EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

Technical Report (T-5.0.0)
Work Package 5 (Graphite Reuse & Recycle)
Summary Report

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Reporting period: 01/04/2008 – 31/03/2013

Date of issue of this report: 31/03/2013

Start date of project: **01/04/2008** Duration: **60 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the CARBOWASTE project	**X**
CO	Confidential, only for specific distribution list defined on this document	

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CARBOWASTE		
Work package: 5 **Task: :** 5.0.0	**CARBOWASTE document no:** CARBOWASTE-0313 -T-5.0.0 (e.g. May 2008 as date of issue: 0805)	**Document type:** T
Issued by: Bradtec Decon Technologies Ltd **Internal no.:** Bradtec Report No		**Document status:** Final

Document title

Work Package 5 (Graphite Reuse & Recycle) Summary Report

Executive summary

This report provides a summary of the activities undertaken over the five year duration of the EC funded Carbowaste project, under Work Package 5, the focus of which is the reuse and/or recycle of irradiated graphite (i-graphite) arising from international decommissioning activities of graphite moderated nuclear power plants and other carbonaceous waste and fuel components of High Temperature Reactors (HTR's).

Work Package 5 consists of four key components, these are [1]:

- Task 5.1: Review of Existing Experience Relevant to Recycling
- Task 5.2: Identification and Making of New Products
- Task 5.3: Separation and Recycle of Radiocarbon
- Task 5.4: Products Evaluation

At the beginning of the Carbowaste Project there had been no significant endeavors in respect of irradiated graphite reuse/recycle. Over the 5 year duration of the project, significant developments in this field have been made both within Carbowaste and other related projects (e.g. US DoE Deep Burn Project) which have provided valuable insight and supporting data to substantiate irradiated graphite reuse/recycle opportunities across the nuclear industry.

Applicable products consisting wholly or partially of recycled graphite have been identified, and agreed production pathways established, from source material (i-graphite) to recycled intermediate (such as carbon black). The route to recycled product (e.g. complete gasification and redeposition via the Sabatier Bosch reaction enables the source material to be largely decontaminated of key radionuclides (^{60}Co, ^{3}H, etc.) prior to its inclusion in new products. Partial decontamination is a key requirement for the graphite manufacturers, as a reduced radionuclide inventory simplifies any industrial process and associated production facility. Pilot scale recycled graphite artifacts have been produced, tested and evaluated under Tasks 5.2 and 5.4.

Due to industrial uses of radiocarbon (^{14}C) in areas such as the radiopharmaceutical industry and the concentrated nature of the ^{14}C in irradiated graphite, Task 5.3 investigated the potential for separation of the ^{14}C component of the graphite (isotope separation), and the viability of producing a product of sufficient purity for recycle into ^{14}C products.

The key findings from this work are that graphite recycle is technically achievable and that various products of value to the nuclear industry could be produced wholly or partially from recycled graphite. However, further work is required in order to both optimise and industrialise reuse or recycle processes.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	31st March 2013	Final report	Jon Goodwin	D Bradbury	D Bradbury	D Bradbury

Contents

Executive Summary 6
1 Introduction 7
1.1 Background to Work Package 5 (Recycle & Reuse) 8
1.2 Participants of Work Package 5 10
1.3 Objectives of Work Package 5 11
1.3.1 Task 5.1 – Review Existing Experience Relevant to Recycling 12
1.3.2 Task 5.1 – Identification and Making of New Products 12
1.3.3 Task 5.3 – Separation & Recycle of Radiocarbon 13
1.3.4 Task 5.4 – Products Evaluation 13
2 Existing Experience Relevant to Recycling 14
2.1 Nuclear Graphite Manufacture 14
2.2 Conventional Graphite Management 15
2.3 Alternative Graphite Management Approaches 15
2.3.1 Graphite Gasification 16
2.3.2 Graphite Decontamination by 'Roasting' 19
2.3.3 Carbon Re-deposition following Gasification 21
2.3.4 Chemical Decontamination 21
2.3.5 Intercalation / Exfoliation 22
2.3.6 Direct Reuse of Graphite 22
2.4 Intermediate Choice for Recycle 23
3 Graphite Recycle to Nuclear Grade Graphite 26
3.1 New Product Production 26
3.2 Properties and Characterisation 28
3.3 Product Evaluation 30
4 Graphite Recycle to Electrodes for Waste Vitrification 32
4.1 New Product Production 32
4.2 Properties and Characterisation 34
4.3 Product Evaluation 38
5 Graphite Recycle into Silicon Carbide 39
5.1 New Product Production 39
5.2 Product Evaluation 42
6 Graphite Reuse for Decontamination of Waste Streams 45
6.1 Removal of Soap Detergents 45
6.2 Removal of Radionuclides from Liquid Waste Streams 46
6.3 As Absorbent to Remove Nuclides from Gaseous Waste Streams 51
7 Direct Reuse of Graphite for Various Applications 53
7.1 Graphite Reuse as Electrodes to Dissolve Spent Fuel 53
7.2 Graphite Reuse as a Crucible Material to Dissolve Spent Fuel 55
7.3 Graphite Reuse as Disposal Containers for Solidified Matrices 56
7.4 Graphite Reuse for the Manufacture of Nanotubes 56
8 Isotope Separation 59
8.1 Methods of Radiocarbon Isotope Separation 59
8.1.1 Pressure Swing Absorption (PSA) 59

8.1.2 Gas Centrifuge 67
8.1.3 Amine/Carbamate Separation 73
8.1.4 Cryogenic Distillation 74
8.1.5 Diffusion 75
8.1.6 Carbon Tetrafluoride Distillation 76
8.1.7 Isotope Separation by Laser 77
8.2 Isotope Separation Summary 79
9 ^{14}C Recycle & Supply 80
10 Conclusions 82
Glossary 86
References 89

Executive Summary

This report provides a summary of the activities undertaken over the five year period, under Work Package 5 of the EC funded Carbowaste project, the focus of which is the reuse and/or recycle of irradiated graphite and other carbonaceous waste arising from international decommissioning activities of graphite moderated nuclear power plants, fuel components of High Temperature Reactors (HTR).

Work Package 5 consists of four key components, these are [1]:

- **Task 5.1**: To review existing graphite waste management methods and graphite manufacturing technology to establish and existing experience relevant to the development of recycle pathways.
- **Task 5.2**: To identify new product production pathways and make new products from recycled irradiated graphite materials.
- **Task 5.3**: To establish methods for separating ^{14}C for recycle and to match the resulting separated product to the market needs.
- **Task 5.4**: To evaluate products produced from recycling activities for fitness for purpose.

At the beginning of the Carbowaste Project there had been no significant endeavors in respect of irradiated graphite reuse or recycle. Over the 5 year duration of the project, significant developments in this field have been made both within Carbowaste and other projects (e.g. US DoE Deep Burn Project) which have provided valuable information and data to substantiate potential opportunities to recycle/reuse of graphite in the nuclear industry.

The key findings from this work are that graphite recycle/reuse is technically achievable and that various products of value to the nuclear industry could be produced wholly or partially from recycled graphite. However, for this approach to be adopted there would need to be additional regulatory, political and commercial drivers in place to encourage adherence to the principles of the waste hierarchy.

1 Introduction

A large volume of irradiated graphite (~250,000 tonnes) will arise as a result of decommissioning of nuclear reactors across the globe, and this is a significant issue affecting the nuclear industry.

In addition to this, there are plans to construct new designs of graphite moderated High Temperature Reactors (HTR's). Considerable volumes of graphite will arise from spent fuel components from the new generation of reactors. To give an idea of the volumes considered; a 160 MW Pebble Bed Modular Reactor (PBMR) may produce approximately 2.5 million spent fuel pebbles over a 40 year period. 92% of this volume comprises of carbon/graphite while the remaining 8% is spent fuel.

A 1000 MW Pressurized Water Reactor (PWR) by comparison produces only a few hundred tonnes of fuel waste over its generating lifecycle. Ways need to be found to recycle and reuse the graphite, not only for legacy materials, but for the new types of reactor as well. The efforts to find ways to recycle graphite are also an important goal in achieving sustainable management of this type of waste stream in line with the "waste hierarchy" principles, where disposal of waste is seen as the last option only to be pursued after efforts to achieve other options or uses have failed.

The task of achieving recycle of graphite, while being extremely important as noted above, is also problematic. Amongst the difficulties to be faced, manufacturers of graphite products have not in general been used to working with radioactive materials and do not have appropriately licensed facilities.

Graphite has been used in more than 100 nuclear reactors. It is used primarily as a neutron reflector or neutron moderator, although graphite is also used for other features of reactor cores, such as fuel sleeves. Many of the graphite-moderated reactors are now reaching the end of their lives, and some have already shut down. Therefore radioactive graphite dismantling and the management of radioactive graphite waste are becoming increasingly important issues.

The radioactive graphite coming from nuclear installations has different characteristics from other radioactive waste due to its physical and chemical properties. In addition,

the graphite waste contains after irradiation, a significant amount of long-lived radioisotopes, such as ^{14}C having a half-life of 5,730 years, and ^{36}Cl having a half-life of circa 300,000 years. Many short-lived isotopes are also important, such as tritium (^{3}H), having a half-life of 12.3 years.

1.1 Background to Work Package 5 (Reuse & Recycle)

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.

Work package (WP5) of CARBOWASTE is concerned with creating opportunities to reuse or recycle graphite, or constituents of graphite such as ^{14}C. Because of the structural changes which occur in graphite through extended neutron irradiation it is thought that the major opportunities are associated with recycling rather than reuse, although any opportunities identified to reuse graphite in its existing form have been considered.

There are many potential uses for recycled carbon other than for new reactor graphite. Examples would be its use in graphite electrodes for the immobilization by high temperature processing (e.g. Vitrification) of certain nuclear wastes, or in components such as activated charcoal filters. Opportunities may be more limited, but the technical quality of the required materials may be less demanding than for reactor applications and hence easier to achieve. One key target for any recycle effort will be to use the recycled carbon for production of silicon carbide. Silicon carbide (SiC) has many potential uses in high temperature reactor technology and also in nuclear waste management (e.g. use as an encapsulant). Calcium carbonate has also been considered as a possible use for recycled carbon, but there may be only limited uses for this.

Besides the production of new products for use in their own right, graphite might be used as a component of other products. An example of this is the use of "graphite mortar", as developed by the Paul Scherrer Institute in Switzerland [2]. In this case waste graphite is used as part of a formulation for the grouting of other radioactive wastes.

The objectives of Work Package 5 can only be met by considering all the steps between irradiated graphite arising as waste and its supply in new products. There will be many challenges, for example any manufacturer who wishes to produce recycled graphite products will almost certainly need to have a portion of their production facilities designed and licensed to handle radioactive material. Because of this restriction it is likely that any recycled graphite products will require simple manufacturing processes. However, any radiation protection complications can be lessened by ensuring an efficient degree of decontamination of the precursor materials before manufacture commences. The efficient removal (by decontamination) of gamma activity, with its associated requirements for heavy radiation shielding, will be a particularly important matter.

Because of the presence of the radionuclide ^{14}C and its chemical congruence with the bulk of the graphite, it is unlikely that irradiated graphite could ever practically be decontaminated to such an extent that it could be regarded as non-radioactive. Accordingly, it seems reasonable to restrict consideration of recycle routes to those which would be producing products for controlled uses in radioactively-licensed facilities.

There is one more principle to consider, and that is the issue of partial recycling. It is unlikely that any one recycling route will be able to handle *all* the graphite arising from legacy wastes. That does not mean that the examination of recycle routes is futile. Far from it, the identification and extraction of a portion of the waste which is economically re-useable may be the key to persuading stakeholders that the remainder of the material is beyond redemption and can appropriately be disposed of. In separating particular entities for recycle (e.g. ^{14}C) the substrate waste material to be processed may be very specific, for example graphite having a very high ^{14}C content by virtue of its

manufacture or irradiation history. From this graphite itself only the "roasted" fraction (see later) may be useful. It does not matter that such recycle opportunities do not deal with all the waste, provided that an economic use for at least some of the waste can be found. In summary, it is the waste producers' duty to consider seriously new uses for every part of the waste which they can, before pursuing a disposal philosophy.

At the start of the Carbowaste project, 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 the work undertaken under Work Package 5 has been to seriously consider the potential for i-graphite reuse/recycle and the pathways required to enable it to happen.

1.2 Participants of Work Package 5

Work Package 5 is managed by Bradtec Decon Technologies, primarily through the Work Package Leader, David Bradbury. However, in line with one of the key principles of Carbowaste, David has been responsible for the technical development of a successor, Jon Goodwin (now also of Bradtec) to continue his work in the field of graphite management, to ensure and support knowledge transfer to the next generation of graphite specialists, a key aim of the Carbowaste project. Jon has developed over the duration of the Carbowaste project, and has been largely responsible for the day to day management of WP5 up to its completion at the end of March 2013.

Bradtec is supported by other organisations who are contributing to the work undertaken under WP5, these are listed overleaf [1]:

- UCAR snc – Groupe GrafTech International Ltd (GrafTech)
- SGL Carbon GmbH (SGL Group)
- Nuclear Research and Consultancy Group (NRG)
- University of Manchester (UoM)
- Pebble Bed Modular Reactor (Pty) Ltd (PBMR)
- Hyder Consulting (UK) Ltd (Hyder)
- South African Nuclear Energy Corporation Limited (NECSA)
- Studsvik AB (Studsvik)
- Forschungszentrum Juelich GmbH (FZJ)
- AREVA Nuclear Power (AREVA NP)
- Association pour la Recherché et le Développement des Méthodes et Processus Industriels (ARMINES)

1.3 Objectives of Work Package 5

Work Package 5 is split into 4 distinct areas these are [1]:

- Task 5.1 - Review Existing Experience Relevant to Recycling
- Task 5.2 - Identification and Making of New Products
- Task 5.3 - Separation & Recycle of Radiocarbon
- Task 5.4 - Products Evaluation

Each of these tasks (and their subtasks) are summarised in more detail in the following sections. Additional information in the form of either Reports or Technical Documents which have been produced during the course of the Carbowaste project are referenced throughout this summary report to direct the reader to those areas of specific interest to them. The purpose of this report is to provide an overview of the work undertaken under WP5, as well as draw together the conclusions of this work.

1.3.1 Task 5.1 – Review Existing Experience Relevant to Recycling

There is 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 this task was to review existing experience relevant to the potential development of reuse or recycling pathways, and not to review the development of processing and disposal technology in its entirety. Under this task both GrafTech and SGL Carbon provided support on the product production aspects in order to define the recycle pathway developed. A further more detailed account of the work undertaken under Task 5.1 is provided within technical reports 5.1.1[3] and 5.1.2 [4].

