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-5.3.2)
Report on Carbon Isotope Separation Methods

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Reporting period: e.g. 01/04/2010 – 31/03/2011

Date of issue of this report: 13/04/2010

Start date of project: **01/04/2008** Duration: **48 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		
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Work package: 5 **Task: :** 5.3.2	**CARBOWASTE document no:** CARBOWASTE-1103 -T-5.3.2 (e.g. May 2008 as date of issue: 0805)	**Document type:** T
Issued by: Bradtec (UK) **Internal no.:** Bradtec Report No 03/11		**Document status:** Final

Document title

Report on Carbon Isotope Separation Methods

Executive summary

This final report is a review of isotope separation techniques which have the potential for use in the separation of ^{14}C from ^{13}C and ^{12}C; a key part of the graphite management process being developed under Work Package 5.

In preparing this report, input was obtained from the participants of both Work Package 5 and Work Package 4. In particular, discussions and meetings held with NECSA, PBMR, FJZ, Studsvik and URENCO have been instrumental in the production of this report. In addition, discussions have been undertaken with suppliers/users of ^{14}C which include GE Healthcare, Bioquotient Research and American Radiolabeled Chemicals Inc (ARC) to assess the potential for supplying ^{14}C derived from i-graphite treatment to the radio-pharmaceutical industry.

Initially the report considers the context of isotope separation and the value of its use as part of the graphite management plan being considered under Work Package 5. The report then considers the preceding stages to isotope separation, which are responsible for generating the feedstock (e.g. carbon monoxide containing a mixture of ^{14}C, ^{13}C and ^{12}C). The preceding steps include conversion of the graphite to the gas phase through a process of steam reformation (gasification, partial oxidation); and the use potential value of "roasting", which can separate graphite into isotope-rich and isotope-lean fractions.

The various isotope separation techniques which have potential for the separation of carbon isotopes are then discussed and where relevant, the results of ongoing work to develop some of these techniques are given. The scaling of the techniques is considered and the potential to undertake a two stage approach to isotope separation is discussed. The potential option for applying a direct chemical reaction to the graphite, such as the fluorination of carbon into carbontetrafluoride is mentioned.

The report concludes that current commercial development of the isotope separation techniques of gas centrifuge and pressure swing absorption is ongoing, and initial results for both these methods are promising. In addition, the benefits of applying an initial 'roasting phase' to the treatment process considered and the potential viability of a recycle route for the ^{14}C is discussed.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
1	31st April 2011	Final report	Jon Goodwin	D Bradbury	D Bradbury	D Bradbury
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Contents

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initial ‘roasting phase’ to the treatment process considered and the viability of a recycle route for the ^{14}C is discussed.

1 Introduction

The objective of this final report is to establish the role of carbon isotope separation within the process of graphite management, particularly in the recycle and reuse of graphite, and to summarize the key isotope separation techniques which could potentially be applied for the purpose of separating the isotopes of ^{14}C from ^{12}C and ^{13}C. Prior to applying isotope separation, the graphite is required to be transformed, for example form a solid into a gas, via a process, such as gasification.

Isotope separation is the process of concentrating specific isotopes of a chemical element by removing other isotopes, for example separating natural uranium into enriched uranium and depleted uranium. When considering its potential application for the separation of ^{14}C from ^{12}C and ^{13}C as part of the graphite management plan (see Figure 1.1 overleaf) being considered under Work Package 5, the benefits of applying this process include:

- The potential production of a ^{14}C rich (ideally pure) product which can be used as an alternate source of the ^{14}C isotope used for medical and other purposes, thereby negating the need (either wholly or partially) for this isotope to be manufactured on demand. This potentially alternative source of ^{14}C may reduce the requirements on reactors such as the Petten High-Flux Reactor (HFR) to produce ^{14}C, thereby increasing the opportunity to increase production of other radioisotopes.

- Minimising the ^{14}C content and therefore the radiological implications of the majority of the gasified graphite.

Through gasification (partial oxidation or partial gasification) of the graphite and subsequent re-deposition in a form such as carbon black, it is possible to produce new carbon products (e.g. Graphite electrodes used in the vitrification of some nuclear wastes) from irradiated graphite with very efficient decontamination from all isotopes other than ^{14}C. Special additional processing may be required to separate ^{14}C from ^{12}C, other than that achieved through the roasting process (in which ^{14}C is released selectively from graphite by initial heating). This isotope separation is the subject of this final report.

