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Review of Existing Experience Relevant to Recycling

Executive summary

This report is a review of existing experience relevant to the recycling of graphite. Work Package 5 is concerned with establishing ways of recycling graphite and the objectives can only be met by considering all the steps between irradiated graphite arising as waste and its supply in new products. Due to the limited experience with recycling and reusing irradiated graphite it has been decided to widen the scope of the review to include a discussion of those pathways for graphite management which hold the most potential, but require further work before they can be proven valid.

In preparing this report input was obtained from the participants of the Work Package (which is gratefully acknowledged). In particular discussions and meetings have been held during this first year of the programme with GrafTech, SGL, Studsvik, NECSA, PBMR and others.

Initially the report considers the properties of irradiated graphite in as far as they will affect the subsequent steps of recycle. The report then goes on to consider the steps necessary to prepare graphite for recycle, such as the appropriate removal (by decontamination) of radioactivity. This may involve conversion of the graphite to the gas phase and re-deposition as carbon. The potential value of “roasting” is considered, which can separate graphite into isotope-rich and isotope-lean fractions. Graphite manufacturing techniques are then considered to discuss what types of product or processes might be applicable. Other types of recycled product are then considered, including the sale of ^{14}C as a product. This option will almost certainly require separation of carbon isotopes, and the techniques for accomplishing this are discussed.

One conclusion of this report is that carbon black is a favoured intermediate for production of recycled products, although other possible intermediates, such as high molecular weight organic compounds, are not ruled out.

Out of this work a forward programme for the Work Package is developed.

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Executive Summary

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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. Avoidance of all this radioactive waste makes finding ways to recycle and reuse the graphite important, 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. It is the purpose of this review to highlight both pre-existing and potential opportunities which could be utilised for graphite recycle and reuse.

The task of achieving recycle of graphite, while being extremely important as noted above, will also be extremely difficult. 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 shutdown. 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 300,000 years. Many short-lived isotopes are also important, such as tritium (^{3}H), having a half-life of 12.3 years.

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 will be associated with recycling rather than reuse, but any opportunities identified to reuse graphite in its existing form will be included.

There are many potential uses for recycled carbon other than 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 the reactor application 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 [1]. 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 his 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 health physics 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 seems too optimistic to consider 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 introduce before the discussion which follows, and that concerns 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. There need be no concern 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 just pursuing a disposal philosophy.

There is rather 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 will be 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 [2].

Due to the limited experience with recycling and reusing irradiated graphite it has been decided to widen the scope of the review to include a discussion of those pathways for graphite management which hold the most potential, but require further work before they can be proven valid.

2 Summary of Characteristics of Irradiated Reactor Graphite

When considering the potential for graphite recycle or reuse it is important to understand the characteristics exhibited by irradiated reactor graphite as they might affect the recycle process. Graphite has particular characteristics that make it a special and difficult waste form, some examples include:

- The phenomenon of stored 'Wigner energy', which contributed to the Windscale Pile 1 accident of 1957 and which exists to a much lesser extent in the lower regions of Magnox-reactor graphite cores;
- The perceived possibilities of fire and graphite dust deflagration during dismantling of reactor cores or handling of graphite;
- Problems associated with the potential release over geological timescales of labile isotopes such as ^{14}C and ^{36}Cl;
- The presence of these isotopes together with shorter-lived isotopes such as ^{3}H and ^{60}Co may require the treatment of much of the graphite as intermediate level waste (ILW);
- The perceived destiny of graphite (in the UK at least) is stabilisation, encapsulation, containment, and deep storage of an exceedingly large volume of material. This option is extremely expensive;
- There is no long term facility available at present for the acceptance of the graphite waste.

The composition of the reactor graphite varies from reactor to reactor; it also varies slightly within a single reactor. This is mainly due to the nature of the feedstock which is input into the manufacturing process. As a result of this variation, some reactors are affected with increased levels of activation products; for example, higher than average levels of ^{60}Co present in the Heysham and Hartlepool Advanced Gas-Cooled Reactors (AGRs).

