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Data for Comparison of New Management Methods with Existing Practice

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 5.1.2 – 'Data for Comparison of New Management Methods with Existing Practice'. The comment and discussion contained within this report relates to the potential recycle pathways developed under Work Package 5 since the start of the Carbowaste project in April 2008. Detailed information relating to basis of the recycle pathways is provided in T.5.1.1 'Review of Existing Graphite Waste Management Methods'[1], with detailed overviews of the production of products resulting from either graphite recycle or direct reuse approaches covered under the deliverables for Task 5.2 (5.2.1 to 5.2.5) [2, 3, 4, 5, 6]. In addition the properties and characteristics of these products are covered in T.5.4.1 [7], with evaluation of the products covered under 5.4.2 [8].

As stated in within T5.1.1 [1], very little experience existed in the field of i-graphite reuse/recycle prior to the commencement of the Carbowaste project. Therefore it is not possible to compare the status of development of recycling to that which existed before, simply because i-graphite recycle had not been previously investigated.

The basis of this report is therefore to summarise the routes to recycle developed under Work Package 5. These include:

- Graphite Gasification leading to Carbon Black as an intermediate for recycle
- Direct reuse of i-graphite
- Conversion of i-graphite to Silicon Carbide
- Discussion of recycle and reuse options

Revisions

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2						

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1 Introduction

Good environmental practice requires that disposal of waste should be the last resort selected only after preferable alternatives have been considered. These alternatives include minimisation of waste generation, reuse of the materials in their current form or recycling the materials through appropriate processing to form new products. CARBOWASTE's Work Package 5 is concerned with creating opportunities to reuse or recycle graphite, or constituents of graphite such as ^{14}C. It was thought that the major opportunities would be associated with recycling rather than reuse, but any opportunities identified to reuse graphite in its existing form would be included [9].

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.

This short report provides a basic summary of the recycle options for irradiated graphite identified throughout the duration of the Carbowaste project under Work Package 5, and directs the reader to the various reports under which each of the options are covered in detail.

The key recycle/reuse pathways summarised in this short report are:

- Graphite gasification and redeposition into Carbon Black as the recycle intermediate for inclusion into new graphitic products. Carbon black was chosen by both GrafTech and SGL as the intermediate for recycled graphite production in Work Package 5.
- Direct reuse of irradiated graphite for the production of Silicon Carbide for use as a repository packing medium or as a component of fuel pebbles for HTR reactors.
- Direct reuse of irradiated graphite, for example under the Deep Burn Project, which has been running in parallel to the Carbowaste project, but which provides additional external data relevant to that considered under Work Package 5 .

2 Routes for Graphite Recycle & Reuse

As shown through the work undertaken under Work Package 5 of the Carbowaste project, various approaches to graphite recycle and reuse are possible. Key examples of these which have been investigated over the course of the project are covered over the following sections.

2.1 Graphite Gasification and Redisposition

Gasification through the process of steam reforming or reaction with oxygen is a viable first step for the recycle of graphite. It can be utilised for dealing with the legacy of graphite moderated reactors, but could be also useful for processing graphite materials (for example, graphite and carbon content from spent TRISO fuel particles) from the future graphite moderated reactor designs such as the PBMR or Gas Turbine–Modular Helium Reactor (GT-MHR). The gasification process allows effective decontamination for radionuclide's other than ^{14}C. In any scenario for gasification of graphite, the intention is to retain the radioactivity in solid form for disposal as radioactive waste, whilst further processing of the synthesis gas through methods such as isotope separation prior to re-deposition of solid carbon for subsequent addition as a raw material into the manufacturing of recycled graphite.

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

(1)

$$C + H_2O \longrightarrow CO + H_2$$

The carbon monoxide can be separated or the gases further oxidised in the same reactor with oxygen to form carbon dioxide and water (see equation 2). The water can be recycled, allowing the collection of tritium released from the graphite.

(2)

$$CO + H_2 + O_2 \longrightarrow CO_2 + H_2O$$

Steam reforming technology has been in widespread industrial use for decades, and was, for example, the basis for the production of “town gas” (hydrogen and carbon monoxide) from the reaction of steam with coke for the public gas supply. Town gas has now been replaced by the introduction of natural gas (methane).