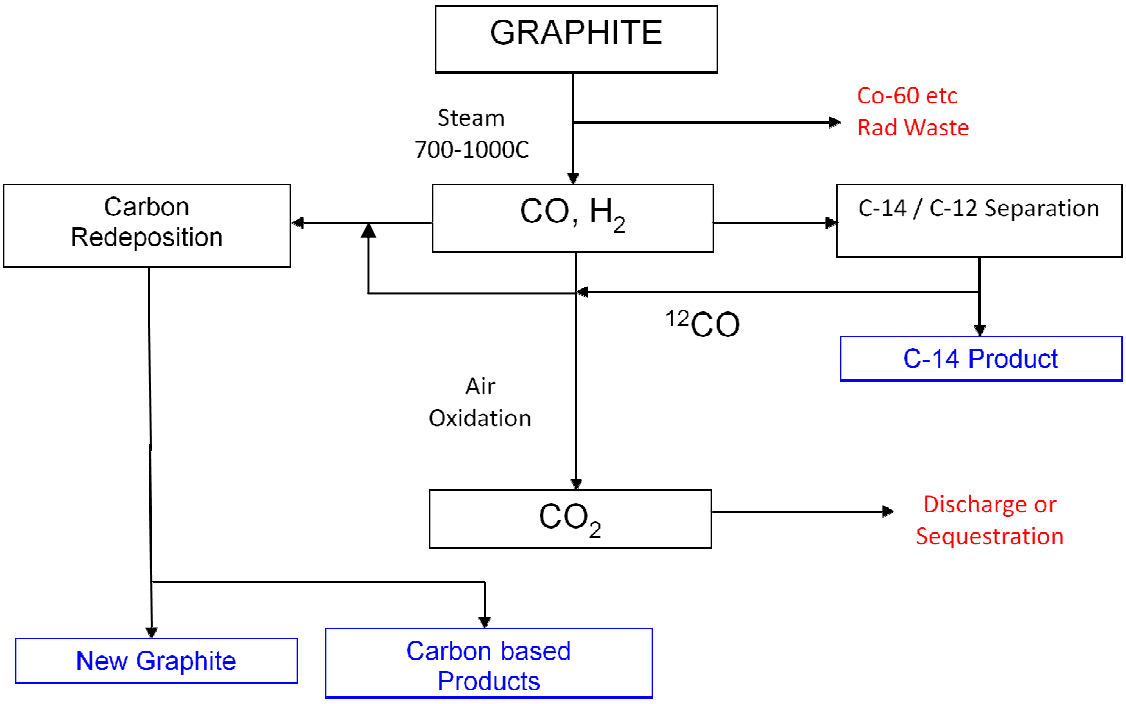

Figure 1.1 - Graphite Gasification Options [1]

There are various isotope separation technologies which have the potential to separate the isotopes of ^{14}C from ^{12}C and ^{13}C, including Pressure Swing Absorption, Cryogenic Distillation and Gas Centrifuge. This report endeavors to describe the approach of each of the technologies and to give an indication as to their current potential for use in separating the isotopes of ^{14}C from ^{12}C and ^{13}C.

This final report is the deliverable for Task 5.3.2, part of Task 5.3 (Separation and Recycle of Radiocarbon) of Work Package 5 and also includes the results of discussions undertaken for Task 5.3.3 (Comparison of ^{14}C production methods and suitability for market needs) of the Carbowaste project. The participating organisations under the Carbowaste project for Task 5.3 are Bradtec, FZJ, Studsvik, PBMR and NECSA, with input recived from organizations including include GE Healthcare, Bioquotient Research and American Radio-labeled Chemicals Inc (ARC).

2 Graphite Gasification

In order to reach the stage where isotope separation is applied, the graphite is required to be transformed, for example from a solid into a gas. The conversion of the graphite into the gas phase results in the retention of the less labile radioisotopes such as ^{60}Co in the solid residue. This can then be packaged and grouted ready for long term storage. The gas (CO, H_2) resulting from the gasification process, will have lost a significant proportion of the radionuclides, but ^{14}C and ^{3}H remain. ^{3}H can be readily removed from the process in the form of water. The removal of the ^{14}C from ^{12}C and ^{13}C could be undertaken by applying a suitable isotope separation technique, or techniques. Figure 2.1 below highlights the gasification stage of the graphite management plan.