The physical, chemical and radiological characteristics of irradiated reactor graphite are now briefly considered:

2.1 Physical

The important physical and mechanical properties which are characteristic of irradiated reactor graphite and need to be understood prior to considering recycle/reuse are discussed below:

2.1.1 Wigner Energy

Wigner energy (or "stored" energy) occurs in graphite under neutron irradiation because atoms are displaced from their normal lattice positions into configurations of higher potential energy. The quantity of accumulated stored energy is a function of fast neutron flux, irradiation time, and temperature. The higher the irradiation temperature, the lower is the amount of "stored" energy. In all cases, a saturation point may be achieved in terms of the total amount of stored energy for long periods of irradiation.

Stored energy can be released if the graphite is heated above its irradiation temperature (50K above is typical to achieve a significant release rate); although a temperature in excess of 2000°C is required before all the energy can be released.

Reactors which are potentially affected by Wigner energy issues include the Hanford reactors, early Russian and Chinese production reactors and G1 in France. In Soviet-designed Reaktor Bolshoy Moshchnosti Kanalniy (RBMK) reactors, a small amount of graphite in contact with cool water tubes in control and instrumentation channels is operated at a sufficiently low temperature to accumulate significant Wigner energy [3].

2.1.2 Dimensional Changes

Nuclear graphite components are polycrystalline in nature and their physical irradiation property changes are dominated by irradiation-induced changes to the graphite crystallites. The effect of irradiation on the crystallites is to expand in one direction and shrink, to a lesser extent, in the other direction. The consequence of this crystal dimensional change on the polycrystalline graphite component is critically dependant on the manufacturing route and the irradiation temperature.

Many components were manufactured by extrusion. This leads to large differences in both the non-irradiated and irradiated properties parallel and perpendicular to the extrusion direction. These highly anisotropic graphites have been used in all of the early graphite-moderated reactors. Other later graphites are moulded and manufactured from special cokes and as a result are much more isotropic in nature.

At low temperatures (less than 300°C) most anisotropic graphite shrinks with irradiation parallel to the extrusion direction and expands in the perpendicular direction. At higher temperatures (above 300°C) anisotropic graphites shrink in both directions. Isotropic and near-isotropic graphites generally initially exhibit shrinkage in all dimensions under all irradiation conditions [3].

2.1.3 Modulus and Strength

Irradiation-induced changes significantly modify both the modulus and strength of nuclear graphite. These changes have implications related to core removal, treatment and disposal of graphite waste.

Non-irradiated graphite has a non-linear stress-strain characteristic with significant hysteresis. However, a small irradiation dose leads to a much more linear stress-strain characteristic and a significant increase in modulus. With increased irradiation the modulus further increases until at very high doses the graphite structure starts to degenerate and the modulus falls significantly. The initial increase in modulus is accompanied by an increase in strength, which with continued irradiation follows a similar pattern to the modulus until the graphite degenerates at very high doses. Thermal and radiolytic oxidation also reduces the modulus and strength [3].

2.1.4 Thermal Conductivity

When considering radioactive waste disposal, particularly in deep geological formations, the thermal conductivity of the graphite waste is an important factor, since a small amount of fast neutron damage significantly decreases the thermal conductivity of graphite. With increased irradiation flux (fluence rate) the thermal conductivity remains at the low value until, at high doses, the structure of the graphite starts to

degenerate. There is then another significant decrease in thermal conductivity. Values as low as 2 or 3 W.m-1.K-1 compared with non-irradiated values of around 100–200 W.m-1.K-1 can be achieved in graphite irradiated at low temperatures. Thermal and radiolytic oxidation also reduces the thermal conductivity of graphite as an exponential function of weight loss [2].

2.1.5 Other Properties

The coefficient of thermal expansion and the electrical properties, including electric resistance, are also changed by irradiation. However, fast neutron irradiation, or moderate radiolytic oxidation, does not markedly change the specific heat capacity.

During reactor operation these changes in the physical and mechanical properties lead to brick stresses which eventually can lead to brick failure. [3].

2.2 Chemical

Graphite is a material of low chemical reactivity and generally benign properties. Graphite has been demonstrated to be innocuous under extreme conditions, such as in projector-lamp arcs, electric motor brushes, electrodes withdrawn from arc furnaces at temperatures in excess of 3000°C, components in space vehicles re-entering the atmosphere, and in the use of graphite-fibre reinforcements in, for example, jet engines.