Reaction of graphite with pure oxygen achieves the same overall result as Reactions 1 & 2 above. Unlike incineration in air there is no inert carrier (e.g. nitrogen) involved in either process, so the process can take place more or less in an enclosed system, if so desired. With liquefaction of carbon dioxide or reversal of gasification by the Sabatier or Bosch reactions there need not necessarily be any release of gas to atmosphere as a result of the process. This obviously allows for tight control of radionuclide release.

The first (optional) step of the thermal treatment would be to raise the temperature of the graphite to 400 to 1000°C and roast at that temperature to allow the volatile gaseous radioactive materials on the surface of pores of the graphite matrix, predominately ^{14}C, ^{3}H and ^{36}Cl, to migrate out of the graphite in a low volume gas stream. The ^{3}H and ^{36}Cl would be removed through condensation and wet scrubbing of the process off gases with a chilled water solution. This process is referred to as “roasting”.

The remainder (or all, if no roasting is done) of the graphite can then be thermally destroyed via gasification of the graphite in the steam reforming process. This process utilizes a fluid bed system (Stage 2 Thermal Treatment) to gasify the graphite and release the remaining fraction of ^{3}H, ^{36}Cl, ^{14}C and separate non-volatile radionuclides (^{60}Co, ^{55}Fe, etc.) that are contained in the graphite structure. Destruction of the graphite is achieved through heating of the graphite to 900 to 1100°C in a steam and/or oxygen rich environment, which gasifies the graphite into CO_2. The outlet gases from the reformer are cooled to remove steam and the balance of ^{3}H as water vapour from the gas stream. The cooled gas stream is then filtered to remove non-volatile radionuclides and any fine graphite particles from the gas stream. The fine graphite particles are returned to the reformer for gasification. The dry gas stream comprises a low volume CO_2-rich gas with residual ^{14}C as CO_2 [10, 11, 12].

Figure 2.1 below is a basic flowchart which details the potential routes from graphite gasification though to recycled graphite/carbon product.

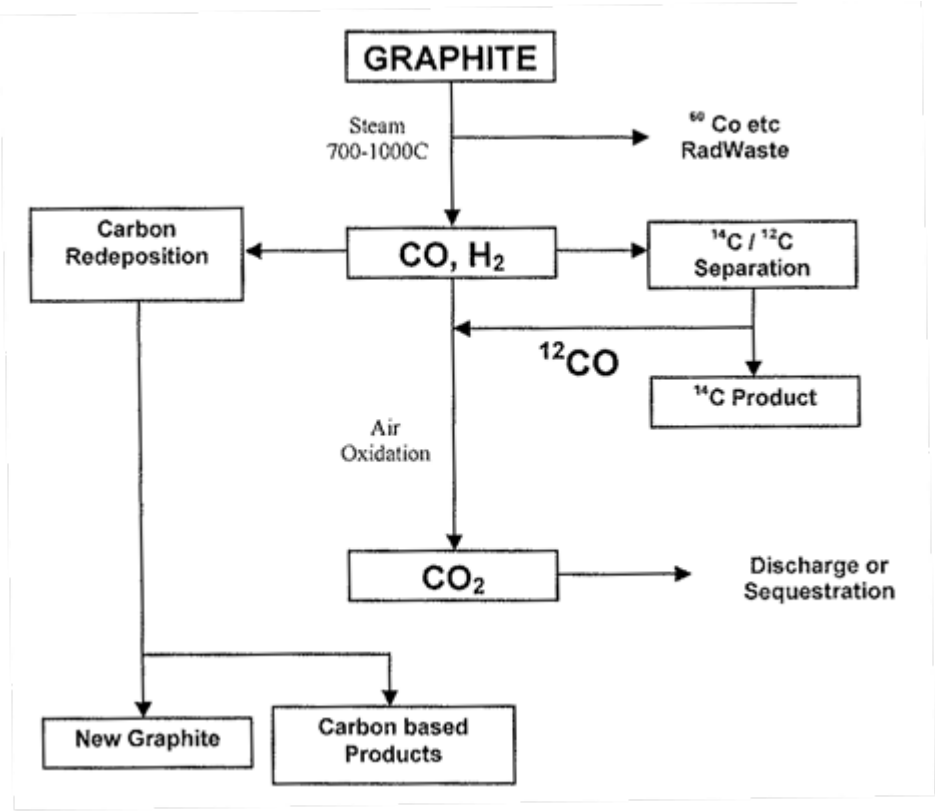

Figure 2.1 - Flowchart detailing routes from graphite gasification to recycled product. [14]