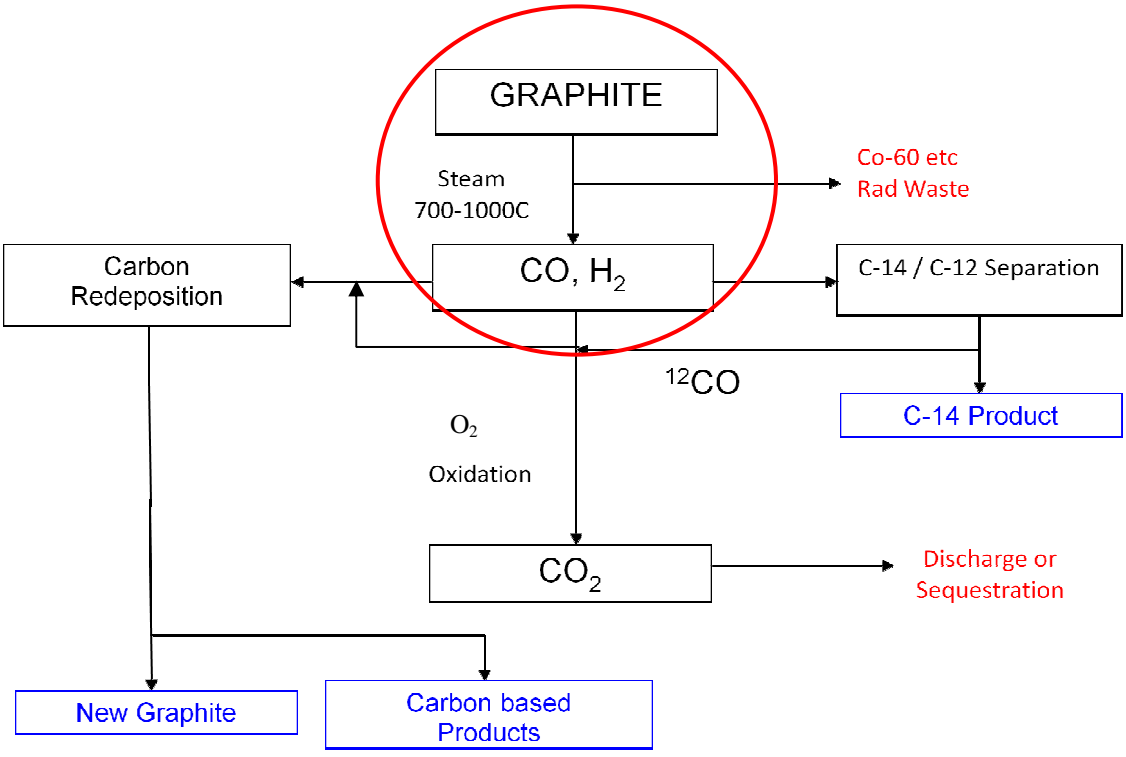

Figure 2.1 Graphite Management Plan, with Gasification Phase highlighted. [1]

There are potentially many reaction schemes to convert solid carbon (in graphite form) into gaseous oxides of carbon, in addition to the steam reforming scheme shown in Figure 2.1. However, the constraints of processing many thousands of tonnes of material (and issues associated with radioactive inventory) mean that only simple and

established reaction schemes with inexpensive reactants are likely to prove practical. There are two principal options:

- React the graphite with air or oxygen (incineration).
- The carbon can be reacted with steam, using the well established "steam reforming" reaction.

Incineration of graphite is difficult; mainly because nuclear graphite is extraordinarily resistant to oxidation [2, 3]. This means that the deliberate usage of incineration to dispose of irradiated graphite by oxidation presents a considerable technical challenge for conventional incineration processes. However, it has been achieved, on a pilot-plant scale, by Framatome at Le Creusot utilising a fluidised-bed approach [4, 5].

Of these two options, the use of the steam reforming process is probably the most suitable due in large part to its ability to be undertaken within a closed system, which when compared to the continuous air flow required for incineration and its difficulties in holding back volatile radionuclides, this is a distinct advantage. Development of the steam reforming process for graphite gasification is well advanced with trials being undertaken currently by Studsvik in the USA, the results of which are deemed to be encouraging [6].