2.2.1 Oxidation of Bulk Graphite

Chemical reaction in graphite takes place only with extremely powerful reagents. Considering aspects related to safe-storage of graphite cores and eventual decommissioning and disposal, the most relevant oxidation reaction in solution which could conceivably occur during storage in moist air in a radiation field — i.e. with the graphite remaining in an air-filled reactor vessel — is with nitric acid. However, in practice, the nitric acid concentrations attainable are orders of magnitude below those which could give rise to exfoliation reactions and structural collapse in the graphite. The reaction is inconceivably slow under storage conditions (either in the reactor vessel

or subsequently in a separate storage facility), and the most likely impurities (oxygen and water vapour) are known to inhibit the reaction as does prior irradiation.

Oxidation of graphite by water vapour is minimal below 1000°C unless a catalyst is present and, even then, no significant reaction has been reported below 400°C. The presence of water may, however, influence the behaviour of catalysts with respect to oxidation of graphite in air.

Measured oxidation rates in irradiated graphite are found also to be elevated as a consequence of modest amounts of inorganic catalysts. The effect of such catalysts is to increase the graphite-oxidation rate above its normal value at any particular temperature. The most potent catalysts are transition-metal compounds and compounds of elements (such as lead), where there is a possibility of transfer between two oxidation states in the metal oxide. Mild catalysts (alkali and alkaline earth compounds) are present in most graphite irradiated in UK reactors but in no case has reactivity in air risen beyond the limits imposed by a successful safety case for accidental air ingress.

Graphite cores irradiated in carbon-dioxide-based coolants will also include a proportion of more chemically reactive deposit carbonaceous materials. These tend to be associated with localised areas on the geometrical surfaces of components (e.g. the lower temperature end of fuel and interstitial channels in which there is a gas flow); they derive from radiolysis of carbon monoxide (which is itself produced by radiolytic oxidation of graphite by the carbon dioxide) to form polymeric materials with a variable oxygen content. Localised concentrations of up to 3% by weight have been found in Magnox reactors.

A related higher-reactivity material, essentially paracyanogen, is found on graphite which has been irradiated while under a nitrogenous cover gas such as in the CANDU annulus-gas space. In this case, the carbon source in the deposit is from $^{14}N_2$ after neutron irradiation, and is essentially entirely ^{14}C, which needs to be borne in mind when decommissioning [3]. It is also believed to be the case that ^{14}C produced from impurity $^{14}N_2$ in the coolants of carbon-dioxide-cooled reactors will result in

concentration of ^{14}C in the carbon deposits on internal pore and geometric surfaces of graphite components: it should be noted however than an EdF theoretical analysis of source terms in UNGG reactors leads, at the present time, to an alternative view.
Two types of oxidation need to be considered, radiolytic and thermal; these are discussed below:

2.2.2.1 Radiolytic Oxidation

Fast neutron irradiation and radiolytic oxidation radically change the physical and mechanical properties of nuclear graphite. In reactors where the graphite operates in an inert atmosphere, such as the light water graphite moderated reactors (LWGR), or the high temperature helium cooled reactors (HTR), radiolytic oxidation is not an issue. However, in gas or air-cooled reactors extensive radiolytic oxidation can take place. For example, French Magnox reactor Bugey 1 has parts of the core which had reached 35% weight loss at the end of life and similar graphite weight losses are now being encountered in some of the UK Magnox and AGR reactors.

Radiolytic oxidation takes place within the accessible graphite pores and does not preferentially attack the graphite component surface. For this reason the component's shape and size will not be greatly affected by radiolytic oxidation during the operational life [3].

2.2.2.2 Thermal Oxidation

Thermal oxidation is only likely to be of concern in reactors, where accidents have occurred. For example, in the fire-affected zone of the Windscale Piles the thermal oxidation is known to have increased the channel size and weakened some of the components. As an example, there are visible penetrations between certain horizontal fuel channels and vertical shut-down-rod channels [3].

2.2.2 Graphite Dust Deflagration

Graphite dust must be distinguished from other impure carbonaceous dusts (like coal dust) which are easily explosible. Whereas there has never been a recorded dust explosion in a graphite manufacturing or machining plant, dust explosions in coal mines have been relatively common. Nuclear graphite dusts are found to be much less reactive, and it is a combination of chemical purity (lack of volatile content) and particle size, which is primarily responsible for the difference in behaviour between graphite dust and other impure carbonaceous dusts.

