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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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- Identification of Requirements for Intermediates Needed for New Products Synthesis -

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Identification of Requirements for Intermediates Needed for New Products Synthesis

Executive summary

CARBOWASTE's Work Package 5 is concerned with creating opportunities to reuse or recycle graphite, or constituents of graphite such as ^{14}C. 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. In principle, the simplest method of recycling graphite is to re-form new graphite from old without any intervening chemical transformation. Unless the graphite is decontaminated first, the recycle production facilities would have to be fully qualified to handle gamma emitting isotopes, which would involve considerable complication and expense. The other option would be to use alternative intermediate materials for production, which could be produced in decontaminated form from irradiated graphite.

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

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1	December 09	Final Report	J.C. Goodwin	D. Bradbury	D. Bradbury	D. Bradbury
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Executive Summary

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1 Introduction

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

Before the start of CARBOWASTE there was very limited experience with recycling or reusing irradiated graphite to date. 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.

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This short report describes the issues involved in manufacture of recycled products and records the outcome of discussions with Work Package Participants which led to their choices of intermediates for recycled products.

- Carbon black was chosen by both GrafTech and SGL as the intermediate for recycled graphite production in Work Package 5.
- NRG chose to use irradiated graphite directly for production of silicon carbide.
- Although these choices were made for the WP5 programme for the reasons stated in the report, this does not imply that this is the only, or even the correct, choice for the future.
- New methods of graphite decontamination suggest that future work should re-consider using decontaminated irradiated graphite as the intermediate material.

2 Main Body of Report

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

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

Heating graphite can, at least in some cases, lead to selective loss of isotopes (particularly tritium and ^{14}C) from the graphite structure. This phenomenon has the potential to be utilised both for a form of partial decontamination of graphite in advance of recycle, and for the production of a fraction of gas concentrated in radioisotopes for particular recycle opportunities.

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

- Isotopes formed in the bulk gas phase may diffuse into the pore volume and deposit on the pore surfaces.

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

Any of the above mechanisms may yield a pore surface layer enriched in radioactive isotopes, which might then be released by gasification, by heating either in an inert atmosphere or one which encourages gasification of carbon, such as steam. This "roasting" procedure might then yield a small fraction of the graphite as gaseous forms of carbon containing a significant proportion of radioactive isotope inventory, which would be a most desirable outcome – effectively partially decontaminating the majority of the graphite.

Graphite purification by treatment with halogen gases is well established as a precursor to reactor applications. A similar technique might be used to reduce the residual contamination of radionuclides such as ^{60}Co.

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

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

It is worth drawing attention to the fact that ^{14}C is a low energy "soft-beta" emitter and hence the radiation from it has very little penetrating power.

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

Petroleum Coke

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

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

Pitch Coke

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

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

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

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

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

Carbon Black

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

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

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

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

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

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

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

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

3 Conclusions

- Carbon black was chosen by both GrafTech and SGL as the intermediate for recycled graphite production in Work Package 5.
- NRG chose to use irradiated graphite directly for production of silicon carbide.
- Although these choices were made for the WP5 programme for the reasons stated in the report, this does not imply that this is the only, or even the correct, choice for the future.
- New methods of graphite decontamination suggest that future work should re-consider using decontaminated irradiated graphite as the intermediate material.

4 References

5 Glossary

CPC	Calcined Petroleum Coke
NRG	Nuclear Research & Consultancy Group
SGL	SGL Carbon GmbH
SiC	Silicon Carbide
PSA	Pressure Swing Absorption