1.3.2 Task 5.2 - Identification and Making of New Products

This task included the production (pilot scale) of candidate products (e.g. moderator graphite, silicon carbide, etc.) from simulated or real recycled carbon. It also addressed how to make candidate products directly from graphite without chemical transformation / decontamination. The production of materials which are suitable for use in disposal sites as backfill or encapsulants was also investigated. In addition to graphite for new reactors, moderators, fuel components, other graphite and carbon based products were considered, for example, the use of graphite electrodes for the immobilisation by high temperature processing of certain nuclear wastes, or alternatively their use as an absorbent for radionuclides (replacing expensive resins) or use within activated charcoal filters. Under this task, NRG focused on the formulation of silicon carbide, GrafTech and SGL Carbon on the development of new graphite candidate products, and NECSA on the potential use of irradiated graphite as an absorbent material. A further more detailed account of the work undertaken under Task 5.2 is provided within technical reports 5.2.1 [5], 5.2.2 [6], 5.2.3 [7], 5.2.4 [8] and 5.2.5 [9].

1.3.3 Task 5.3 - Separation & Recycle of Radiocarbon

When considering the potential recycle of ^{14}C, the isotope must first be separated from irradiated graphite and prepared in a form suitable for industrial users of the isotope to accept. This task involved a study of the different possible isotope separation technologies, such as pressure swing absorption, cryogenic distillation and amine/carbamate separation. In addition to this assessment, URENCO (under subcontract from FZJ) considered the use of gas centrifugation. Additional supporting work external to WP5, was undertaken by NECSA/PBMR on potential microbial methods of isotope separation. A further more detailed account of the work undertaken under Task 5.3 is provided within technical reports 5.3.1[10], 5.3.2 [11] and 5.3.3 [12].

1.3.4 Task 5.4 – Products Evaluation

The properties and characteristics of the recycled materials produced under Task 5.2 - Identification and Making of New Products, have been assessed to understand their fitness for purpose for their chosen application. It was initially envisaged that the evaluation of the products would be undertaken by participants external to the manufacturing process, however as the project developed it was clear that those best placed to undertake the evaluation were the graphite manufacturers themselves. A further more detailed account of the work undertaken under Task 5.4 is provided within technical reports 5.4.1[13], 5.4.2 [14] and 5.4.3 [15].

2 Existing Experience Relevant to Recycling

At the start of the Carbowaste project initial work under WP5 was focused on identifying previous experience in the field of graphite reuse/recycle which could inform options developed under the project. An extensive desk based review was undertaken to consider:

- The properties of irradiated graphite in as far as they will affect the subsequent steps to recycle.
- The steps necessary to prepare graphite for recycle, such as the appropriate removal (by decontamination) of radioactivity. This included the conversion of the graphite to the gas phase and re-deposition as carbon, as well as the potential value of 'roasting', which can be used to separate graphite into isotope-rich and isotope lean fractions.
- Graphite manufacturing techniques to establish what types of product or processes may be applicable for graphite recycle.
- Other types of recycled product, including the sale of ^{14}C as a product. This option requires separation of carbon isotopes to achieve the required purity.

The output of this work is reported as part of Task 5.1 within T5.1.1 'Review of Existing Experience Relevant to Recycling'[3].

2.1 Nuclear Graphite Manufacture

A key component of the initial work undertaken in WP5, was to review graphite manufacturing techniques, and specifically the inputs into graphite formula. Valuable insight and direction was provided by the graphite manufacturers SGL Carbon and GrafTech who have both been manufacturing nuclear grade graphite since the early in the nuclear programme. This interaction provided technical direction as to the form, quantity and properties required of the recycled component included within a formulation for new graphite. At the start of the project, the graphite manufacturers had no experience with the recycle of irradiated graphite into new products. The only related experience they had was the practice of including small amounts of scrap, virgin

graphite as a raw material for production of new graphite products. The review of graphite manufacturing techniques and its raw materials are covered in Report 5.1.1 [3].

2.2 Conventional Graphite Management

Conventional graphite management is limited to two general approaches, the selection of which is largely due to the level and nature of the radioactivity associated with the graphite, as well as the volume of the specific graphite waste stream.

The primary approach relates to the encapsulation of the graphite waste for long term storage within a suitable repository environment. The second approach, which is only suitable for lower activity graphite from, for example test reactors, is to incinerate it, and to discharge the resultant gas to atmosphere.

Both of these approaches have inherent issues associated with them which alternative emerging graphite management approaches, such as decontamination, are attempting to address.

2.3 Alternative Graphite Management Approaches

The primary issues associated with long term storage of graphite relate to its radionuclide inventory (specifically certain key labile radionuclides with long half-lives such as ^{14}C and ^{36}Cl), and the large volumes of graphitic wastes. Various different approaches have been investigated as part of the Carbowaste project which are applicable for the decontamination of irradiated graphite.

The potential benefits of graphite decontamination include the potential to reduce the radionuclide inventory of the graphite to enable its reuse through its recycle into 'new' nuclear graphite (or other related achievable materials, such as SiC), or its potential down classification (e.g. ILW to LLW) to enable reduced management requirements for its long term storage.

Other potential benefits of decontamination include the opportunity to derive valuable radioisotopes from the irradiated graphite (e.g. ^{14}C), which have potential marketable end uses such as tracers for the radiopharmaceutical industry. It is important to

understand the various decontamination methods when considering the potential recycle of graphite, as:

- they are critical for firstly removing a substantial proportion of the radionuclide inventory to simplify the inclusion of carbonaceous materials within an industrial recycling process,
- they dictate the form and properties of the recycled end product, and
- they define the form and nature of the waste streams produced.

The following sections provide a basic summary of the various decontamination approaches which have potential applicability as a precursor to the recycle of irradiated graphite to produce new carbonaceous nuclear products.

2.3.1 Graphite Gasification

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 (GTMHR). The gasification process allows effective decontamination for radionuclides 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 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.

$$\mathbf{C + H_2O \longrightarrow CO + H_2} \qquad \textbf{(1)}$$

The carbon monoxide can be separated or the gases further oxidised in the same reaction vessel 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)

$$\mathbf{CO + H_2 + O_2 \longrightarrow CO_2 + H_2O}$$

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 controls on 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, referred to as "roasting" is discussed in more detail in the following section.

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 [16, 17, 18].

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

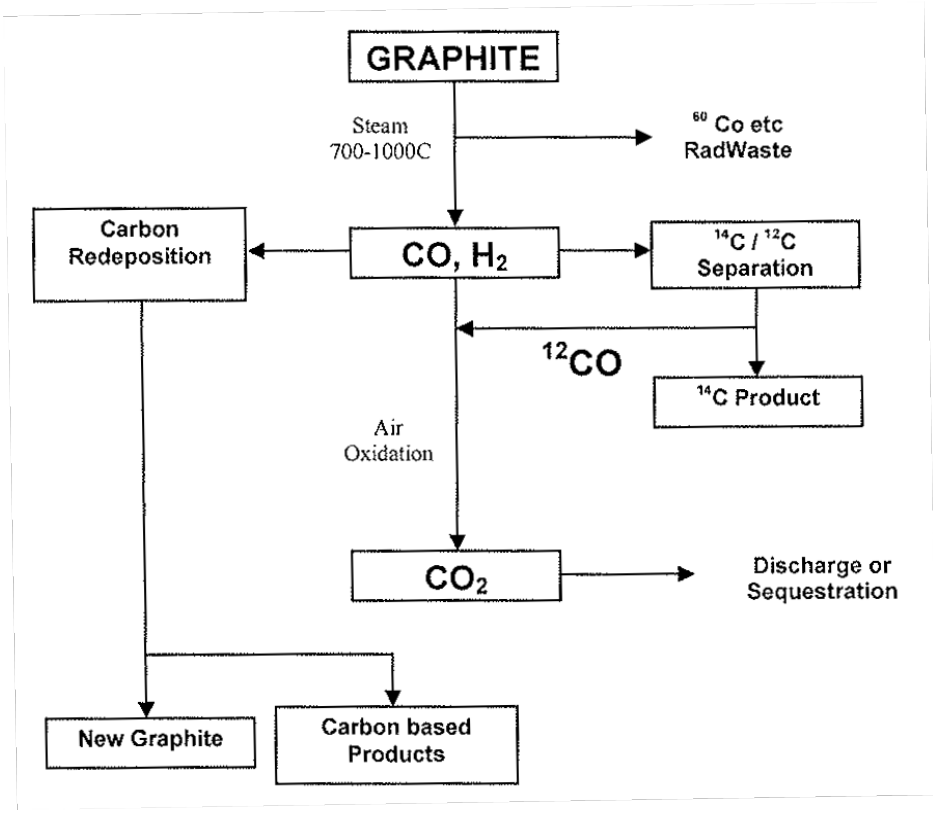

Figure 2.1: Flowchart detailing routes from graphite gasification to recycled product. [19]

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 these 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 [20]. ^{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.

2.3.2 Graphite Decontamination by 'Roasting'

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.

Unfortunately, there are likely to be limitations on what can be achieved by roasting. Some of the contamination mechanisms described above will be relevant to the closed pores, which may not release their inventory during the heating procedure. Furthermore there are isotopes formed by activation of bulk materials and impurities in the graphite during reactor operations. Enhanced release in an early fraction will not be possible for the isotopes that are locked into the non-porous graphite matrix.

It seems unlikely (however carefully it is optimised) that more than about 60% of the ^{14}C and 80% of the tritium can be released in the first few per cent of carbon lost. This observation is confirmed by preliminary work on blocks removed from the UK GLEEP reactor [21]. This might nevertheless be a useful result and important when considering its potential as part of the graphite recycle process, since any ^{14}C contamination of new products will need to be kept to the minimum possible. The roasting procedure might be used to yield an isotopically concentrated fraction which provides the starting point

for isotope separation (e.g. PSA) to produce a high purity ^{14}C for use by the medical industry as a radiological tracer.

2.3.3 Carbon Re-deposition Following Gasification

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. Discussions were held with the graphite manufacturers on the feasibility of introducing the powdered carbon (carbon black) as a component of the manufacturing process of new graphite.

2.3.4 Chemical Decontamination

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. This area has been investigated under Work Package 4.

2.3.5 Intercalation / Exfoliation

Intercalation / exfoliation of the graphite provides an opportunity to significantly increase the surface area of the graphite accessible, therefore providing the potential for optimised removal of key radionuclides (e.g. ^{14}C, ^{3}H), a notable percentage of which would otherwise be inaccessible within the graphite lattice and closed pore structure.

This approach has been investigated as part of WP2 of the Carbowaste project, with a specific focus on the potential recycle of irradiated HTR graphite. One of the conclusions from this area of work, which is reported under Work Package 2 is that the industrial recycling of graphite separated from TRISO particles via preparation of graphite intercalated compounds (GIC's) may be an attractive way to recycle the graphitic waste for industrial and environmental applications, especially when considering the high quality of the GIC's and exfoliated graphite (EG) obtained at room temperature as part of this test programme.

2.3.6 Direct Reuse of Graphite

In addition to GrafTech's work under Carbowaste, they have also been involved in the Deep Burn project, working closely with Oak Ridge National Laboratory on behalf of the US Department of Energy.

Deep Burn reactors can handle a variety of fuel sources and be of several reactor designs, but all require nuclear grade graphite as a moderator. Over the life of the reactor the significant quantities of nuclear graphite components will need to be replaced, creating a radioactive materials management issue: storage, transportation, and burial, all with associated costs and environmental implications. One method for addressing the irradiated graphite management issue is to reuse/recycle the graphite. Reuse of irradiated graphite could be as straightforward as shuffling the graphite components within the reactor to maximize the useful life of that material, or to use an expended block as the raw material for making a new graphite component. This latter option is essentially the production of a new graphite component through a true recycle process.

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.

Initial results from the work to date 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 be unlikely to include graphite irradiated to a higher irradiation dose [22, 23].

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 of the full radionuclide inventory from the used irradiated graphite moderator block to the new nuclear graphite product, and thereby would require 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.

2.4 Intermediate Choice for Recycle

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 had a preference for carbon black, since this can most readily be produced from the gasification route (which provides optimal decontamination, specifically in relation to gamma emitters).

Although both manufacturers have considerable experience of incorporating non-radioactive graphite into new products, they were concerned about the practicality of

working with un-decontaminated graphite itself. They therefore chose to use inactive carbon black as a simulant for carbon black derived from gasification and re-deposition.

SGL Carbon assessed the behaviour of carbon black vs. coke upon heat treatment in order to provide baseline data on its properties, characteristics which in turn informed the proportion which could be incorporated into new graphite without significant negative effect to resultant products performance. This work showed that carbon black cannot replace coke due to its poor graphitizability and its negative impact on thermal conductivity.

Upon thermal treatment at 3000 ºC, a noticeable graphitization of the coke sample was observed whereas the carbon black sample only marginally responded, resulting still in a calculated negative degree of graphitization. Therefore, carbon black can indeed be considered as "non-graphitizable", i.e. unable to contribute to the desired pronounced graphite character of nuclear graphite, reflected in its high thermal conductivity.

In addition, the measured density of carbon black does not considerably change from 2100 to 3000 ºC heat treatment temperature. A typical graphitizable coke shows the same behaviour as the tested "nuclear coke": density increases with temperature, with levelling out around 3000 ºC. Synthetic graphite based on well-graphitizable needle coke typically shows a density value of around 2.24 g/cm^3 [24].

Furthermore, due to the very low particle size and different pitch take-up and wetting behaviour compared to coke dust, there is a practical limit for carbon black addition for producing nuclear graphite for moderator and fuel. This limit is estimated to be in the range of 10-15% in the dry material aggregate, taking also into consideration that coke flour will be replaced by carbon black, where replacement is constrained by overall (coke) flour quantity in the formulation.

On the other hand NRG and NECSA chose to investigate the recycle of irradiated graphite (without decontamination) directly into other graphitic artefacts, or in the case of NRG into silicon carbide. This choice to work with irradiated graphite was supported by the availability of fully-radiation-shielded laboratory facilities on both the NECSA and NRG sites.

Despite these preferences other possible intermediates should not been ruled out from consideration. There is a possibility, for example, 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.

3 Graphite Recycle to Nuclear Grade Graphite

SGL Carbon produced pilot scale candidate products of nuclear grade graphite (NBG-18), which included a proportion of simulant recycled material (carbon black). This work was undertaken at their Raciborz Facility in Poland. The purpose of the work was to understand whether the inclusion of recycled materials within new nuclear grade graphite (for use in moderator or fuel) would be achievable, and the end product still be viable for its intended purpose. Further more detailed information pertaining of this work is provided in reports 5.2.1, 5.2.2, 5.2.3, 5.4.1 and 5.4.2 [5, 6, 7, 13, 14].

3.1 New Product Production

The non graphitizable nature, poor thermal properties, 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 both moderator and fuel.