Nevertheless, this may not be the case of reactor graphite in the presence of large amounts of stored (Wigner) energy. In the UK, when planning the decommissioning of the Windscale Piles, the question of the explosivity of impure graphite dust containing stored energy, and its relevance for graphite-handling operations during reactor decommissioning and subsequent graphite storage or disposal, arose.

The criteria which must be simultaneously satisfied if a dust explosion/deflagration is to result are:

- The dust must be combustible;
- The dust must be airborne, implying a need for a turbulent gas flow or some mechanical action producing levitation;
- The particle size must be optimized for flame propagation;
- The dust concentration must fall within an explosible range (i.e. neither too high or too low);
- An ignition source of sufficient energy to initiate flame propagation must be in contact with the dust suspension; (the use of thermal cutting devices should be avoided);
- The atmosphere in which the dust is suspended must contain sufficient oxygen to support combustion.

Additional factors which also have an effect are moisture content, hybrid mixtures with flammable gases (e.g. use of cutting devices in the dust laden environment) and impurities (e.g. organic matter producing volatiles) [4]

2.2.3 Galvanic Corrosion

Graphite may react electrochemically with other materials. Acting like a “noble” metal, graphite can promote accelerated corrosion of other metals by electrical (galvanic) coupling, in which local electrolytic cells driven by potential differences lead to increased dissolution and oxidation of less noble metals. Graphite is more electronegative even than stainless steel, so that direct contact between graphite wastes and stainless steel containers can lead to premature penetration and loss of integrity. Experimental studies have shown that corrosion rates can be increased by factors of up to ten. A number of preventative measures have been identified, including use of cement grouts and baskets to isolate graphite from stainless steel waste containers [3].

2.3 Radiological

The nuclear graphite in most reactors will have been exposed to very high flounce (up to 5 x 10^{22} n/cm2) and has a significant radionuclide content arising both from the activation of impurities in the original graphite and from material transported from other parts of the reactor circuit (e.g. steel-oxidation products) which has also become activated and is held on or within the graphite components. Before disposal of the graphite, the radionuclide content must be estimated in order to determine the most appropriate disposal route.

Depending on the graphite source (moderator, reflector or fuel-element components), different quantities of relatively long-lived radionuclides may be present — mainly ^{14}C and ^{36}Cl after a short decay time. Isotopes arising from other sources, such as corrosion products and lesser impurities, include ^{3}H, ^{60}Co, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{110m}Ag, and ^{109}Cd. In addition to these, quantities of fission products (^{90}Sr, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{113m}Cd, ^{121m}Sn, ^{129}I, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{147}Pm, ^{151}Sm, $^{152, 154, 155}Eu$, etc.), as well as some uranium and transuranium elements (mainly ^{238}Pu, ^{239}Pu , ^{240}Pu, ^{241}Pu, ^{241}Am, ^{243}Am, ^{242}Cm, ^{243}Cm and ^{244}Cm), will arise as a result of fuel failures during operation of the

reactor, or just from traces of uranium carried into the core on fuel-element surfaces after fabrication [5]

It should be stated that there is considerable variation in the radiological inventory of the graphite's between reactors, one such example is the variation in ^{60}Co activity between the first and second generation of British reactors. The graphite from the second generation reactors (AGR's) was given a revised specification which allowed an *increase* in impurity cobalt to that which was present in the first generation graphite reactors, and which has resulted in severe difficulties in handling even small quantities of graphite present in containers of monitoring samples due to the elevated activity levels derived from the increased concentrations of ^{60}Co.

Another issue which has arisen is due to the use of either chlorine gas or freons in the purification process to remove certain metallic impurities as their volatile chlorides, leading to residual ^{36}Cl contamination. This isotope has an extremely long half life, and this means that the graphite must have multiple safety barriers against diffusion and leaching if it is subjected to repository disposal

2.4 Summary of Relevance of These Properties to Recycle

The irradiation of graphite in reactor cores changes the properties of the graphite markedly as described above. Most of the properties described above are more relevant to behaviour of graphite during the early stages of a recycle operation (such as retrieval from the reactor or pre-processing) rather than in the later stages which lead to an end product. Some, such as the reduction in thermal conductivity due to irradiation, may actually enhance the processing by gasification. Gasification and re-deposition of carbon may be seen as a particularly valuable processing step not only for the decontamination which it affords, but also for the removal of concerns about many of the other issues such as Wigner Energy.