For the graphite moderator blocks to be gasified effectively, they must be size reduced in order for the feedstock to be within the optimal particle range (<50mm). This process can be undertaken by one of two mechanisms, firstly, the blocks can be removed from the reactor intact (current baseline approach) and then fed through a crusher (or crushers); or the moderator graphite could be size reduced as part of the process of retrieval from the reactor (e.g. Nibble and Vacuum approach).

Another potential option may be to utilise a direct reaction such as conversion of the graphite into the intermediate form of CF_4; this option is currently being investigated to assess its viability. Although such direct reaction paths may not be appropriate for treating the full quantity of graphite waste, they may nevertheless be useful for generating small scale feedstock for isotope separation.

2.1 Steam Reforming Process

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

$$C + H_2O \longrightarrow CO + H_2 \quad \textbf{(eq.1)}$$

The CO can be separated or the gases further oxidised with oxygen to form carbon dioxide and water. The water can then be recycled, allowing the collection of the tritium released from the graphite.

$$CO + H_2 + O_2 \longrightarrow CO_2 + H_2O \quad \textbf{(eq.2)}$$

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).

Unlike incineration in air there is no inert carrier (nitrogen) involved in the 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 [7]. This obviously allows for tight control of radionuclide release. Another advantage of steam reforming is that it can utilise the phenomenon of "roasting", which is discussed in detail in Section 2.2.

2.2 Roasting for Enhanced Radionuclide release

It has been noticed that the heating of graphite can, at least in some cases, lead to selective loss of isotopes (particularly tritium and ^{14}C) from the graphite structure [8]. This phenomenon is a result of the slight (partial) oxidation, and is worthy of study since it might be exploited as a form of partial decontamination of graphite in advance of disposal or recycle. It also represents an initial form of isotope separation but which on its own is not sufficient.

Graphite has a porous structure. A proportion of the pore volume is open, meaning that 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
- Neutron irradiation of gases in the pore volume may yield isotopes absorbed on the pore surfaces
- Species absorbed on the surface of the pores during the 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.

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.

Initially it was thought that there would 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. It might be expected that non-volatile radionuclides would be retained in the graphite matrix but it should be noted that there may be mechanisms (such as gas phase decontamination) by which these radionuclides could be released.

The loss of tritium and ^{14}C from graphite during the heating was the subject of a detailed preliminary study at FZJ [9]. The conclusions of this initial study are as might be expected, namely that a carbon fraction enriched in ^{14}C and tritium can be released by heating the graphite to about 1100°C in various atmospheres. The degree of enrichment achievable is dependent on the temperature profile and the gas composition, and more remains to be learned about the mechanism to optimise this. It seemed 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 percent of carbon lost (see Figure 2.2). This observation is confirmed by preliminary work on blocks removed from the UK GLEEP reactor [10].

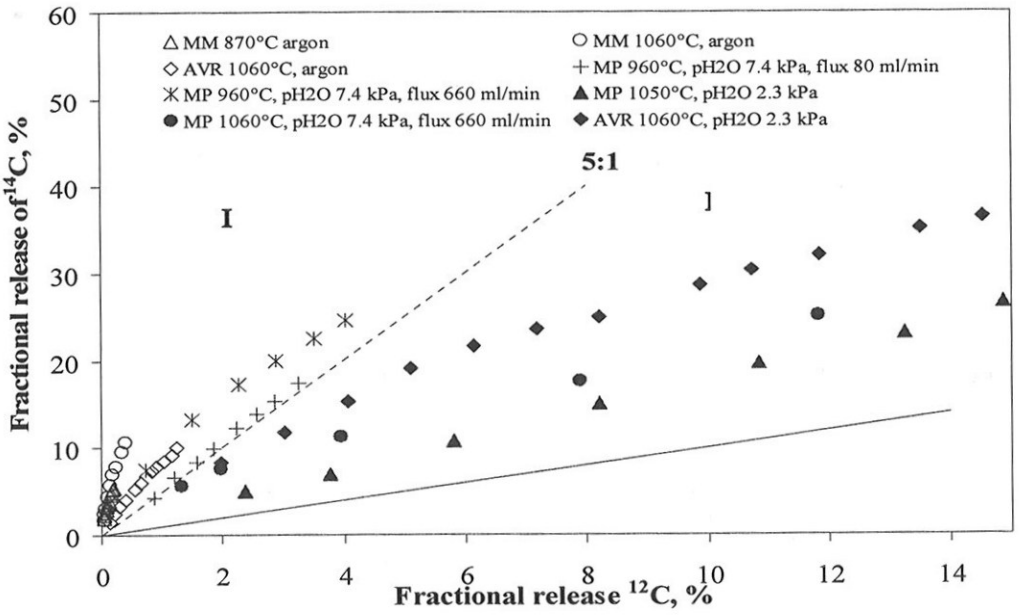

Figure 2.2 – Selective Release of Radiocarbon from Merlin and AVR Graphite[1]