Therefore, the pilot plant trials utilized 7.5 and 15 % carbon black, replacing coke flour in a standard nuclear graphite formulation. As base formulation, SGL's standard nuclear graphite NBG-18 with 1.6 mm maximum grain size of isotropic coke was selected. Three variants were produced using comparable processes to that of industrial production (see Figure 3.1 overleaf), these were:

- Reference: standard NBG-18 formulation, i.e. 100 % coke in dry aggregate
- Trial 1: 92.5 % coke, 7.5. % carbon black in dry aggregate
- Trial 2: 85 % coke, 15 % carbon black in dry aggregate

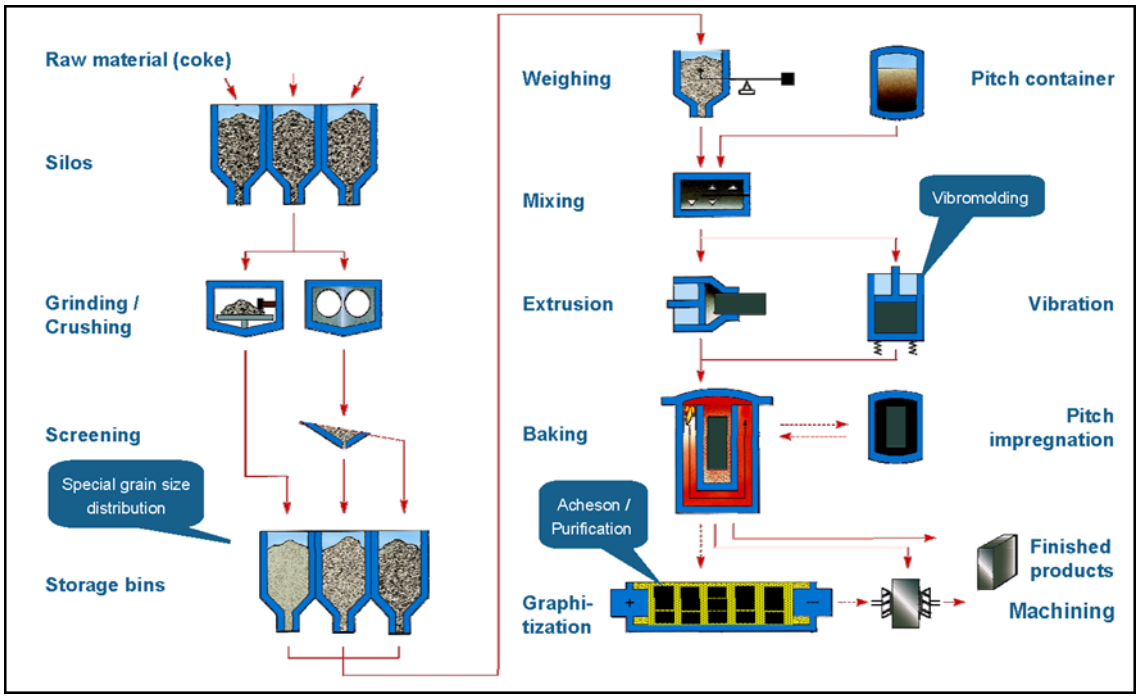

Figure 3.1: Industrial Nuclear Graphite Production Process (schematic)

The pilot plant process followed the principle route of industrial nuclear graphite production (Fig. 3.1 and [25]), which consists of raw material preparation by crushing and screening, mixing in defined proportions with pitch, shaping by extrusion or vibro-molding, baking the resulting green product, densifying by pitch impregnation/rebaking, and finally graphitising the artefact in an Acheson graphitization furnace. In contrast to the industrial process, block-pressing was used in pilot plant scale instead of vibro-molding to avoid additional experimental scattering through the forming process and no purification technique was applied during graphitization. With regard to the task, these aspects are considered non-significant for the objective of this activity. Iso-molding was not considered as this requires a completely different raw material preparation and green process, and moreover, no internal reference was available.

The dry components were mixed with coal-tar pitch to form a carbonaceous paste which was shaped into rectangular blocks of dimensions 200 x 200 x 220 mm (Figure 3.2) by uniaxial hydraulic block-pressing. Trial 2 required approx. 15 % more binder addition.

Figure 3.2: Samples after block-pressing (from left to right: Reference, Trial 1 with 7.5 % carbon black, Trial 2 with 15 % of carbon black)

After baking at 850 °C, blocks were twice impregnated with coal-tar pitch and rebaked to improve mechanical strength and provide a good thermal conductivity after graphitization. Finally, the blocks were graphitized in an Acheson lab graphitization furnace at 2900 °C. After cooling down, cores were drilled from the lab samples for analyses (Figure 3.3).

Figure 3.3: Samples after graphitization (from left to right: Reference, Trial 1 with 7.5 % carbon black, Trial 2 with 15 % of carbon black), with core samples already taken

3.2 Properties and Characterisation

The cores taken from the nuclear graphite blocks were subjected to laboratory analysis to determine the properties and characteristics of the recycled graphite artefacts. The testing covered parameters which are key to the performance of a nuclear graphite, these included apparent density, specific resistivity, Young's modulus and coefficient of thermal expansion. Table 3.1 overleaf provides the testing data associated with the reference, 7.5% and 15% carbon black content samples.

Table 3.1: Laboratory data for pilot plant trial materials

Base Grade	Recipe	No of sample	Apparent density	Specific resistivity	Compressive strength	Flexural strength	Thermal conduct.(at 30°C)	Coeff. of lin.ther.exp. (20-200°C)	Young's Modulus
			g/cm³	Ω·µm	MPa	MPa	W/m.°K	µm/(K·m)	kN/mm²
NBG-18	Reference	1 - with grain	1,78	7,9	62,1	23,4	153,1	3,8	10,3
		3 - against grain	1,78	8,2	53,1	18,7		4,1	9,4
	7.5 pp of carbon black	1 - with grain	1,77	9,5	50,6	11,7	136,1	3,8	9,5
		3 - against grain	1,78	10,7	50,6	11,3		4,1	7,6
	15 pp. of carbon black	1 - with grain	1,79	13,1	43,3	5,5	104,5	3,8	6,8
		3 - against grain	1,79	13,6	43,2	6,9		4,1	5,5

There is considerable impact on the mechanical and thermal properties of the graphite material. The addition of 15 % carbon black considerably decreased mechanical strength – both compressive and flexural – by up to about 70 % and thermal conductivity by 32% vs. Reference. Apparent Density remained practically unaffected from the addition of carbon black.

Overall, one can conclude from the trials that maximum only 5-10 % of carbon black can be tolerated from process requirements, in particular in industrial scale, 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.

3.3 Product 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 radionuclides which constitutes a particular issue when producing moderator/reflector graphite in industrial scale of several hundred tons. It is possible 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 [1].

4 Graphite Recycle to 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].

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.

The work was undertaken at their facility located in Cleveland, Ohio, USA. A detailed overview of this work is provided in Report 5.2.4 'Other Graphite and Carbon Based Products' [8].

4.1 New Product Production

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. The electrodes were 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~~

GrafTech fabricated 5 different varieties of graphite material that are made with 0 to 10 % carbon black (% carbon black was 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 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, and which could easily lend itself to automated radiologically controlled manufacturing.

The amount of pitch in each mixture was optimized for the manufacturing conditions and the varying fraction of carbon black. For example, artifacts made with higher amounts of carbon black required 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 in Table 4.1 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 artefact becoming very brittle.

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 [13].

4.2 Properties and Characterisation

Optical microscopy images taken of representative areas of the final graphitic artifacts produced for this work are shown in Figure 4.1 below:

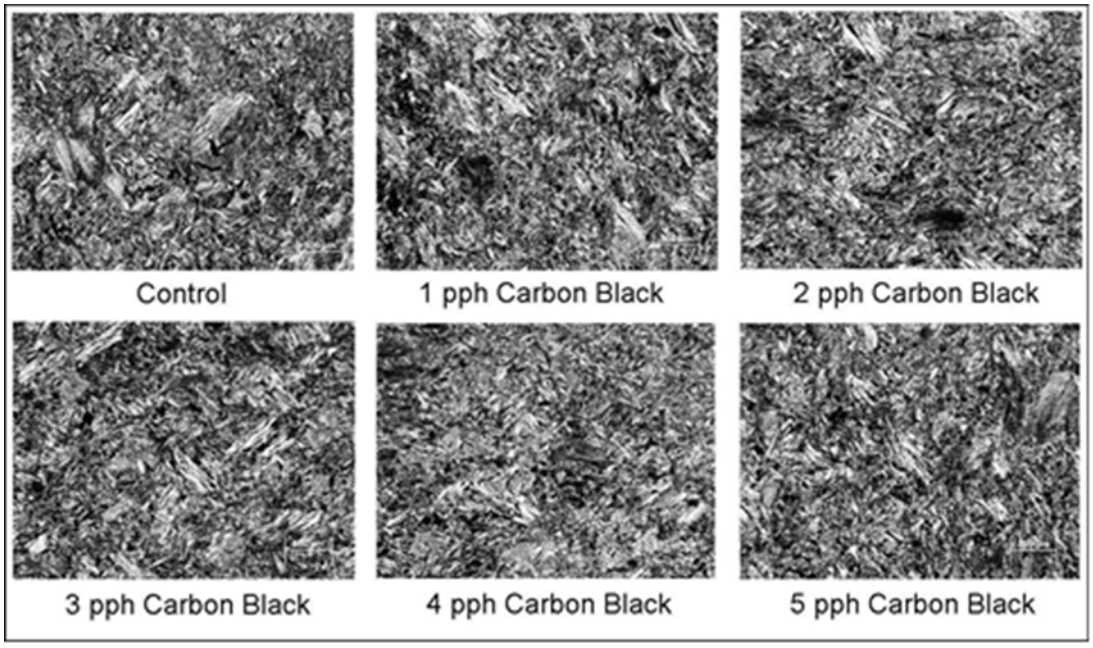

Figure 4.1: Comparison of graphite artifacts made with varying concentrations of carbon black. Images show uniform areas of graphitized material

Uniform structure is evident in the artefact, aside from aggregates of carbon black that seem to appear with increased loading of the non-graphitizable particles, as seen in Figure 4.2 overleaf.

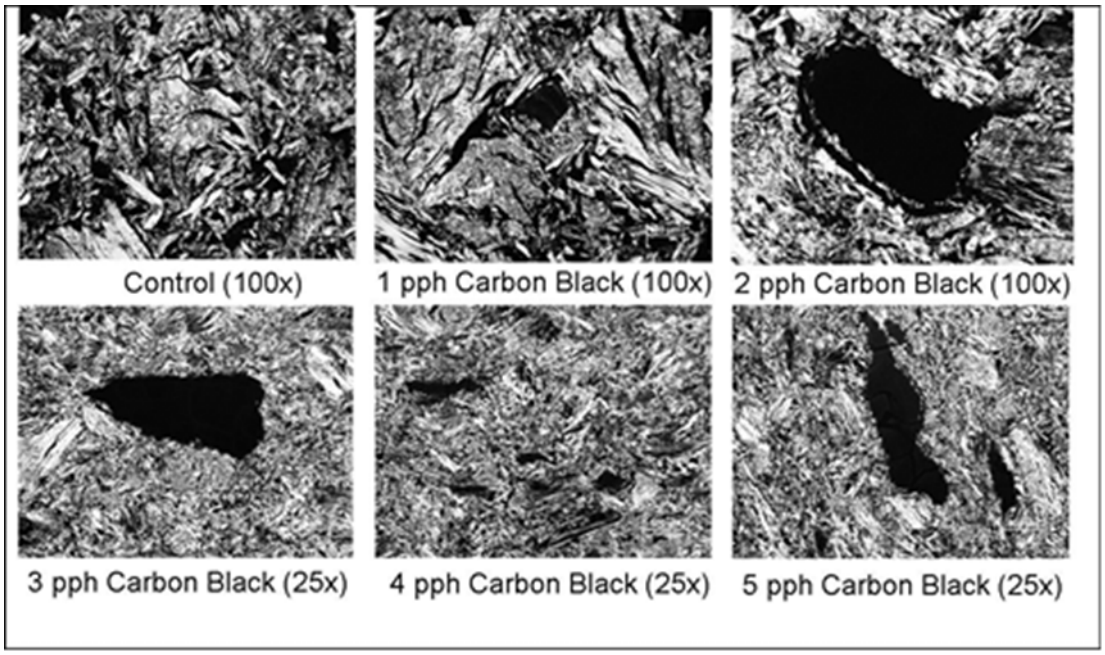

Figure 4.2: Optical microscopy images showing aggregation of carbon black due to lack of sustained mixing. Carbon black aggregates show as dark areas in polarized light

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 4.3), coefficient of thermal expansion (Figure 4.4), thermal conductivity (Figure 4.5), Young's modulus and specific resistance (Figure 4.6). All figures show two samples tested for each value of carbon black loading.

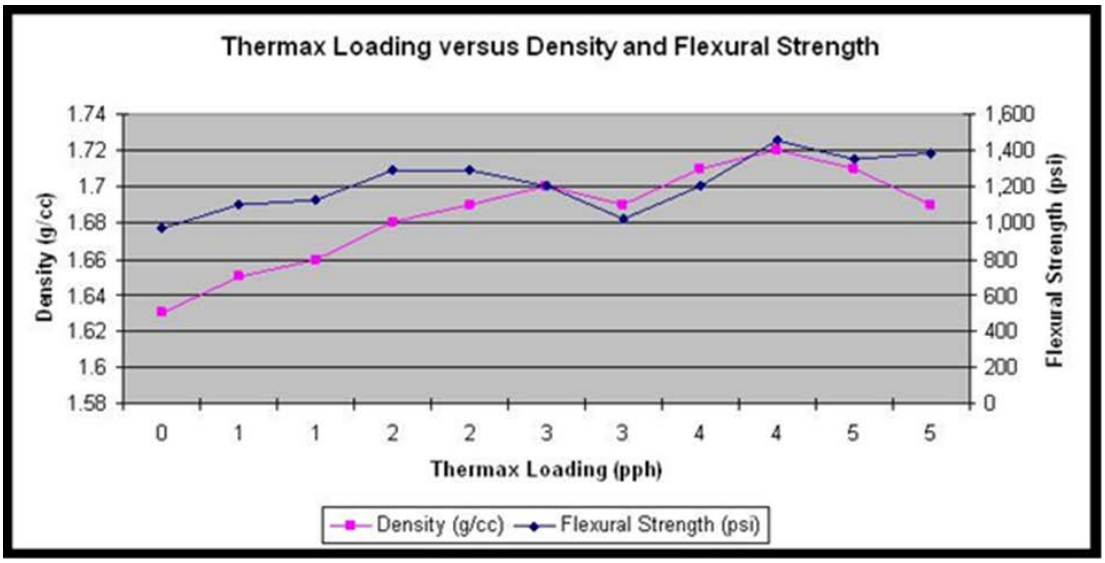

Figure 4.3: Results of measured density and flexural strength at various levels of carbon black loading.