3 Preparing Graphite for Recycle

There are several stages required when preparing graphite for recycle. These will include at least some of the following:

- Good radiological characterisation of the graphite is required prior to removal from the reactor core
- Graphite extraction from the reactor core
- Size reduction of the graphite into a suitable form (i.e. particulate) for further processing
- Decontamination of the graphite without gasification, or
- Gasification of the graphite with or without the addition of a 'roasting' phase
- Carbon deposition after gasification via the Sabatier/Bosch Reactions
- Carbon isotope separation e.g. Pressure Swing Absorption (PSA)

These stages are discussed in more detail over the following pages.

3.1 Radiological Characterisation of the Graphite

A good radiological characterisation of the graphite waste is needed before proceeding with treatment or conditioning. The characterisation of radioactive graphite is complex due to many variables between nuclear plants. Not only is nuclear graphite sourced from a variety of locations; other variables such as operational lifetimes, reactor assembly, core temperature, fuel, coolant composition and shut down periods must be considered.

Throughout the life of many nuclear reactors (although this is not the case for all reactors), extensive sampling and measurement of graphite has taken place in order to substantiate the continued operation of the reactors. When considering the Magnox fleet of reactors in the UK for example, good data exists on the physical, mechanical and chemical characteristics of graphite and its evolution through reactor life; however there is little information to hand on the isotopic content of the graphite. Isotopic content is however a key parameter in graphite management and disposal.

Significant work is being undertaken by both operators of the various reactors and academic organisations in attempting to accurately model and define the changes to the graphite reactors both structurally and isotopically. It is critical when considering the potential for recycle and reuse of reactor graphite that the radiological content is fully understood so that appropriate processing stages can be developed to separate the radiological inventory in a safe and controlled manner.

Characterisation is covered fully in CARBOWASTE Work package 3.

3.2 Options for Graphite Extraction from Reactor Core

The retrieval of the graphite from the reactor core is the first stage in preparing the graphite for recycle. As a result of its residence time in the reactor core the physical and mechanical properties of the core may have significantly changed during operation. Stresses will have developed in the fuel channel bricks, which in a few extreme cases may have lead to a significant amount of failed components. Irradiation growth and shrinkage may have lead to significant channel degradation or even to whole core deformation.

Specific reactor decommissioning experience suggests the process of graphite removal is undertaken in two alternative operational conditions, which are:

- **Dry removal** – undertaken in air e.g.Windscale Advance Gas-Cooled Reactor (WAGR), Graphite Low Energy Experimental Pile (GLEEP) in UK or perhaps with an inert gas.
- **Wet removal** – undertaken with the reactor flooded (e.g. Fort St Vrain, French proposals for the later UNGG plant.

The preferred methodology for core removal will strongly depend on the characteristics of the core design, the general geometry and construction of the nuclear reactor containment, supporting facilities available on site, the timing of the operation and the radiological environment. The current methodology generally anticipated for the retrieval of the graphite from the reactor cores relies on the graphite being removed

brick by brick. This is a difficult and expensive process as the reactor is required to be "opened up" to allow for the removal of the large graphite blocks.

The retrieval of graphite from reactor cores is addressed in Work Package 2 and therefore it is not deemed appropriate to cover this area in detail within this report. It should be noted that novel methods for graphite retrieval are being considered outside of the scope of CARBOWASTE, although these have yet to be fully developed or trialled [6].

3.3 Size Reduction

Preparative treatments of graphite prior to processing should be kept to a minimum, since such treatments will add to the cost and operational radiation exposure associated with the processing of graphite.

Size reduction may be a necessary preparative treatment. Size reduction of graphite poses some problems arising from its properties as a lubricant and its potential for dust formation. Size reduction by conventional apparatus can however be achieved without difficulty in preparing the graphite for the gasification phase. The preferred method used to date is wet grinding of the graphite to sizes of less than 1cm.

When considering HTR reactors, an additional phase of pre-processing must be considered, namely the separation of fuel kernels from the graphite compacts. It has been found that the application of electrical pulses to graphite compacts can efficiently lead to disintegration of the compacts and separation of the fuel kernels.