However, recent supplementary work undertaken at FZJ as part of the Work Package 4 of the CARBOWASTE programme indicate that up to 79% of the ^{14}C can be released through chemical treatment with reactive gases (water steam) within a period of 3 hours, and up to 93% within 7 hours (see Figure 2.3 overleaf). It should be noted, that this result was gained from a sample of Merlin graphite, and the results gained are not necessarily representative of that of other types of nuclear graphite, such as Magnox or RBMK moderator graphite. Further work in this area is ongoing, and it is hoped that further, more comprehensive results will be available prior to completion of the project.

These significant levels of release of ^{14}C from the graphite are currently thought to be a result of two separate mechanisms. The principal one is the ^{14}C derived from ^{14}N; this is thought to reside on the surface of the graphite and within the open pore structure, and is therefore considered to be readily liberated.

The secondary source is from ^{14}C derived from ^{13}C within the graphite matrix. It is thought that a by-product of the conversion of ^{13}C to ^{14}C is 470kJ of excess energy. For completeness, it should also be mentioned that ^{14}C may also be produced from the irradiation of ^{18}O present in the CO_2 coolant gas.

There is currently some debate as to whether or not this energy is sufficient to permit the ^{14}C to move from its original lattice position. If it is sufficient, then this would go some way to explain the improved release rates ^{14}C as exhibited by FZJ's most recent experiments [11].

These recent results are indicating that through a combination of gasification (to remove the majority of radionuclides e.g.^{60}Co etc.) with an initial roasting phase (to remove the vast majority of the ^{14}C) and water retention (to remove ^{3}H); the vast proportion of activity can be removed from the majority of the gas. This significantly widens the potential opportunities for the use recycled graphite derived from carbon redeposition from the gas phase. Additionally, the concentration of ^{14}C in the gas derived from roasting phase will be high, and therefore would provide a convenient low volume feedstock to derive a pure ^{14}C product.

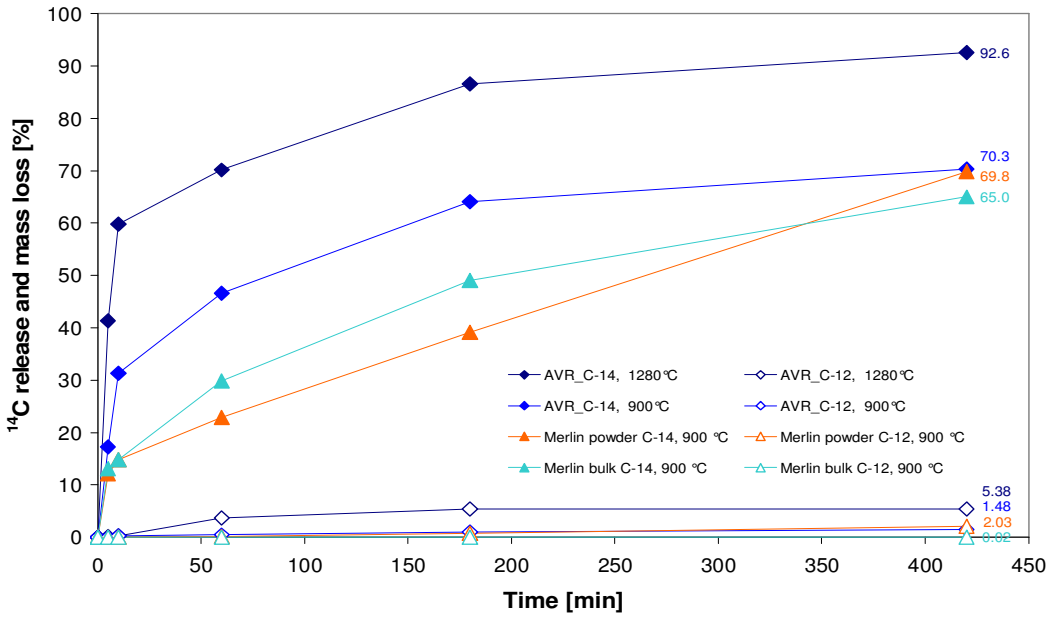

Figure 2.3 – Graph showing initial test results of C-14 release in water steam [12]

This current work by FZJ is ongoing and progress is being closely monitored due to its implications on the work being undertaken with Work Package 5 [12]. It should be noted that FZJ have patents in place covering aspects of this work.