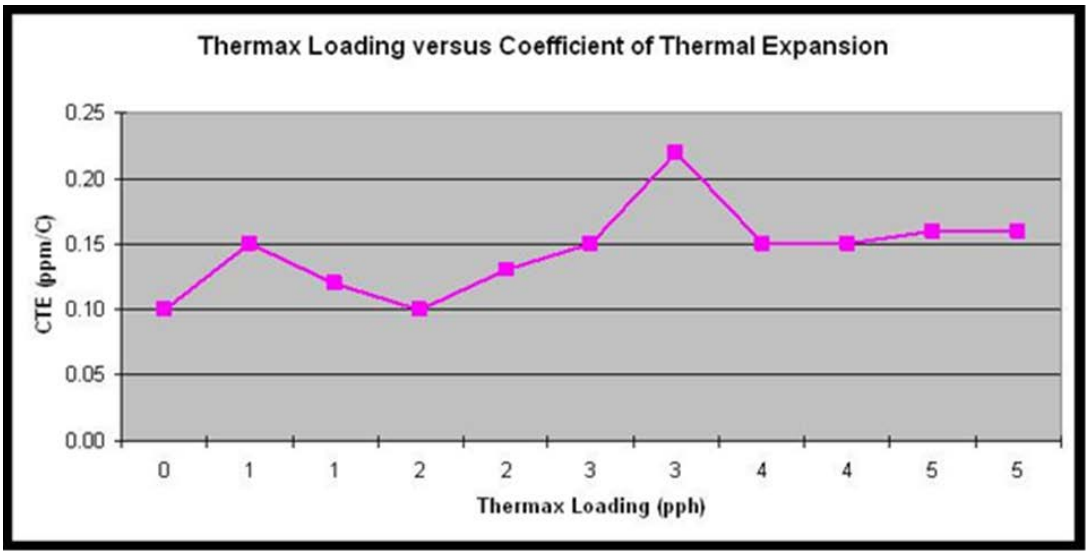

Figure 4.4: Measurement of the slight change in CTE as a function of carbon black loading.

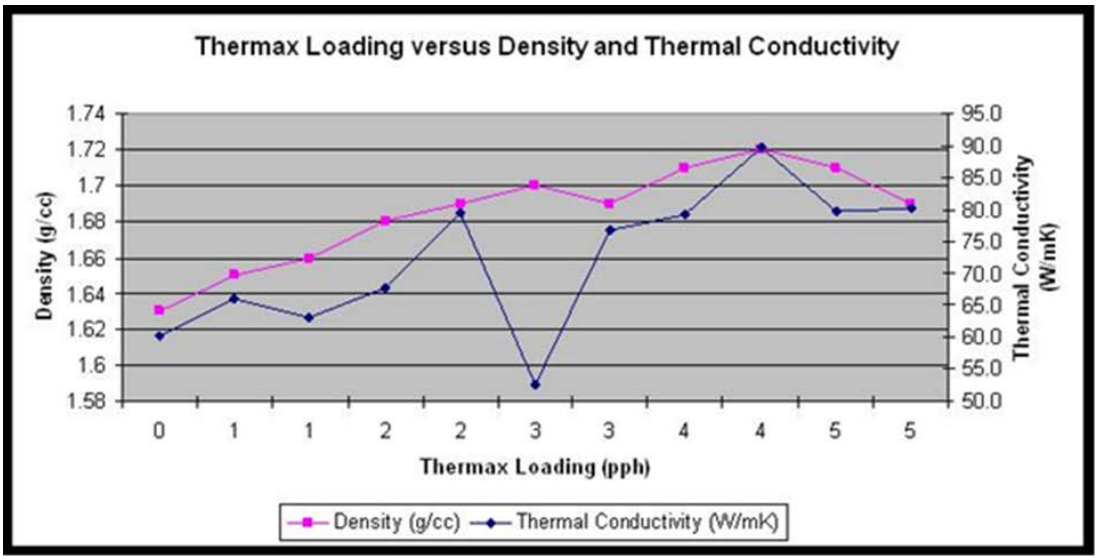

Figure 4.5: Measurement of the density and thermal conductivity of graphite made with varying levels of carbon black.

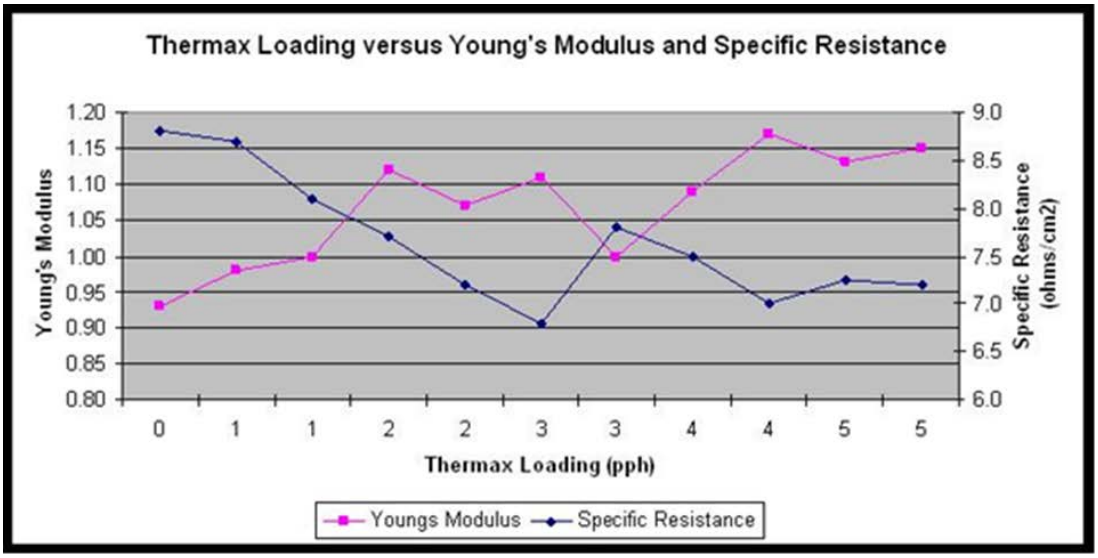

Figure 4.6: Variation in Young's modulus and SR with varying levels of carbon black loading.

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

4.3 Product 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 [14].

5 Graphite Recycle into Silicon Carbide

NRG's contribution to Work Package 5 included 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. This work was undertaken at NRG's Petten Facility in the Netherlands. Further work undertaken by NRG under WP6 has looked at the leaching characteristics under repository conditions of the SiC produced from irradiated graphite under WP5. Results from these tests are reported as part of Task 6.2 'Disposal behaviour of carbonaceous wastes' [1]. A detailed overview NRG's SiC production work is provided in Report 5.2.4 'Other Graphite and Carbon Based Products' [8].

5.1 New Product Production

Literature research on SiC formation from graphite was undertaken, and several suitable methods were found. Finally a technique published by A. Morancais et al. in the J. of Eur. Ceram. Soc. 23 (2003) 1949–1956 [26], was chosen as the method to be tested. In the paper, the method is called "a process involving a Self-Heat Sustaining (SHS) stage."

The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite was studied. Products with very high pore contents (≈80%) were obtained using a process, shown in Figure 5.1 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.

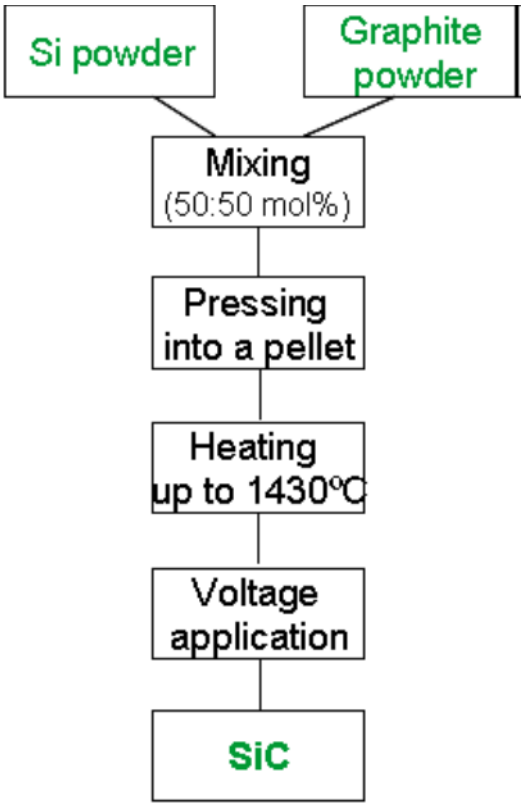

Figure 5.1: Flowchart showing the SiC formation method

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 was undertaken.

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.

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.

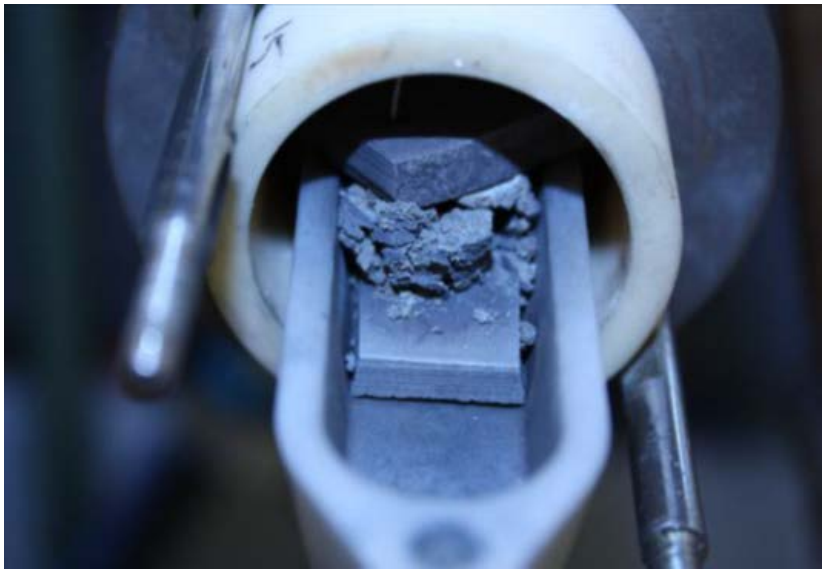

Figure 5.2: A SiC pellet after the Morancais SHS method

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 [13].

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 [27].

5.2 Product Evaluation

The primary focus of the recycle of graphite into Silicon Carbide was focused on its end use as a robust leach resistant material for use as a packing material for wastes under repository conditions. Therefore, a summary of the SiC leaching data is provided below as this forms the basis of its product evaluation.

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}Cwas 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 compared with 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 [28].

6 Graphite Reuse for Decontamination of Waste Streams

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 (covered in this section); the second is the direct reuse of graphite for various applications (covered in the following section).

This section covers the work undertaken by NECSA, in respects to the use of irradiated graphite for the decontamination of both liquid and gaseous waste streams containing certain radionuclides, which include ^{14}C, ^{36}Cl, and ^{129}I.

6.1 Removal of Soap Detergents

At nuclear installations clothing decontamination is achieved with different detergents and the resulting effluent contains organic residues. In order to release this effluent to the environment, the organic contaminants must be removed. Irradiated graphite was used as an adsorption medium to capture known soap detergents which are used in South African Installations. The result indicated in Figure 6.1 below demonstrates that irradiated graphite can be used to remove detergents in question [29].

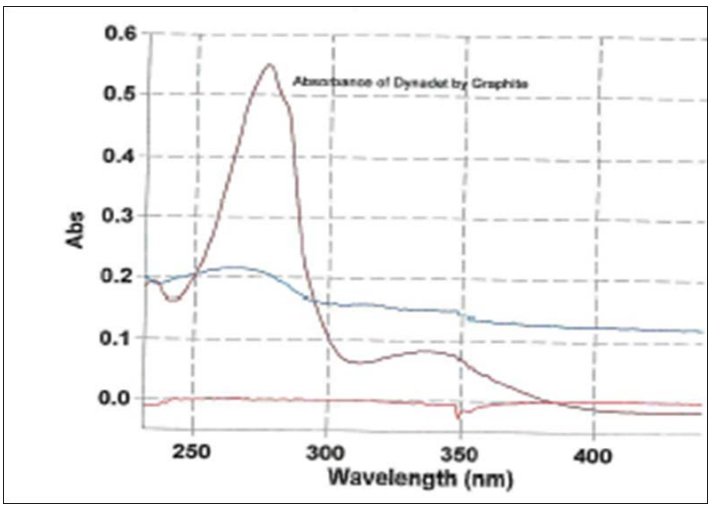

Figure 6.1: UV-spectra of the removal of organic detergents used in South African nuclear industries from effluent waste streams
-Brown: original waste stream with detergent
-Blue: waste stream after 1st absorption
-Red: waste stream after 2nd absorption

6.2 Removal of Radionuclides from Liquid Waste Streams

Research in the past has been focused on improving processes for the removal and recovery of radionuclide's from nuclear waste streams using ion exchange resins. Generally speaking, the expensive resin material is contaminated and has to be disposed of. By replacing the resin with irradiated graphite, contaminated material from the PBMR could be used to recover radionuclides from a PBMR waste stream. The absorption coefficient values for ^{89}Sr (50 000 ml/g), ^{110m}Ag (40 000 ml/g) and ^{131}I (8 000 ml/g) in Figures 6.2 and 6.3, illustrate that irradiated graphite can be used as an ion exchange medium [29].

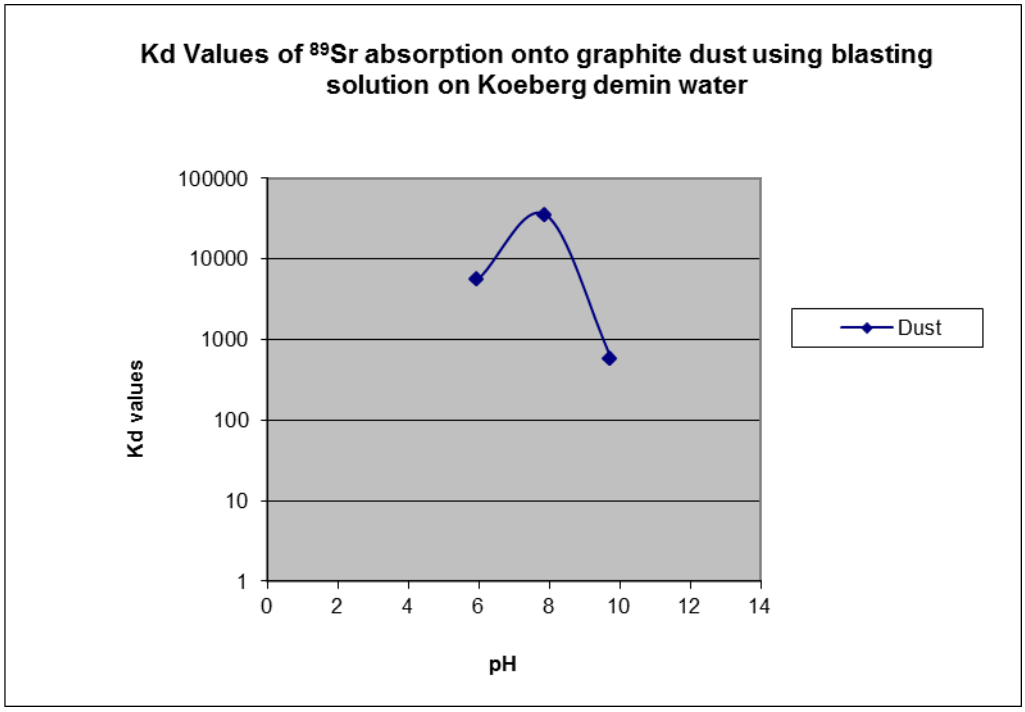

Figure 6.2: Removal of ^{89}Sr from a PBMR waste stream using irradiated graphite as ion exchanger material.