3.4 Decontamination without Gasification

In principle, the simplest method of recycling graphite is to re-form new graphite from old without any intervening chemical transformation. Graphite manufacturers sometimes incorporate some scrap graphite in to their production processes already as a finely-ground flour in the initial coke-pitch mix (see Section 4). The advantage of this option is simplicity, but it is likely to be of rather limited use, because there is no opportunity for significant decontamination of the graphite before recycle, and the

products that can be formed this way may not have suitable properties for many applications.

The major limitation on decontamination of irradiated graphite without the use of the gasification process is its neutron activation and hence the presence of radioactivity throughout the structure. This means that whilst activity can be removed from the graphite surface (and the surface of open pores); activity is still retained in the remaining structure. This would result in a graphite product which has a reduced radioactive inventory, but which is still active and therefore in a form which may only be of limited use [7].

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.

3.5 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 radionuclide's other than ^{14}C. In any scenario for gasification of graphite, the intention is to retain the radioactivity in solid form for disposal as radioactive waste, whilst further processing of the synthesis gas through methods such as isotope separation prior to re-deposition of solid carbon subsequent addition as a raw material into the manufacturing of recycled graphite.

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

(1)

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

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

(2)

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

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

Reaction of graphite with pure oxygen achieves the same overall result as reactions 1 & 2 above. Unlike incineration in air there is no inert carrier (e.g. nitrogen) involved in either process, so the process can take place more or less in an enclosed system, if so desired. With liquefaction of carbon dioxide or reversal of gasification by the Sabatier or Bosch reactions (see Section 3.7) there need not necessarily be any release of gas to atmosphere as a result of the process. This obviously allows for tight control of radionuclide release.

The first (optional) step of the thermal treatment would be to raise the temperature of the graphite to 400 to 1000°C and roast at that temperature to allow the volatile gaseous radioactive materials on the surface of pores of the graphite matrix, predominately ^{14}C, ^{3}H and ^{36}Cl, to migrate out of the graphite in a low volume gas stream. The ^{3}H and ^{36}Cl would be removed through condensation and wet scrubbing of the process off gases with a chilled water solution. This process, 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 [7, 8, 9].

Figure 1 below is a basic flowchart which details the potential routes from graphite gasification though to recycled graphite/carbon product.

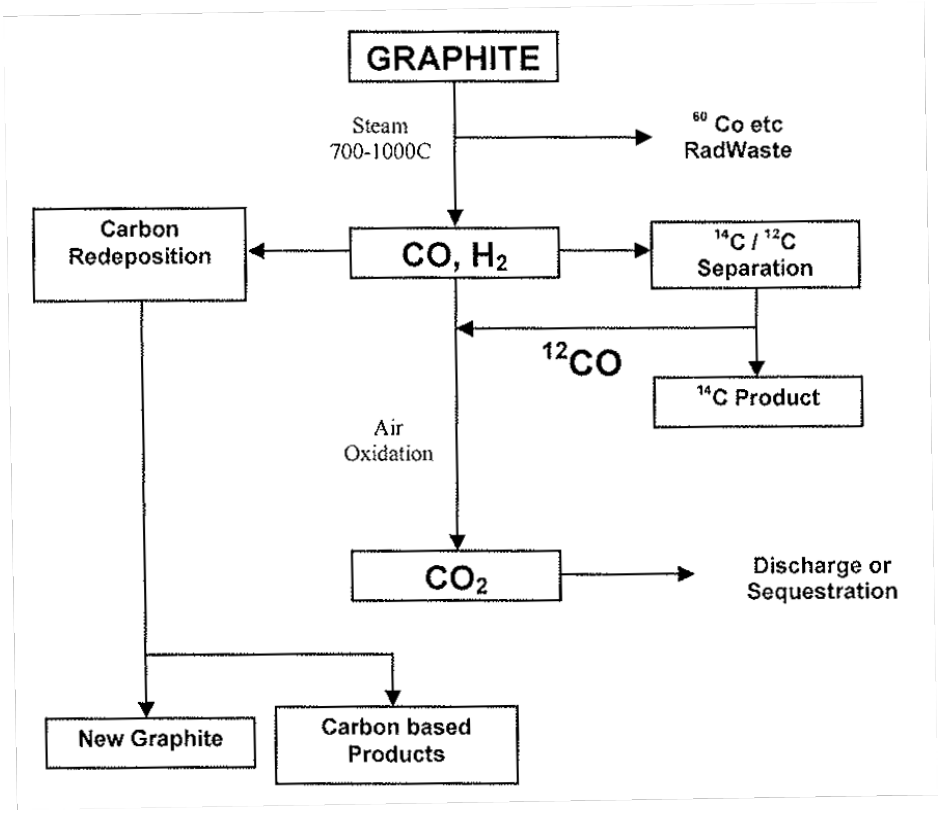

Figure 1 - Flowchart detailing routes from graphite gasification to recycled product. [10]