3 Isotope Separation

Isotope separation stage of the proposed graphite management process is highlighted below (see Figure 3.1); this stage directly follows the gasification of the graphite discussed in Section 2.

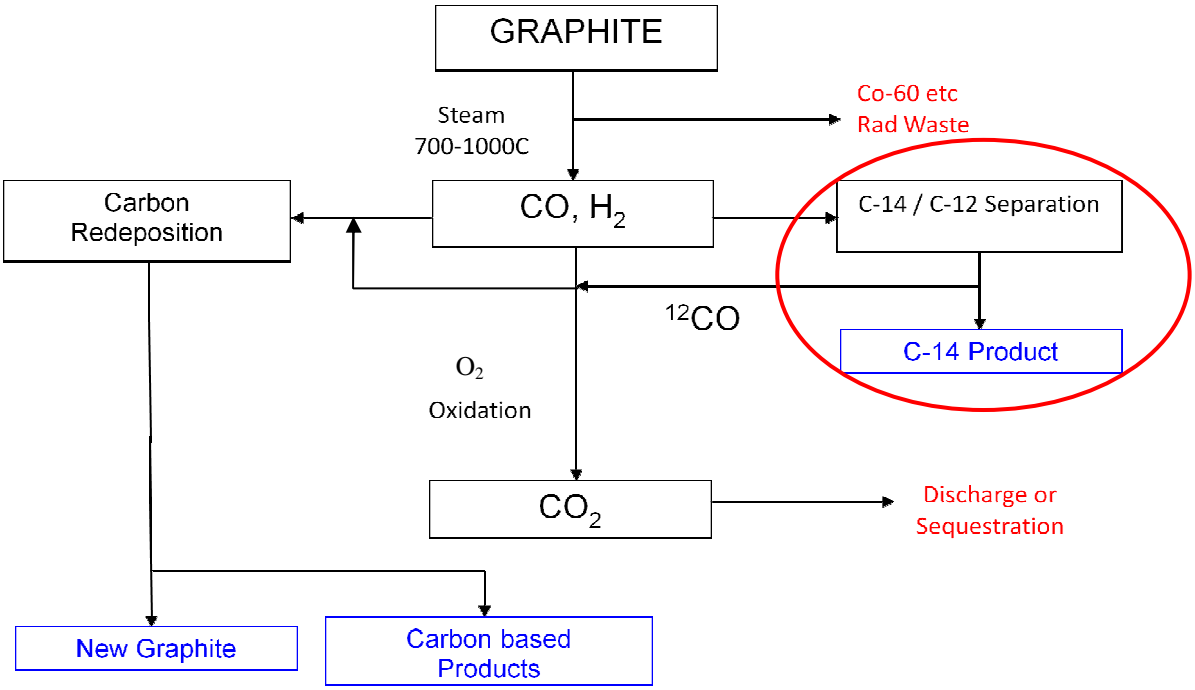

Figure 3.1 Graphite Management Plan, with Isotope Separation Phase highlighted.[1]

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

3.1 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, see Section 3.3);
- Those which rely on the small differences in thermodynamic or kinetic reaction properties of the isotopes (e.g. PSA, see Section 3.2), and
- Those which rely on properties not directly connected to atomic weight, such as nuclear resonances (e.g. SILEX see Section 3.8).

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 discussed in this section.

3.2 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 [1].

