carbonaceous Wastes'

[6] Carbowaste Report D5.2.4 'Other Graphite and Carbon Based Products'

[7] Carbowaste Report D5.2.5 'Use of Graphite Based Products for Decontimation of Waste Streams'

[8] 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.

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