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 thee 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 [11]. ^{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.

3.6 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 [12]. 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 pure ^{14}C for use by the medical industry as a radiological medicine (discussed further in section 6).

3.7 Carbon deposition following gasification

The off-gas (synthesis gas or syngas) produced through the gasification process (discussed in 3.5) 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. Discussion has taken place with graphite manufacturers on the feasibility of introducing the powdered carbon as a component of the manufacturing process of new graphite (see later).

The use of the Sabatier and Bosch reactions are wide ranging in terms of their actual and potential applications. For example the Sabatier and Bosch reactions have been

studied as a way to remove carbon dioxide and to generate clean water aboard space stations.

The Bosch reaction is also being investigated for use in maintaining space station life support. Though the Bosch reaction would present a completely closed hydrogen and oxygen cycle which only produces atomic carbon as waste, difficulties maintaining its higher required temperature and properly handling carbon deposits mean significantly more research will be required before a Bosch reactor could become a reality. One problem is that the production of elemental carbon tends to foul the catalyst's surface, which is detrimental to the reaction's efficiency.

The Sabatier reaction has been proposed as a key step in reducing the cost of manned exploration of Mars (Mars Direct) through In-Situ Resource Utilization [12, 13]

3.8 Carbon Isotope Separation

It has been established above that (through gasification and re-deposition) it is possible to produce carbon from irradiated graphite with very efficient decontamination from all isotopes other than ^{14}C. Special additional processing will be required to separate ^{14}C from ^{12}C, other than that achieved through the roasting process described above.

The cost and complexity of an isotope separation process is such that it is most unlikely ever to be applied to the full quantity of graphite waste arising. There are arguments which suggest that such an objective is not even desirable, even if it were achievable. In disposal sites greater radiological safety is achieved by reducing the specific activity of ^{14}C, not by increasing it. Hence there is no point in concentrating ^{14}C by isotope separation only to dispose of the resulting concentrated product – to do so only increases the potential for radiological consequences if the carbon leaks out of the site.

Isotope separation may, however, be very useful for one of two purposes: producing a very small quantity of isotopically pure ^{14}C for recycle as a product or producing a small amount of carbon from waste graphite at sufficiently low specific activity to enable its use in a particular recycle route. In both cases the isotope separation process is likely to be applied on a relatively small scale.

There are various isotope separation technologies which have the potential to separate the isotopes of ^{12}C and ^{14}C, such as Pressure Swing Absorption, Cryogenic Distillation and Gas Centrifuge. These technologies are discussed in more detail below:

3.8.1 Pressure Swing Absorption

Pressure Swing Absorption (PSA) for carbon isotope separation was initially developed for the separation of ^{13}C from ^{12}C. 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. 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.

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 hydrotreating and hydrocracking 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 geosequestration, 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.

3.8.2 Cryogenic Distillation

A US patent [15] 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. 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 [15]. 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.

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

3.8.3 Amine Carbamate

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 [16]. Although this type of system appears to have been studied quite extensively since the 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 to be somewhat slow.

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

3.8.4 Gas Centrifuge

URENCO has indicated that it is interested in developing a gas centrifuge alternative for carbon isotope separation [17]. A gas centrifuge (or also gas ultra centrifuge) is a machine which physical separates different heavy gases with the help of the centrifugal energy.

This process has been used for uranium enrichment, by separating uranium hexafluoride gas with higher portion of ^{238}U from that containing a higher portion of ^{235}U on the other side. This physical separation of the isotopes by this method is necessary as their chemical characteristics are identical and therefore chemical procedures cannot be effectively utilised in the separation of these isotopes.