If the graphite is completely gasified (e.g. by steam reformation) the remaining non-volatile isotopes will be left behind as a residue, while semi-volatile isotopes (such as ^{137}Cs) may be collected with the non-volatile ones, or in adjacent low temperature zones . Total gasification thus provides the means to collect the isotopes in a concentrated form for waste management. This is a most important outcome, since the non-and semi-volatile isotopes include all the principal gamma-emitting ones, hence allowing all further downstream operations with the carbon to be performed "hands-on".

A critical technical issue involved with the destruction of graphite is the ultimate disposition of the volatile radionuclides, ^{3}H, ^{36}Cl and ^{14}C. The ^{3}H can be simply captured by condensing the ^{3}H water vapour in the condenser/cooler/scrubber unit. The tritiated water can be used for the production of cement matrices for encapsulation of wastes from this or other processes.

The behaviour of ^{36}Cl is not yet fully understood. Evidence of significant and rapid losses of ^{36}Cl following pulverisation of bulk graphite suggest that this phenomenon should be studied much more extensively in order that its potential for concentrated isotopic release easily captured in the scrubber solution and then concentrated and stabilized in a cement matrix [15]. ^{36}Cl collected in the gasification process can be treated in the same way as ^{3}H above

Steam reforming or oxygen oxidation produce a very low volume of outlet gas that contains the ^{14}C in a manner amenable to a variety of disposal or discharge options. These can be optimised to simplify the process system, minimise personnel exposure, and provide for simplified regulatory approval and permitting, and highest level of confidence and approval by stakeholders. This gas is can also be the starting point for producing new recycled products.

The off-gas (synthesis gas or syngas) produced through the gasification process can be reformed into carbon through the use of the Sabatier and Bosch reactions which is in effect a reversal of the gasification process (see Equations 3 and 4 below):

$$CO_2 + H_2 \longrightarrow CO + H_2O \quad (3)$$

$$CO + H_2 \longrightarrow C + H_2O \quad (4)$$

The second (rate determining) reaction can be catalysed by an appropriate transition metal catalyst (e.g. Iron) with the output form being a powdered carbon. This could then be used to generate a family of new carbon based products, which would be used primarily for the nuclear industry to avoid any residual traces of radioactivity escaping to the public domain.

The work undertaken by both GrafTech and SGL Carbon under WP5 of Carbowaste has been focused on the use of carbon black as the intermediate recycled component for new graphite. This work in reported in detail under the suite of reports produced under Task 5.2, which include reports 5.2.3 [4] and 5.2.4 [5].

The key conclusions from this work are:

- Full gasification of the graphite and its redeposition into carbon black for use as the recycle intermediate provides an effective method of decontamination to enable the requirement for only minimal radiological controls associated with the manufacturing infrastructure for the production of recycled products.
- The incorporation of carbon black into new graphite artefacts is viable, however as a result of the carbon blacks properties and characteristics, a maximum limit of ~10% of carbon black can be incorporated into the dry formulation, without significant reduction in the products strength, conductivity and integrity.

2.2 Graphite Decontamination by Leaching/Washing

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.

The underwater decommissioning of the Bugey PWR reactors in France, will provide a valuable insight into the effects of 'washing' the graphite, and understanding as to the release kinetics of key radionuclides from the graphite as well as the potential reduction in activity associated with it post retrieval. Decontamination/leaching of radionuclides from irradiated graphite have been investigated as part of both Work Package 4 and 6.

2.3 Direct Reuse without Decontamination

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.

A primary example of this approach has been demonstrated under the US DoE's Deep Burn Program [16]. The primary goal of this project was to determine if nuclear graphite formed through the normal graphite forming process but using crushed previously irradiated nuclear graphite, could be formed with sufficient mechanical integrity to warrant further investigation.