The absorbed ^{110m}Ag was recovered from the graphite by using an eluting solution of 1M HNO_3 and 2% H_2O_2. The results (Figure 6.4) indicate that more than 95% of the ^{110m}Ag was recovered after one bed volume.

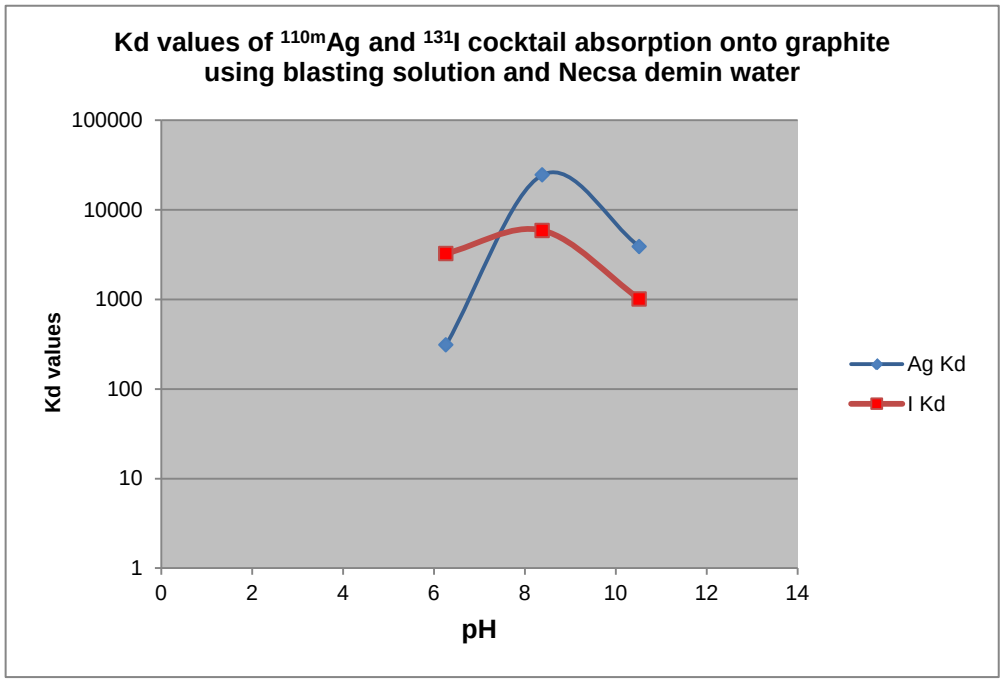

Figure 6.3: Removal of 110mAg and 131I from a PBMR waste stream using irradiated graphite as ion exchanger material

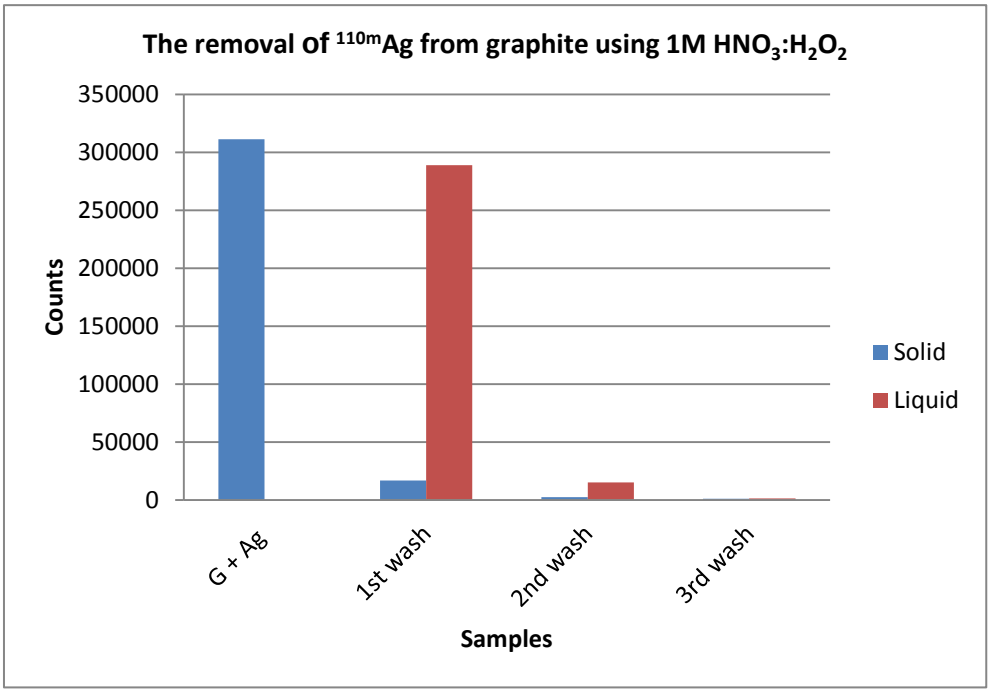

Figure 6.4: The removal of ^{110m}Ag from graphite using 1M HNO_3 and 2% H_2O_2

In addition, the treatment of graphite with silver nitrate was undertaken to enhance the removal of radioactive iodine from waste streams. Preliminary results of experiments to determine the absorption of ^{131}I on the carbon nanotubes were most promising. The Kd value for ^{131}I on carbon nanotubes was about 50 000 units. As the nanotubes were conditioned in an acidic $AgNO_3$ solution for 24 hours, the Kd value for ^{110m}Ag was very low, but it had a substantial effect on the Kd value for ^{131}I.

Preliminary results of experiments to determine the absorption of ^{137}Cs and ^{60}Co on graphite are promising. Results of experiments are summarised in Table 6.1:

Table 6.1: Kd values for ^{137}Cs and ^{60}Co on graphite.

Sample	**K_d**
Cs-graphite (pH<5) treated with $AgNO_3$	5.46
Cs-graphite (pH8-9) treated with $AgNO_3$	3.99
Cs-graphite (pH>12) treated with $AgNO_3$	1.17
Cs-graphite (pH<5)	0.24
Cs-graphite (pH8-9)	0.54
Cs-graphite (pH>12)	10.19
Co-graphite (pH<5) treated with $AgNO_3$	4.2
Co-graphite (pH8-9) treated with $AgNO_3$	153.0
Co-graphite (pH>12) treated with $AgNO_3$	631.2

The results showed that ^{137}Cs could not be absorbed onto graphite, but ^{60}Co is absorbed at higher pH [29].

The considerable amount and number of long-life radioisotopes (e.g. radiocarbon (^{14}C), chlorine (^{36}Cl), iodine (^{129}I), technetium (^{99}Tc), selenium (^{79}Se), caesium (^{135}Cs) etc.) are present in irradiated graphite, due to neutron activation. In order to determine the physical adsorption properties of radiocarbon (^{14}C) onto graphite (important in order to

develop a mechanistic model for impurity removal), experiments were performed to study the adsorption of ^{14}C from a liquid waste stream onto irradiated graphite.

The result in Table 6.2 indicates that the adsorption of ^{14}C onto graphite is minimal and leaching, therefore, poses a huge contamination risk.

Table 6.2: Results of ^{14}C adsorption (on i-graphite)

	Sample	K_d
1.	^{14}C in demin water	3.7
2.	^{14}C in demin water	0
3.	^{14}C in HNO_3	-20
4.	^{14}C in NaOH	0

The negative value in Experiment 3 indicates that the final concentration of ^{14}C in the effluent was substantially higher than the starting concentration of ^{14}C in the effluent after the experiment, indicating the additional release of ^{14}C from the irradiated graphite specimen. To confirm this hypothesis, another experiment was conducted with 1M HNO_3 without any ^{14}C and, after 24 hours of contact time, the solution contained ^{14}C, indicating that ^{14}C leached from the i-graphite.

The results indicate that the ^{14}C resulting from the neutron activation of nitrogen is highly mobile and poses a contamination risk.

Experiments were performed to study the adsorption of different radionuclides (^{60}Co, ^{36}Cl, ^{131}I and ^{22}Na) from a liquid waste stream (acid and alkaline) onto irradiated graphite. The result in Table 6.3 indicated that only ^{60}Co in an alkaline medium will be absorbed onto i-graphite. When the i-graphite is impregnated with Ag, the absorption of ^{36}Cl in acid solution increased.

Table 6.3: Adsorption of different radionuclides onto irradiated graphite

Sample	K_d
i-graphite + ^{60}Co in 0.25M NaOH	3079.3
i-graphite + ^{60}Co in 4M HNO_3	58
i-graphite + ^{36}Cl in 1M NaOH	0.53
i-graphite + ^{36}Cl in 4M HNO_3	3.6
Ag impregnated i-graphite + ^{36}Cl in 1M NaOH	1.3
Ag impregnated i-graphite + ^{36}Cl in 1M HNO_3	469.6
i-graphite + ^{131}I pH 3	4.455
i-graphite + ^{131}I pH 3	4.942
i-graphite + ^{131}I pH 10	0.666
i-graphite + ^{131}I pH 10	0.371
i-graphite + ^{22}Na 1M NaOH	4.0
i-graphite + ^{22}Na 1M NaOH	0.1
i-graphite + ^{22}Na 4M HNO_3	0
i-graphite + ^{22}Na 4M HNO_3	0

6.3 As Absorbent to Remove Nuclides from Gaseous Waste streams

In order to determine the possibility of using irradiated graphite to remove radionuclides from gaseous waste streams, an experimental setup was designed. The requirements of the research equipment required included [30]:

- High vacuum generation + measurement
- Mobile
- Sub-system for desorbing (gaseous) adsorbed species on PTFE filter pieces; max temperature 500°C; desorbed species detected by FTIR.
- Sub-system for determining the absorptive capacity of graphite's towards a number of gases (I_2, CO_2, CO, NO_x, etc) at ambient temperature.

The system used for this work consisted of the following:

- Vacuum system: fore-vac pump, turbo molecular pump + backing pump, liquid nitrogen trap, trolley.
- Vacuum manifold + vacuum and pressure gauges.
- Liquid nitrogen freeze-out container + liquid nitrogen dewar.
- PTFE filter desorption vessel + heating mantle and temp control. An inert gas flush probe is included to facilitate transfer of the desorbed species to the FTIR gas cell. The vessel is connected to a standard 10cm FTIR gas cell. Only IR active species can be detected. The gas cell is connected to the freeze-out vessel.
- Gas supply, flow control and mixing manifold. At least four supply lines, each with mass flow controller, power supply and readout unit, and isolation valves. This system allows accurate mixing and flow control of a test gas with a carrier gas.
- Test vessel for determining the absorptive capacity of graphite towards specified gases. Graphite is contained in a removable canister with screw thread for fixing it vacuum tight to the test vessel. The outlet of the vessel is connected to the FTIR gas cell. The test gas mixture, with known concentration and flow

rate, flows through the graphite canister. The test gas is absorbed by the graphite until it reached saturation. The test gas is then detected by the FTIR. The test gas concentration, flow rate, and flow time to saturation allows the calculation of the test gas absorptivity per mass unit graphite.

The objective of this work was to investigate the rate of mass transfer of CO_2 with respect to interior design and the quality of activated carbon. If the process is successful, it will used to investigate mass transfer of Iodine and Tritium (radioactive).

Results in Figure 6.5 indicated that a fluidized bed design is the optimum design for adsorption compared to stationary columns. During fluidization the activated carbon particles mix with each other (laminar layer that is formed around the particle is always disturb and mixing disturbs the concentration gradient, thus enhancing the rate of mass transfer). In the stationary column the air flow will channel through the path with less resistance (less force per area) and therefore some of the air flow will was not exposed to the activated carbon particles resulting in a decrease in absorption rate.

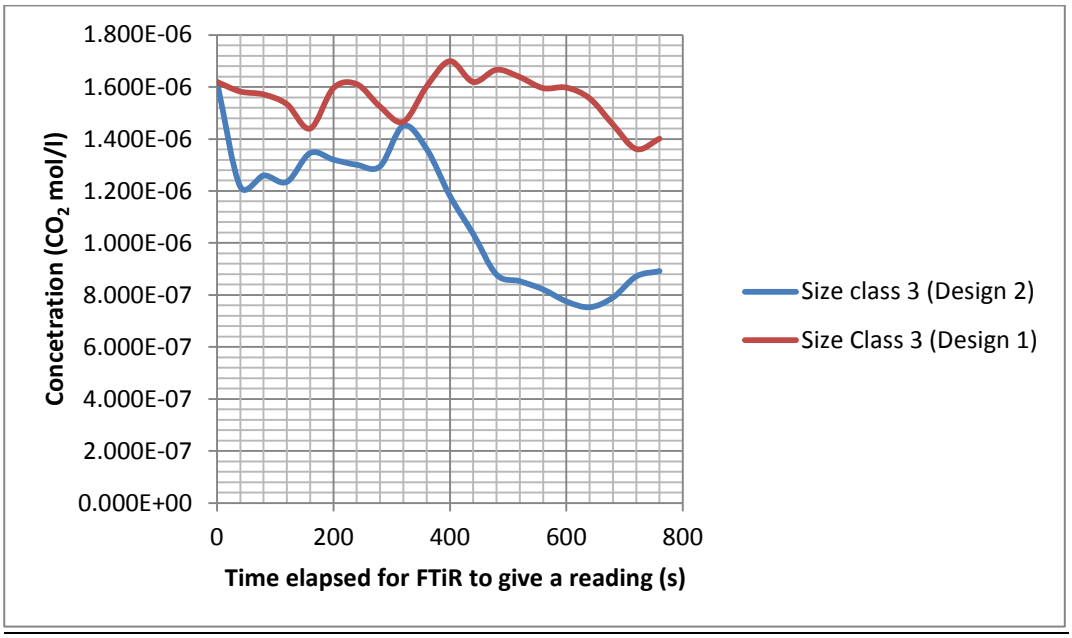

Figure 6.5: Relationship of Carbon dioxide absorption on different designs
-Design 1: Stationary columns
-Design 2: Fluidize

7 Direct Reuse of Graphite for Various Applications

NECSA's contributions to Work Package 5 covered two distinct aspects of graphite recycle and reuse. The work covered in this section relates to the direct reuse of i-graphite in the production of products for use in nuclear waste management.