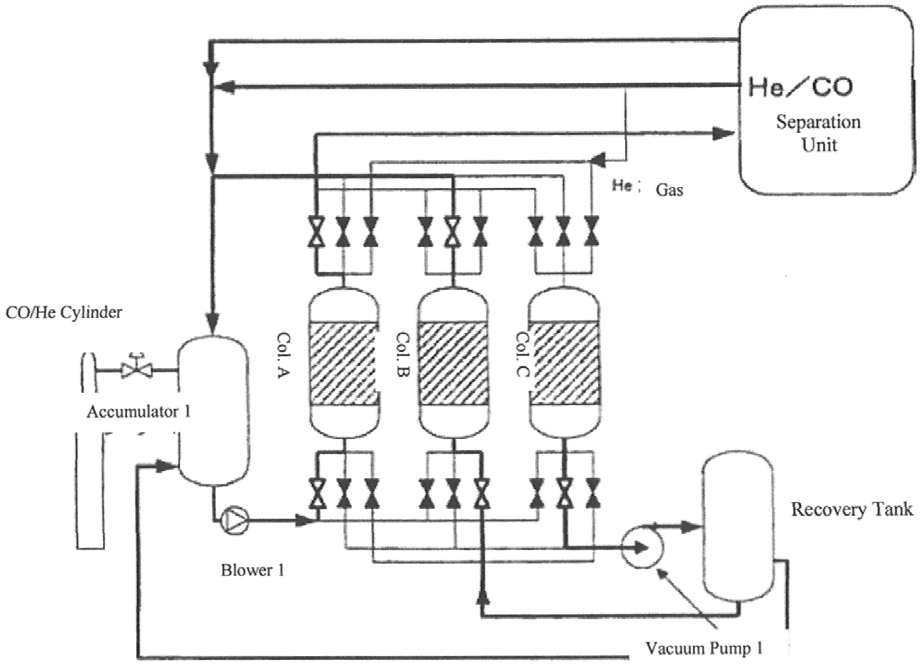

Figure 3.2 – PSA Three Column Stage Diagram[1]

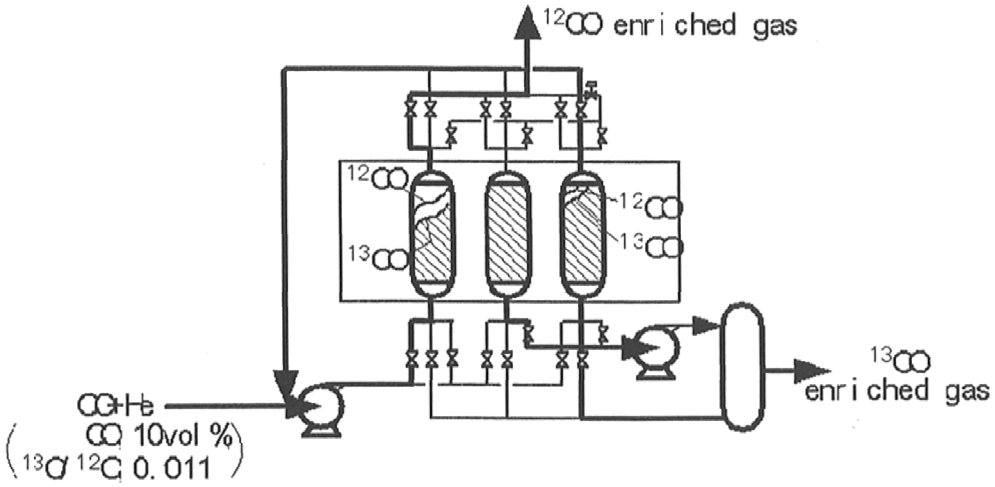

Figure 3.3 – Parallel Purge Operation of Three Column System [1]

3.2.1 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.

3.2.2 Results from the Japanese Tests

A full report of the Japanese tests is available [13], 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 [1].

3.2.3 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.

3.2.4 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 (as discussed in Section 3).

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 repects ro graphite was issued on the 18th August 2010. 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 [Yang, Eun, Lee, and Oh (2005)]. 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."

3.3 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 3.4 below).