Results from this suggest that, within the narrow parameter range studied, the materials could be formed with a level of density, strength, and thermal conductivity to suggest that the recycling process is viable. It is noted that the irradiated materials used in this study were in a moderate range of irradiation associated with graphite densification, and that recycling would likely include graphite irradiated to a higher irradiation dose [4].

It should be stated that whilst this work is very promising, the approach to graphite recycle will be of limited application due to the carryover the full radionuclide inventory from the used irradiated graphite moderator block to the new nuclear graphite product, and thereby requires significant radiological containment for the full process of retrieval, processing, manufacture and installation. The potential use of non-destructive decontamination techniques prior to recycle, such as 'roasting' or chemical decontamination, may enable the radiological protection measures required, to be

downgraded in line with reduction of the graphite radionuclide inventory resulting from its partial decontamination.

In addition, NECSA have considered the direct reuse of irradiated graphite for waste disposal, waste vitrification and as a media for decontamination of waste streams. This work is reported in the Work Package 5 deliverables 5.2.4 [5] and 5.2.5 [6].

2.4 Thermal Decontamination for Recycle

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.

This work has been investigated in detail within Work Package 4.

2.5 Conversion to 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 or within HTR Fuel Pebbles.

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 [15].

This approach to recycle enables the irradiated graphite to be included in new products which have optimised properties and characteristics to its original form which benefits its requirement for long term storage. Whilst the conversion of irradiated graphite into silicon carbide has been demonstrated, further work is required to both optimise and

industrialise this process, as well as understand if the use of silicon carbide produced through this route is viable for use in HTR fuel components.

3 Discussion

The key issue with utilising irradiated graphite as a key component of new products and thereby providing a path to recycle relates its radiological contamination. For direct reuse to be feasible, suitably radiological controlled facilities would be required which cover not only the product manufacture, but also the transport and storage (both pre and post manufacture) and the end use of the material must be compatible with the radionuclides associated with it. This direct reuse whilst potentially feasible in certain circumstances (e.g. Deep Burn) is unlikely to be an option for the vast majority of the irradiated graphite arising from decommissioning activities in the near future.

The option to convert the irradiated graphite to carbon black (or some other potentially suitable intermediate) by passing it through the gas phase (gasification) and subsequent re-deposition provides the most effective means of decontamination to date. This in turn provides a greater degree of flexibility in the choice of products and the manufacturing processes which can be used to produce them, as the reduced activity enables a reduction in the radiological controls required. The use of carbon black as an intermediate to enable recycle, has been demonstrated to have significant limitations, largely related to its material properties and characteristics. Carbon black has been shown to be considered as "non-graphitizable" and therefore cannot fully replace coke in a graphite formulation because it will hardly contribute to the thermal properties required in nuclear graphite. Furthermore, the very low particle size and therefore higher pitch take-up and worse pitch wetting behaviour of carbon black compared to coke flour constitutes a practical limit of carbon black addition for producing nuclear graphite for moderator and fuel. This limit is estimated at around 10% in the dry material aggregate. Whilst results from the work indicate that a degree of optimisation could be applied (e.g. improved dissemination of the carbon black through the formula to avoid aggregations), the upper limit for inclusion is only likely to rise by a very small amount.

Work undertaken outside of the Carbowaste project by GrafTech (e.g. USDoE Deep Burn), has demonstrated that if the recycled intermediate were to be in the form of

graphite, a significantly greater proportion of recycled material could be included within a new product, without a detrimental effect to the products properties and characteristics.

The most opportune route for recycle therefore would be to undertaken a robusty process of decontamination, which could potentially involve multiple stages (e.g. Intercalation, roasting and washing). Significant work has been undertaken under Work Package 4 which has considered various decontamination approaches, the findings from which may enable an optimised approach to graphite decontamination to be developed. This in turn could open the door to irradiated graphite recycle becoming a serious solution for on-going graphite management.

Glossary

GT-MHR	Gas Turbine-Modular Helium Reactor
HTR	High Temperature Reactor
NECSA	South African Nuclear Energy Corporation
PBMR	Pebble Bed Modular Reactor
PSA	Pressure Swing Adsorption
PWR	Pressurised Water Reactor
SiC	Silicon Carbide
TRISO	Tristructural-isotropic
USDoE	United States Department of Energy

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