7.1 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 7.1). 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 7.1: Electrolytic cell, where a graphite piece is the working electrode.

The resulting voltammogram (shown in Figure 7.2), 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.

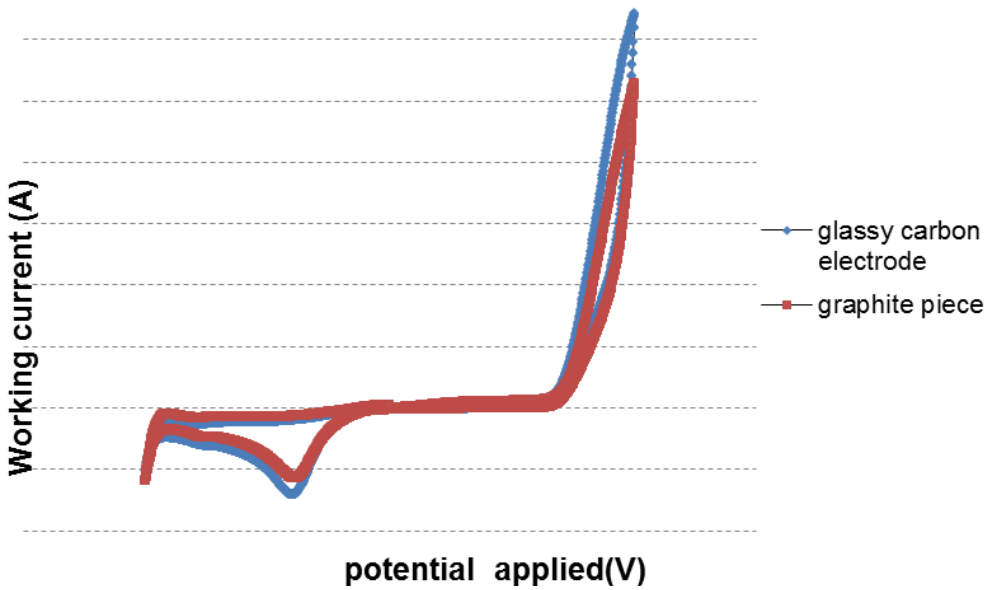

Figure 7.2: Voltammogram showing reactions using different working electrodes

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.

7.2 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 7.3 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). NECSA plan to manufacture crucibles using chemical etching technology which will be subsequently tested as molten salt containers, with specific focus determining if any radionuclide transfer between the graphite and molten salt occurs.

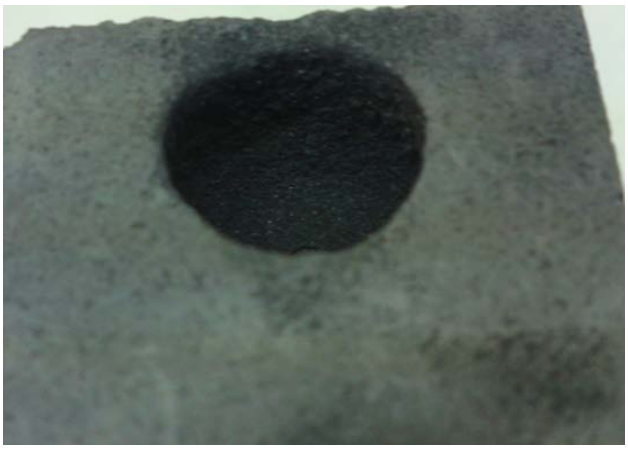

Figure 7.3: Manufacturing of graphite crucibles for molten salt applications using chemical etching technology

7.3 Graphite Reuse as Disposal Containers for Solidified Matrixes

The work undertaken by NECSA, and reported in Section 7.2 above, was considered to have an additional application that being the use of graphite blocks as disposal containers for solidified matrixes.

7.4 Graphite Reuse for the Manufacture of Nanotubes

The manufacture of nanotubes with DC plasma is planned to 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 nanotubes. 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 7.1 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 7.1: 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 7.1 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 ^{36}Cl 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 7.2 overleaf, indicate that there is slight adsorption on the Bayertubes and SWNTs in acidic medium. Measurements are currently underway at pH 7, no further results were available at the time of preparing this report.

Table 7.2: 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

8 Isotope Separation of Radiocarbon

The isotope separation techniques described over the following sections are considered independently of each other, however, it may prove feasible to employ two techniques, firstly one to address the large volumes, and a second to focus on achieving a high purity ^{14}C product (e.g. Gas centrifuge followed by SILEX).

8.1 Methods of Isotope Separation

There are three types of isotope separation technique, these are:

- Those which rely on separation of the isotopes through the variation in their atomic weight (e.g. Gas Centrifuge);
- Those which rely on the small differences in thermodynamic or kinetic reaction properties of the isotopes (e.g. PSA), and
- Those which rely on properties not directly connected to atomic weight, such as nuclear resonances (e.g. SILEX).

Various methods exist for the separation of isotopes although not all of these have been or can be readily applied in the separation of ^{14}C from ^{12}C. Those techniques which exhibit potential (theoretical or proven) for the separation of ^{14}C from ^{12}C are summarized in this section. For a more detailed review of isotope separation techniques please refer to Report 5.3.2 'Report on Isotope Separation Methods' [11].

8.1.1 Pressure Swing Absorption (PSA)

Pressure Swing Absorption (PSA) for carbon isotope separation was initially developed for the separation of ^{13}C from ^{12}C. Researchers at NUPEC and IRI in Japan started to consider the possibility of using it in the late 1990's, for the purpose of processing graphite derived from the decommissioning Tokai Power Station (GCR). It has been proven that the process can be adapted to separate a fraction of ^{13}C plus ^{14}C from ^{12}C, as would be required when separating the isotopes released during the graphite gasification process.

The technology is well established on an industrial scale for achieving separation of gases. The principal is that a gas mixture (often contained in a carrier gas) is absorbed by flowing through a column packed with particles of absorbent. The gaseous components are differentially absorbed on the column packing, which allows a "decontaminated", purified stream to exit the column, while a "concentrated" fraction of the contaminant is retained on the absorption column. The gases absorbed on the column can then be desorbed by reducing the system pressure, which leaves the column particles in a condition ready to begin further absorption duty.

Aside from their ability to discriminate between different gases, adsorbents for PSA systems are usually very porous materials chosen because of their large surface areas. Typical adsorbents are activated carbon, silica gel, alumina and zeolite. Though the gas adsorbed on these surfaces may consist of a layer only one or at most a few molecules thick, surface areas of several hundred square meters per gram enable the adsorption of a significant portion of the adsorbent's weight in gas. In addition to their selectivity for different gases, zeolites and some types of activated carbon called carbon molecular sieves may utilize their molecular sieve characteristics to exclude some gas molecules from their structure based on the size of the molecules, thereby restricting the ability of the larger molecules to be adsorbed.

The whole sequence is operated by pressure changes, hence the name "pressure swing adsorption". Two concepts are useful for further understanding of the technology, namely the "decontamination factor" (DF) and "concentration ratio" (CR). Relating to isotope separation, the DF refers to the ratio of the isotopes in the inlet gas divided by the ratio of isotopes in the outlet gas eluted from the column. Thus, in separating ^{13}C from ^{12}C, if inlet ^{13}C in 1%, and inlet ^{12}C is 99%, outlet ^{13}C is 0.01% and outlet ^{12}C is 99.99%, the DF is 100. The CR refers to the total volume of inlet gas processed, divided by the volume of gas desorbed (together with the contaminant) from the column.

The PSA technique is operated with CO (carbon monoxide) as the chemical form for the isotope separation. It is the interaction between this species and the zeolite absorber which provides the relatively high separation factor. In general the presence of different stable isotopes of additional elements (e.g. ^{17}O and ^{18}O) complicates isotope separation. Hence the use of carbon dioxide in an isotope separation system would exacerbate this problem, even if it were possible to use it. Absorption of the carbon monoxide takes place from an inert gas (helium) carrier gas, which can be simply recycled as part of the process.

Isotope separation technologies usually require many stages for efficient separation, because of the similarity of chemical behaviour of isotopes of the same element. However, chromatographic techniques allow "multiple theoretical plate" separations to occur in a single column, and the PSA system effectively uses a chromatographic technique to separate the isotopes. The most remarkable and critical difference between this technology and many others for isotope separation is that because of the high equilibrium isotope separation factor achievable (α = ca. 1.1 at -30°C) and this chromatographic effect, the Japanese researchers have consistently achieved DF's of about 100 and a CR of 2 – 2.5 in a single, three column, stage.
Thus a seven stage system (each stage being about half the size of the previous one) can achieve a DF of about 100 and a CR of 100. These numbers are consistent with the technique being practical on a large scale.

As is normal for any chromatographic technique, the isotopes progress in bands along the column, and there is an extended band front between the point where the containment begins to be eluted (and hence the DF is reduced) and the column reaches its full isotope ratio in equilibrium with the inlet gas. The Japanese researchers used a column system, eluting and reabsorbing the band front to ensure that only clean gas is eluted, while at the same time the highest possible CR is achieved from each stage by only eluting columns in fully equilibrated condition. To achieve this, part of the eluted gas from the (third) fully loaded column is re-pressurised and passed through the

(second) partially loaded column and from there fed into the inlet gas stream to the first (unloaded) column [31].

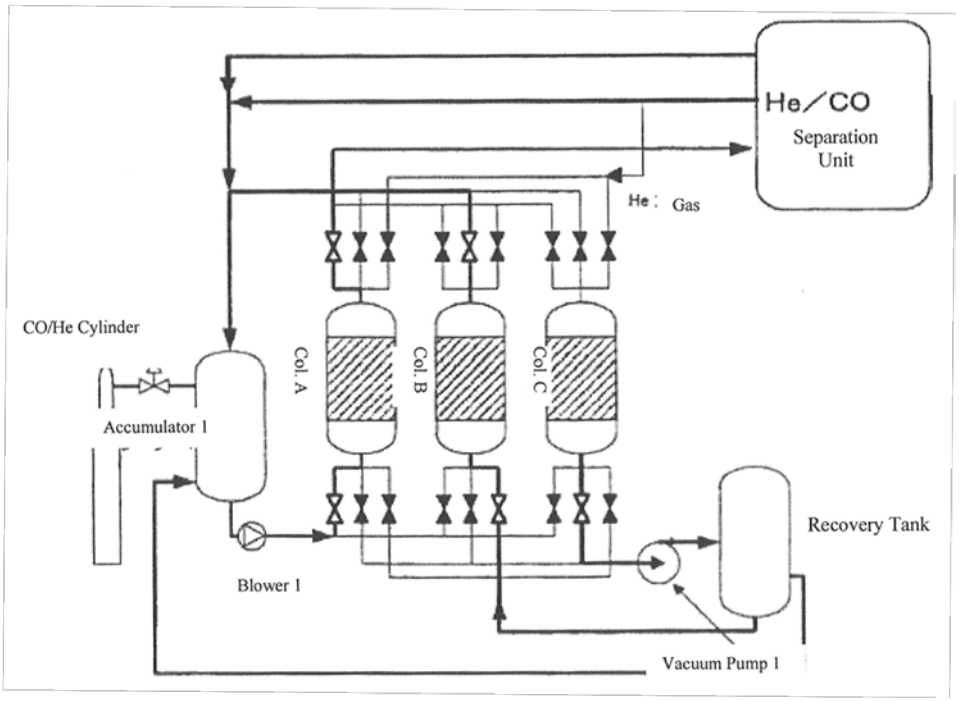

Figure 8.1 – PSA Three Column Stage Diagram [31]

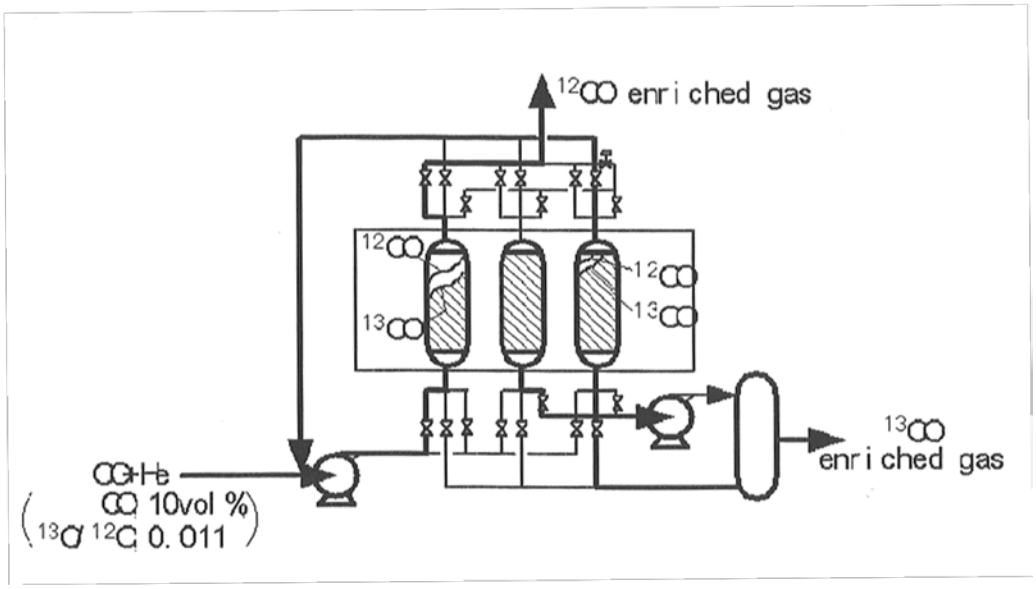

Figure 8.2 – Parallel Purge Operation of Three Column System [31]

Overview of the Japanese Test Programme

Test work has been carried out on the PSA technique. The purpose of this was to establish isotope separation performance for ^{14}C in the graphite incineration off-gas

under real life operating conditions. Obtaining data through basic testing of ^{14}C isotope separation technology with the goal of system conceptualization and real-life application makes it possible to examine the real-life facility concept of the system as a whole. Extensive small scale testing and development of the process has been undertaken.

Results from the Japanese Tests

A full report of the Japanese tests is available [32], and a summary of the results only will be given here.

Choice of Zeolite Absorbent

A variety of potential absorbents were tested, but the test work found at an early stage that Na-X type zeolites were superior to other types tested, and accordingly this type of absorbent was used for all the later test work.