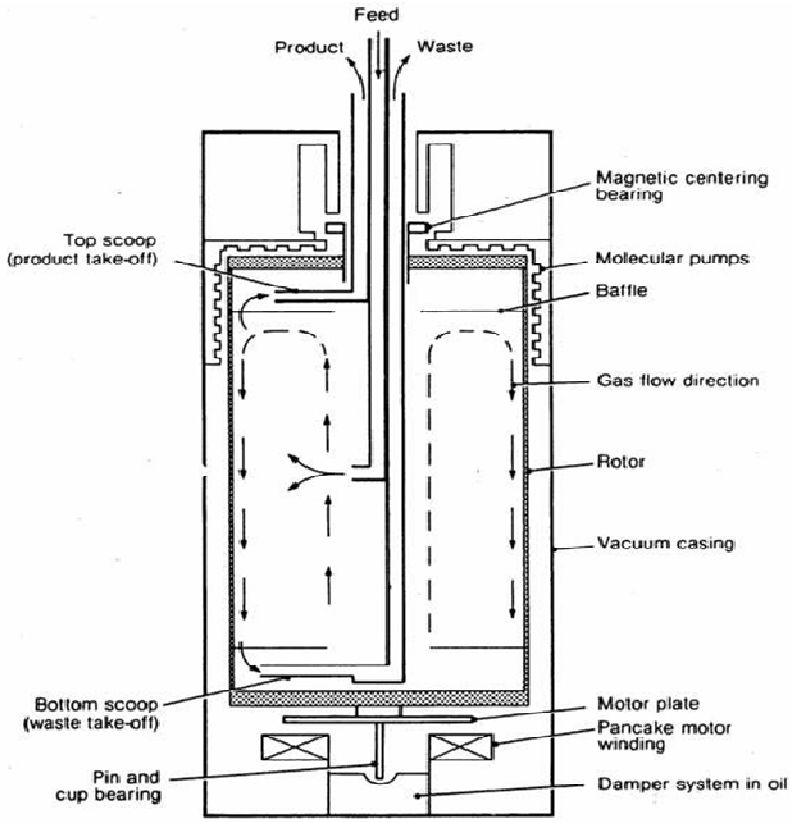

Figure 3.4 - Cross section through a Gas Centrifuge used by URENCO

The enrichment effect of a single centrifuge is small, so they are linked together by pipes into cascades (see Figure 3.5). 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 previous gaseous diffusion process (Section 3.6).

Figure 3.5 - 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.

3.3.1 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).

3.3.2 Results to date

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 3.1, below:

Table 3.1 – Table showing the results of investigation into potential process gases for carbon treatment [14]

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.'

3.4 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 [15]. 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 can not 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[16].

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 [1]. Additionally, the theoretical plateau height is much higher with amine carbamate, than with cryogenic distillation (see section 3.5), which leads to the requirement for larger columns [16, 17].

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 tones of waste. Further information on this technology may come to light through Work Package 4 of the CARBOWASTE programme.

3.5 Cryogenic Distillation

A US patent [18] 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 [16]. 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 [19]. 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.

3.6 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.

3.7 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.

3.8 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 [20].

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.

Attempts are being made to open a dialogue with SILEX in order to keep abreast of any developments pertaining to this technology and how these may relate to the isotope separation required for dealing with the removal of ^{14}C from ^{12}C and ^{13}C [20].

3.9 Isotope Separation Summary

Little information is yet available on the economics of isotope separation, 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) options described in Section 2.3, 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.

4 ^{14}C Recycle and Supply

One of the tasks (T.5.3.3) 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).

5 Conclusions

When considering the management of graphite and specifically its treatment for recycle or re-use; the potential offered by a viable isotope separation process for separating ^{14}C from ^{12}C and ^{13}C is considerable. By being able to isolate the other key radionuclides present in the i-graphite, firstly by the process of gasification (e.g. ^{60}Co, ^{55}Fe), then by scrubbing or other technologies (e.g. ^{36}Cl, ^{3}H), to leave only the issue of ^{14}C, isotope separation could be the critical last step in the development of a viable graphite management process which result in substantial waste minimization through recycle and/or reuse.

The key conclusions reached in this report are:

- 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 (upto 93%).

- 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

CANDU	CANada Deuterium Uranium
CR	Concentration Ratio
DF	Decontamination Factor
ETC	Enrichment Technology (Joint venture between URENCO and AREVA)
FZJ	Forschungszentrum Jülich
GCR	Gas-Cooled Reactor
GE	General Electric Corporation
GLE	Global Laser Enrichment
GLEEP	Graphite Low Energy Experimental Pile
GTMHR	Gas Turbine-Modular Helium Reactor
HEU	Highly Enriched Uranium
LEU	Low Enriched Uranium
NUPEC	Nuclear Power Engineering Corporation
PBMR	Pebble Bed Modular Reactor
PSA	Pressure Swing Adsorption
PWR	Pressurized Water Reactor
SILEX	Separation of Isotopes by Laser Excitation
USEC	United States Enrichment Corporation

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