Separating ^{14}C from ^{13}C and ^{12}C

Although the individual isotopes should be separated from each other by the process, in practice the parameters of separation indicates that the PSA process can be used most efficiently for separating a fraction of ^{13}C plus ^{14}C from ^{12}C. For this reason the researchers concluded that this should be their objective, with the desirable CR to achieve being 100, consistent with the approximately 1% content of natural ^{13}C in graphite carbon. This would obviously lead to useful and satisfactory volume reduction to encapsulate the solid waste (containing ^{13}C plus ^{14}C) for disposal while disposing of the ^{12}C to atmosphere. On the other hand if the objective was to collect pure ^{14}C for use or sale, it should be noted that additional processing (possibly using PSA under different conditions) would be required. Although this sounds complex, once the major bulk of the carbon monoxide has been separated, the remaining processing would essentially be a lab-scale, glove box type operation to purify the final product.

Pressure Dependence

The optimum pressures for absorption and desorption have been established through the test work. Optimum absorption takes place at approximately 120 kPa and desorption at

3 kPa. Clearly these values are convenient for plant applications, since 120 kPa is close to normal atmospheric pressure.

Temperature Dependence

The different isotopes of carbon have different temperature dependence characteristics. $^{13}C/^{12}C$ separation efficiency increases as the temperature is reduced from 0 to -60°C, whereas $^{14}C/^{12}C$ separation efficiency reaches a maximum at -30°C. A plant system would probably operate at this temperature, operating in a "cold room" to allow easy access to plant equipment.

Absorption time, concentration and Desorption Purge ratios

These parameters and many others have been examined and optimised by the Japanese researchers. The absorption time is typically just a few minutes – again this is of practical value for plant applications.

Plant Operability

Because the process only involves accumulation tanks, valves, columns, gas pumps and two chemical species (CO and helium) the entire multi-stage process can be simply operated under automatic control. There would be no need for extensive operator intervention.

Because the process would operate on carbon monoxide already separated from the gamma emitting radionuclides present in graphite, there would be no need for radiation shielding of the plant. It is possible that the plant operation could be limited to a maximum of slightly sub- atmospheric pressure – thereby reducing safety concerns associated with carbon monoxide leaks [31].

Application of PSA

One of the primary applications of PSA is in the removal of carbon dioxide (CO_2) as the final step in the large-scale commercial synthesis of hydrogen (H_2) for use in oil refineries and in the production of ammonia (NH_3). Refineries often use PSA technology in the removal of hydrogen sulphide (H_2S) from hydrogen feed and recycle streams of hydro-treating and hydro-cracking units. Another application of PSA is the

separation of carbon dioxide from biogas to increase the methane (CH_4) content. Through PSA, the biogas can be upgraded to a quality similar to natural gas.

Research is currently underway for PSA to capture CO_2 in large quantities from coal-fired power plants prior to geo-sequestration, in order to reduce greenhouse gas production from these plants. PSA is an economic choice for small-scale production of reasonable purity oxygen or nitrogen from air. PSA technology has a major use in the medical industry to produce oxygen, particularly in remote or inaccessible parts of the world where bulk cryogenic or compressed cylinder storage are not possible.

PSA has also been discussed as a future alternative to the non-regenerable sorbent technology used in space suit Primary Life Support Systems, in order to save weight and extend the operating time of the suit.

Current & Future Work on PSA

Work on developing PSA is currently being undertaken by Studsvik. Information relating to their work is deemed to be proprietary at the current time and therefore details concerning the testing of PSA and the data collected are unavailable. One significant variation in Studsviks' work when compared to the Japanese tests (discussed previously) is that the off-gas which Studsvik is working with is derived from steam reforming whilst the Japanese off-gas is derived from incineration. The use of steam reforming of the graphite has distinct advantages over the use of incineration.

A statement summarizing the position of Studsvik (UK) Ltd in relation to their potential use of PSA as a means of supporting its core waste management activities in respects to graphite was issued on the 18th August 2010 [33]. They stated that:

"Pressure Swing Adsorption (PSA) technology is an industry proven approach for the separation and purification of gases. PSA is potentially applicable to separate ^{14}C components of the outlet gas during the thermal treatment and gasification process of radioactive graphite by concentrating ^{14}C oxides and converting them into a solid form for disposal as an intermediate level waste.

The gasified ^{14}C is converted to CO for separation in the PSA. The concentrated ^{14}CO stream from the PSA unit is oxidized to CO_2 and then converted into solid form in a mineralization unit.

The Pressure Swing Adsorption unit consists of several automated adsorption columns that are filled with a special zeolite (aluminosilicate mineral) media. The CO gases pass through the zeolite adsorption columns at a controlled temperature and pressure and the entire CO flow (both ^{12}C and ^{14}C oxide forms) is adsorbed on the zeolite. The process flow is then reversed and the pressure adjusted such that the ^{14}C carbon monoxide (^{14}CO) is preferentially released by the zeolites.

Based on previous work in Japan, it is estimated that the Japanese pressure swing adsorption process will remove and concentrate at least 40% to 60% of the radioactive ^{14}C [34]. The PSA unit for separation ^{12}CO and ^{14}CO isotopes has only been demonstrated at lab-scale.

In addition to the Japanese work, Studsvik has sponsored research and development studies and adsorption modeling that indicates that up to 90% removal efficiency of ^{14}CO from ^{12}CO is possible using special adsorption media and column operations. Significant additional theoretical and laboratory work will be required to demonstrate the suitability of the process at an industrial scale with a mixed gas stream.

As roasting the graphite has shown a very high potential for separating the ^{14}C from the graphite without destroying the graphite structure, further PSA work has not been conducted by Studsvik. The roasted graphite that has minimal levels of residual ^{14}C can then be gasified.

The THOR® treatment process coupled with a qualified PSA system for separation and concentration of the ^{14}C fraction of the waste will reduce the volume of the final post treatment stabilized wastes."

8.1.2 Gas Centrifuge

The gas centrifuge technique was specifically developed to separate the isotopes of ^{235}U from ^{238}U, and was developed to replace the gaseous diffusion method of ^{235}U extraction. The gas centrifuge relies on the principles of centripetal force accelerating molecules based upon mass. It comprises an evacuated casing containing a cylindrical rotor which rotates at high speed in an almost friction-free environment. The uranium is fed into the rotor as gaseous uranium hexafluoride (UF_6) which also rotates. The centrifugal forces push the heavier ^{238}U closer to the wall of the rotor than the lighter ^{235}U. The gas closer to the wall becomes depleted in ^{235}U whereas the gas nearer the rotor axis is enriched in ^{235}U. UF_6 depleted in ^{235}U flows upwards adjacent to the rotor wall, while UF_6 enriched in ^{235}U flows downwards close to the axis. The two gas streams are removed through small scooped pipes, called "scoops (shown in Figure 8.3 below).

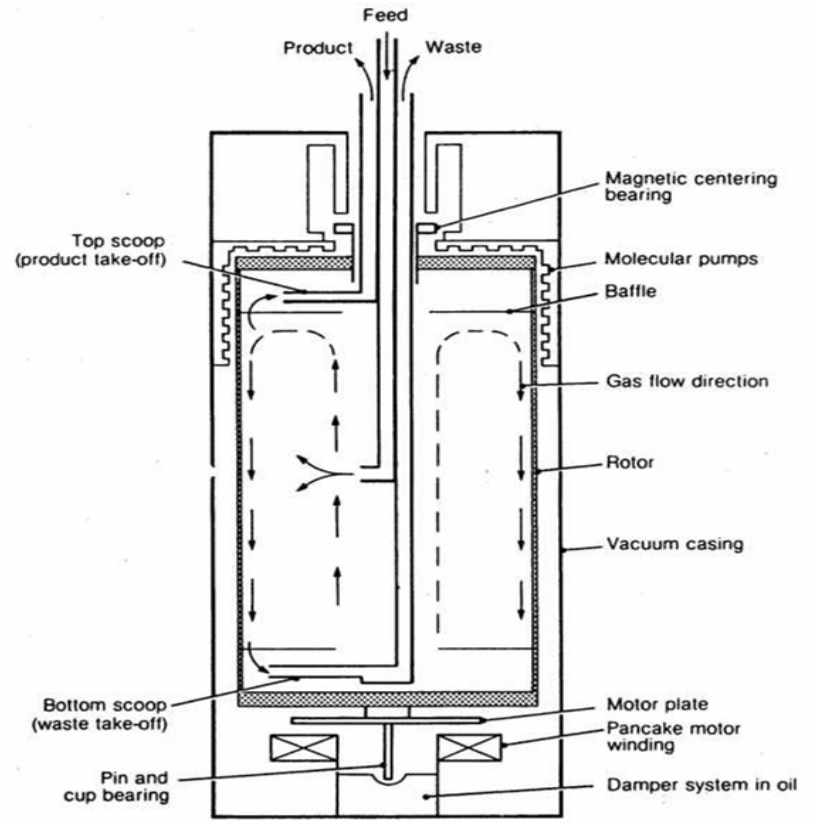

Figure 8.3: Cross section through a Gas Centrifuge used by URENCO

The enrichment effect of a single centrifuge is small, so they are linked together by pipes into cascades (see Figure 8.4). Through the utilisation of these cascades, the process yields higher concentrations of the ^{235}U isotopes with significantly less energy usage and smaller scale plant compared to the gaseous diffusion process.

Figure 8.4: A cascade of gas centrifuges at a URENCO plant.

Once started, a modern centrifuge runs for more than 10 years with no maintenance. An advantage of the centrifuge process is its low energy consumption.

Gas Centrifuge work under Carbowaste

The use of gas centrifuges for the purpose of separating ^{14}C from ^{12}C is a recent endeavor which is being driven, in part, by the Carbowaste programme, as a means of treating the potential off-gas produced through steam reformation of the graphite as part of its potential management plan.

As part of a joint venture between URENCO and AREVA, work is being undertaken through URENCO's subcontract to CARBOWASTE on the feasibility of ^{14}C

enrichment with state-of-the art gas centrifuges from Enrichment Technology (ETC). The aim of this work is to check the feasibility and estimate the cost of ^{14}C enrichment by gas centrifuges developed by ETC for the enrichment of ^{235}U.

The basic separation effect in a centrifuge depends on the absolute difference in molecular weights M_{iC} of the isotopes (isotope abundance $R = N_{14C}/N_{12C}$, circumferential speed: υ_θ

$$\alpha_{ideal} = \frac{R|_{Product}}{R|_{Tails}} \approx \exp\left[\frac{(M_{14C} - M_{12C})\,\upsilon_\theta^2}{2\Re T_0}\right]$$

Enrichment Technology (ETC) centrifuges designed for UF_6 processing (M_{UF6} = 352 g/mol) yield a good performance for process gases with a mean molecular weight above 100 g/mol; lighter process gases increase the effort needed for sealing the rotor from the casing. A low mass fraction of the isotope in the process gas molecule increases the required separative work (per mass of pure substance).

Results

ETCs centrifuges have proven in laboratory settings to yield similar basic separation factors (with respect to a molecular weight difference of 1 g/mol) for a wide range of process gases. These potential process gases which have been identified to use in carbon treatment are given in Table 8.1, below:

Table 8.1: Table showing the results of investigation into potential process gases for carbon treatment [35]

Process Gas	Mean Mol. Weight	Mass Fraction of Carbon	Assessment
CF_3I	195,9 g/mol	6,1 %	Proven in laboratory
CH_2IF	160 g/mol	7,5 %	Very likely to work
CF_4	88 g/mol	13,6 %	Lowest limit for UF_6 design
CO_2	44 g/mol	27,3 %	Ligand isotopes; low weight
CH_4	16 g/mol	75,0 %	Not feasible in UF_6 design

Since issuing the Interim report on Isotope Separation in March 2010, the work by URENCO developed to consider aspects including:

- quantitative estimate of the separative work needed as function of process gas and the degree of ^{14}C enrichment
- rudimentary cascade design (number of stages) for a multi-isotope feed with isotopes ^{12}C, ^{13}C, and ^{14}C
- estimate of the enrichment cost based on the current market price for Uranium enrichment
- the additional cost for the preparation/conversion of the process gas has to be considered.

A report detailing the findings of URENCO's work entitled 'Estimate of the feasibility and the cost for the enrichment of the Carbon isotope ^{14}C with gas centrifuges' was issued in the summer of 2010. The German Federal Ministry has placed restrictions on the use of this report by participants of the Carbowaste project due to the similarities in the process to that used in the enrichment of uranium. Whilst the full report is unavailable for use at the time of production of this report, an abstract of the URENCO report has been supplied. The abstract reads:

'The study deals with the feasibility of the enrichment of the ^{14}C isotope contained in graphite left over from nuclear power plants by means of gas centrifuges that are designed for the enrichment of natural Uranium.

The machines that have been optimized for Uranium enrichment can be used for this purpose without major design changes if the process gas has a molecular weight of not much less than 100 g/mol. Tetrafluoromethan (CF 4) and Trifluorojodomethan (CF3J) have been identified as suitable process gases with a clear cost advantage for the lighter gas. Some machine parameters such as the heat management would have to be optimized by means of laboratory experiments for these process gases.

By comparison and extrapolation from the current market price for Uranium enrichment (162 US $ per SWU) the cost for the enrichment of the 14C molar fraction in 1 g Carbon from 10-5 to 10-3 is estimated as 250 US $ for CF 4 and as 570 US $ for CF3J. Here, it is assumed that the feed is available in unlimited amounts and that the left over (waste) is not much depleted. Most importantly, the cost for the production (conversion of raw graphite or output of the pre-enrichment step) of the process gas is not considered in this estimate.

As a side effect the isotope ^{13}C with an initial concentration of 1,1 % in the graphite reaches a concentration of about 27 % in the product stream when ^{14}C is enriched by two orders of magnitudes.

As a main cost driving factor, the mass fraction of the Carbon atom in the process gas molecule has been identified, making it desirable to use lighter process gases such as CO2 or CH4. The centrifuges built by Enrichment Technology that have been optimized for Uranium separation on base of the process gas UFs (M = 352 g/mol) would need a significant design modification in order to be able to deal with these gases with molecular weights below 50 g/mol and the performance would be limited.

A more realistic assessment of the cost requires precise estimates for the cost of conversion from the output of the pre-enrichment process into a suitable process gas and for the transformation of the process gas into a desirable product. Also, it must be assessed whether the amount of material to be processed is enough to make it worth to enrich in a single large cascade or whether the desired product concentration can be more economically achieved by re-feeding the material several times in a smaller cascade.'

8.1.3 Amine/Carbamate Separation

Isotope separation has been reported in a liquid/gas exchange system utilising the marginal differences in partition of carbon dioxide between the gas phase and an aqueous phase enhanced by the presence of a variety of amines [36]. This process takes place at almost ambient temperature, but involves boiling and cooling, which entails significant energy costs which could be limited by the use of an appropriate heat exchange system.

The separation factor for ^{14}C with the amine carbamate exchange process is 1.02 (the same as with cryogenic distillation). It should be stated however, distillation and gas liquid exchange cannot go further than separating ^{13}C and ^{14}C together from ^{12}C; the reason for this is there will always be much more ^{12}C and ^{13}C, than ^{14}C. This therefore shifts the process towards endlessly separating ^{12}C from ^{13}C, and not ^{14}C from them [37].

Although this type of system appears to have been studied quite extensively since this initial paper, there are as yet no reports of any scale-up applications. One problem appears to be that the separation efficiency depends on rapid transfer of carbon dioxide between the gas and liquid phases, and this transfer appears somewhat slow [31]. Additionally, the theoretical plateau height is much higher with amine carbamate, than with cryogenic distillation, which leads to the requirement for larger columns [37, 38].

Following lab scale trials by a UK company which proved unsuccessful, a Romanian laboratory is assessing this potential technology and claims to have had considerable more success with the process. It is important when considering the cost of this technique, to factor in the cost of the eventual dismantlement of the sizeable columns which is likely to generate thousands of tonnes of waste.

8.1.4 Cryogenic Distillation

A US patent [39] refers to the cryogenic distillation of carbon monoxide as a means of enriching ^{14}C in a single stage. Although simpler than the PSA technology, the very low temperatures required for this process are a drawback. It is important to note that the initial ration of ^{14}C:^{12}C considered in this patent is much higher than one would obtain from a graphite-incineration process (for example) and thus that the number of distillation stages required, and hence the cost, would be very high. The separation factor for ^{14}C with the cryogenic separation exchange process is 1.02 [37]. This procedure was further developed by Ontario Hydro for the separation of ^{14}C from CANDU resin beds used as clean up for the annulus-gas system [40]. In this application the separation is effected as the dioxide, using a recirculating system on successive batches of resin until the ^{14}C in the dioxide builds up to a sufficient concentration using an adaption of the pressure-swing absorption technology. At this point, separation can be effected, again as the monoxide, using zinc as a reductant.

It should be taken into account that this technology has great difficulty in recovering pure carbon monoxide if relatively large volumes of nitrogen are present due to carbon monoxide and nitrogen having very similar boiling points which are -191.5°C and -195.79°C respectively.

8.1.5 Diffusion

Often done with gases, but also with liquids, the diffusion method relies on the fact that in thermal equilibrium, two isotopes with the same energy will have different average velocities. The lighter atoms (or the molecules containing them) will travel more quickly and be more likely to diffuse through a membrane. The difference in speeds is proportional to the square root of the mass ratio, so the amount of separation is small and many cascaded stages are needed to obtain high purity. This method is expensive due to the work needed to push gas through a membrane and the many stages necessary.

Diffusion is unlikely to be a viable option for the separation of ^{14}C and ^{12}C, as it has been superseded by isotope separation by the gas centrifuge technology which has lower energy requirements as well as the required plant having a significantly smaller footprint.

8.1.6 Carbon Tetrafluoride Distillation

There is as yet no known experience of this technique, but there might be some benefit in considering it by analogy with the production of boron isotopes. Enriched ^{10}B is produced for application as a chemical shim in PWR reactors on a (relatively small) industrial scale by the distillation of boron trifluoride etherate. Fluorine is commonly selected as a counter-atom for isotope separations of this kind because it has only one stable isotope, and this avoids complications when trying to separate isotopes by differences in physical properties of a combined molecule.

Carbon tetrafluoride is an easily prepared substance with a convenient boiling point. There is no *a-priori* reason why distillation with a very efficient high-theoretical-plate fractionation system should not be used to separate carbon isotopes. It may be that there are reasons why this option is impractical, but it would seem to be worth considering.

8.1.7 Isotope Separation by Laser

SILEX is an acronym for Separation of Isotopes by Laser Excitation, a technology developed in the 1990s for isotope separation to produce enriched uranium using lasers. The SILEX process was developed in Australia by Silex Systems Limited; a publicly listed high technology innovation company founded in 1988, and was invented by Dr Michael Goldsworthy and Dr Horst Struve.

In November 1996, Silex Systems Limited signed a license and development agreement for the application of SILEX technology exclusively to uranium enrichment with the United States Enrichment Corporation (USEC) avoiding any problems for Australia under the Nuclear Non-Proliferation Treaty. Silex Systems Limited concluded the second stage of testing in 2005 and began enacting its Test Loop Program.

In 2007, an exclusive commercialization and licensing agreement was signed with General Electric Corporation. The Test Loop Program was transferred to GE's facility in Wilmington, North Carolina. Also in 2007, GE-Hitachi signed Letters of Intent for uranium enrichment services with Exelon and Entergy - the two largest nuclear power utilities in the USA. Together with development partners, SILEX is leading the world in developing technologies to create and utilise a new generation of ultra-pure "isotopically engineered" materials.

The SILEX Uranium Enrichment Process is the world's only third generation laser-based technology under development today. The SILEX technology is marketed as having a number of potential advantages over existing isotope separation processes which include it having lower power consumption and capital costs compared to alternative methods; and its modular nature provides it with versatility in its deployment. It should be stated that these claims are related to its use for uranium enrichment only.

Currently, this technology is still under development, with the initial focus of its application being on the enrichment of uranium. The Uranium application of SILEX is currently in the third and final stage of development - called the "Test Loop". In accordance with the SILEX- General Electric Company (GE) Agreement, the Test Loop program is being fully funded by Global Laser Enrichment (GLE), a subsidiary of GE (51%) formed in partnership with Hitachi (25%) and Cameco (24%). The Test Loop, which is being built at GE's nuclear (Fuel Fabrication) facility in Wilmington, North Carolina, USA, will verify performance and reliability data for full scale (commercial-like) facilities. This key engineering demonstration programme is scheduled to be completed at the end of 2009 [41].

Other Applications for SILEX

SILEX technology utilises lasers to separate or enrich the naturally occurring isotopes of an element to create ‘new’ materials with different qualities and therefore may be applied to applications other than uranium enrichment, these include:

- Enriched Silicon-28 for use in advanced semiconductor applications
- Carbon enrichment for the production of synthetic diamond for its improved thermal conductivity
- Carbon–12 enrichment with production of a Carbon–13 ‘by-product’ for medical applications
- Oxygen-18 production for use in Positron Emission Topography (PET) medical imaging.

8.2 Isotope Separation Summary

Little information is yet available on the economics of isotope separation as applied to radiocarbon, but it is likely that any isotope enrichment process will be relatively expensive and unlikely to be applicable to the majority of the graphite waste. However, isotope separation could be important for certain graphite wastes, or fractions thereof. For example, if a small ^{14}C rich fraction were released from graphite by the heating (roasting), this fraction could undergo isotope separation to yield a pure ^{14}C product.

The ^{14}C could potentially be sold to users of the isotope (such as producers of isotopically labelled chemicals), thereby displacing alternative production of ^{14}C for these purposes.

Another potential use of isotope enrichment would be where a particular waste stream just fails to achieve acceptable limits for release to atmosphere. The removal of some of the ^{14}C by isotope separation would then allow release of the remaining bulk.

The scale of the isotope separation techniques vary greatly; some can be applied to relatively large volumes of feedstock such as PSA or gas centrifuge; other techniques such as SILEX are better suited for processing relatively small volumes but are able to produce very high concentrations. It may therefore be viable to use two isotope separation techniques instead of one, in order to produce an ideally pure ^{14}C product.

Of those isotope separation methods which have been discussed, it is clear that some of these are unlikely to be ideally suited for the separation of ^{14}C from ^{12}C. Those methods which do exhibit significant potential are currently being investigated under the CARBOWASTE programme.

9 ^{14}C Recycle and Supply

One of the tasks (T.5.3.3) [12] of the CARBOWASTE Recycle Work Package is to examine the potential for recycle of ^{14}C. The presence of the isotope ^{14}C is usually considered as a problem in the management of irradiated graphite waste. However, the isotope is used in many applications of chemistry and medicine and is used in quite significant quantities, not grossly dissimilar to the inventory of the isotope in graphite moderated reactors. In order to achieve such recycling two developments would need to take place. First there needs to be an efficient means of separating the ^{14}C from the graphite, and second the resulting product needs to have the right characteristics of chemical form, isotopic purity and quantity for supply to the market. It also needs to have the right price.

The workscope included a sub-task which stated "The organisations promoting and marketing ^{14}C (e.g. GE Healthcare, in the UK) will be contacted with a view to matching the isotope product to the market need."

The key findings of the brief report for T.5.3.3 are that:

- The potential industrial recycle of ^{14}C over a number of years could use a significant proportion of the total i-graphite inventory, although it is most unlikely that most or all ^{14}C in irradiated graphite could be recycled. For example one UK manufacturer of products annually uses approximately 0.3% of the inventory of UK's Magnox reactors.
- Although ^{14}C is produced for manufacturers by reactor irradiation of nitrogen species and hence is available to them in high isotopic purity, the discussions revealed that a lower specific activity (i.e. isotopic dilution) would nevertheless be acceptable to manufacturers as input material for some applications. The possibility of recycling material directly from irradiated graphite (without isotope separation) was therefore examined. This would involve using "roasting" techniques to produce a fraction with the highest possible specific activity of ^{14}C from i-graphite, and selecting graphite with the highest possible ^{14}C activity for recycle. Unfortunately the gap is probably too large to bridge this way, since the specific activities required by the manufacturers are the order

of 10^7 to 10^8 Bq/g compared with 10^5 Bq/g typical i-graphite inventory. Recycle of ^{14}C from graphite will therefore almost certainly require purification by isotope separation.

- The appropriate choice of graphite (and a "roasted" fraction from it) would allow any isotope separation process to be conducted on a small physical scale, thereby making the process more economic. More results will be required from "roasting" research to determine the maximum specific activity which can routinely achieved by this process, and this will ultimately determine the economics of recycle.
- There is no problem in producing from graphite fractions the chemical form of carbon needed for recycle. Benzene is a key intermediate for production of products, but this can be produced from inorganic substances (e.g. the calcium carbide/acetylene route).

10 Conclusions

- 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. These include the recycle of i-graphite into components for nuclear applications, such as graphite electrodes for waste vitrification, new moderator graphite its or conversion to silicon carbide.

- The use of carbon black as an intermediate for recycling irradiated graphite is viable, although there are significant limitations on the proportion which can be included within 'new graphite' which if exceeded would have significant consequences on the final products properties and characteristics (e.g. strength, thermal conductivity 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.

- 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. This is not a surprising conclusion, since the recycle of a certain proportion of non-irradiated graphite has been a routine part of manufacturing processes for many years [12].

- The uptake of graphite recycle on an industrial scale requires 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 have been significant developments in the decontamination approaches for 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 work 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

    - Carbon black (or other achievable intermediates) 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.

    - Using graphite which has been extensively decontaminated using the new techniques (e.g. ‘Roasting’) or

    - Using irradiated graphite (with no decontamination) and bearing the full cost of radiological protection of the manufacturing facilities.

- 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.

- NECSA under Work Package 5 has considered the direct reuse of i-graphite for various applications. Key conclusions from their work include irradiated graphite can be used to remove detergents used in South African nuclear installations, and work is progressing in RSA on the use of i-graphite as a container for molten salts as well as for the manufacture of carbon nanotubes.

In terms of isotope separation, the key conclusions drawn include:

- Enhanced isotope removal is achievable though the mechanism of 'roasting', in which an initial small fraction of the graphite is gasified, but which contains a significant proportion of the radioactive isotope inventory.

- Through a combination of roasting and efficient isotope separation, suitable concentrations of both ^{14}C and ^{13}C (e.g. 99% pure) may be achievable. These could be utilized as an additional/replacement source of medical radioisotope.

- The various isotope separation techniques have potential for application in the separation of ^{14}C from ^{12}C and ^{13}C, these include.PSA, gas centrifuge, amine carbamate separation, cryogenic distillation, diffusion, carbon tetrafluoride distillation and separation of isotopes through laser excitation (e.g. SILEX).

- Currently the most appropriate techniques appear to be that of Pressure Swing Absorption and Gas Centrifuge. This assessment is primarily based on the fact that

they are being developed by commercial companies with the express aim of applying the techniques to separate the isotopes of carbon being considered.

- Alternative options to may exist which require further development; these include aspects such as chemical transformation (e.g. Fluorination of carbon to produce carbontetrafluoride).

- Use of more than one technique for isotope separation may be more appropriate, for example, initial use of a large scale technique which can be applied to large volumes of gas (e.g. Gas centrifuge), followed by a smaller scale technique (e.g. SILEX) focused on producing a pure ^{14}C product which could potentially have commercial value, for examples as a labeled radiochemical for AIDS and cancer research.

- In order to assess the viability of one isotope separation technique against another, additional information is required, such as their associated costs, achievable concentration ratios, process rates, and the timescales involved in their development for separating ^{14}C from ^{13}C and ^{12}C.

Glossary

AREVA	AREVA Nuclear Power
ARMINES	Association pour la Recherche et le Développement des Méthodes et Processus Industriels
CANDU	Canada Deuterium Uranium Reactor
CNT	Carbon Nanotubes
CR	Concentration Ratio
DC	Direct Current
DF	Decontamination Factor
EC	European Commission
EdF	Électricité de France S.A.
EG	Exfoliated Graphite
ETC	Enrichment Technology Company Limited
FTIR	Fourier Transform Infrared Spectroscopy
FZJ	Forschungszentrum Juelich GmbH
GCR	Gas Cooled Reactor
GE	General Electric
GIC	Graphite Intercalated Compound
GLE	Global Laser Enrichment
GLEEP	Graphite Low Energy Experimental Pile
GrafTech	UCAR snc - Groupe GrafTech International Ltd
GTMHR	Gas Turbine-Modular Helium Reactor
HEU	Highly Enriched Uranium
HTR	High Temperature Reactor
ILW	Intermediate Level Waste
IR	Infrared

LEU	Low Enriched Uranium
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MW	Mega Watt
MWCNT	Multi Walled Carbon Nanotubes
MWNT	Multi Walled Nanotubes
NBG	Nuclear Block Graphite
NECSA	South African Nuclear Energy Corporation Limited
NRG	Nuclear Research and Consultancy Group
NUPEC	Nuclear Power Engineering Corporation
PBMR	Pebble Bed Modular Reactor
PET	Positron Emission Topography
Pph	Parts Per Hundred
PSA	Pressure Swing Adsoption
PTFE	Polytetrafluoroethylene
PWR	Pressurised Water Reactor
RRT	Round Robin Test
SEM	Scanning Electron Microscope
SGL	SGL Carbon GmbH
SHS	Self Heat Sustaining
SiC	Silicon Carbide
SILEX	Separation of Isotopes by Laser Excitation
SWCNT	Single Walled Carbon Nanotubes
SWNT	Single Walled Nanotubes
TRISO	Tristructural-isotropic Fuel

UNGG	Uranium Naturel Graphite Gaz
UoJ	University of Johannesburg
UoM	University of Manchester
URENCO	Urenco Enrichment Company Ltd
US DoE	United States Department of Energy
USEC	United States Enrichment Corporation
WP5	Work Package 5
XRD	X-ray Diffraction

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