Further information on this technology may come to light through Work Package 4 of the CARBOWASTE programme, specifically Task 4.2.

3.8.5 Thermal Diffusion

Thermal diffusion is another potential technology: this requires significant energy input, however at present the efficiency of the process is unclear.

If a temperature difference is applied to a uniform mixture of two gases, the mixture will partially separate into its components, with the heavier, larger molecules usually (but not invariably) concentrating at the lower temperature. Thermal diffusion can be used to separate isotopes. The amount of separation for any reasonable temperature difference is quite small for isotopes, but the effect can be amplified by combining it with slow thermal convection.

This is likely to be considered in more detail under Work Package 4 of the Carbowaste programme.

3.8.6 Microbial Isotope Enrichment

Graphite decontamination by microbiological treatment is an option being developed in the Republic of South Africa (RSA). Nature has evolved micro-organisms that survive in extreme environments which include micro-organisms acclimated to radioactive environments. An example of radiation resistance in micro-organisms is demonstrated in *Deinococcus radiodurans*, which has been studied extensively with radiation doses up to 5000 times higher that the lethal dose to humans. Additionally, some micro-organisms have been shown to carry out biotransformation and detoxification of several organic and inorganic pollutants. This technology is aimed at reducing the volume of nuclear waste in order to allow full recycling of contaminated graphite for possible reuse in new reactor applications, but which could potentially also be utilised in decommissioning the current fleet of post generation reactors.

To date, some microbiological selectivity in uptake of carbon isotopes has been reported and it is the scope of Task 4.4 of the Carbowaste programme to consider this potential option is more detail.

3.8.7 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.

3.9 Discussion of Desirable Intermediates for Graphite Recycle

Initial discussions have been 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 have indicated that they have a preference for carbon black (see below), since this can most readily be produced from gasification routes. Although both manufacturers have considerable experience of incorporating non-radioactive graphite in products, they are concerned about the practicality of working with un-decontaminated graphite itself.

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

4 Graphite Manufacturing Processes, and Adaptation for Recycle

The manufacturing process of both new graphite and that produced in part from recycled graphite is almost identical, with the notable exception being that concerning the mitigation against the radiological aspects of recycled graphite such as ^{14}C (see Section 4.7). The manufacture of graphite is discussed in detail throughout this section, with comments made as to where potential exists to incorporate recycled graphite into the manufacturing process.

4.1 Raw Materials

The raw materials used for the manufacture of synthetic graphite are discussed below,

4.1.1 Petroleum Coke

Petroleum Coke (often abbreviated petcoke) is a carbonaceous solid derived from oil refinery coker units or other cracking processes. Calcined petroleum coke (CPC) is manufactured by heating green coke to approximately 1300-1400 C in a rotary kiln. This affects the removal of virtually all residual hydrocarbons and moisture. The final calcined product contains only a trace of volatile matter, and 0.3-6% sulphur, depending on the petroleum base used to make the coke. Calcined and green petroleum cokes are inherently low in ash constituents. The fixed carbon content of most calcined petroleum coke products ranges from approximately 97-99.5%.
Through discussions with the GrafTech it has been confirmed that they have experience of adding both graphite and lampblack to the coke mixing stage of the graphite manufacturing process. It has been agreed in principal that a substitute derived in part from recycled graphite could used in place of the petroleum coke. This would require further work and trials to demonstrate if this could work in reality.

4.1.2 Pitch Coke

Pitch coke is a high purity carbon residue manufactured by the destructive distillation (coking) of coal tar pitch. Coal tar pitch is a by-product resulting from the thermal distillation of bituminous coal. Because it is condensed from the gas phase, coal tar

pitch is inherently low in ash and other mineral impurities. Therefore, the resultant coke is low in impurities.

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

Gilsonite, an asphalt naturally occurring coke which is mined in the USA is also used in the manufacture of some nuclear graphite. The graphite's produced with Gilsonite tend to be isotropic, with higher density and strength, and lower porosities and radiolytic oxidation rates compared to equivalent graphites. The key microstructural feature of graphites produced using Gilsonite is the "onion skin" structure exhibited by the coke particles.

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

4.1.3 Carbon Black

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

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

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

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

4.1.4 Natural Graphite

Naturally occurring graphite exists in 3 main forms:

4.1.4.1 Flake graphite

This occurs mostly in metamorphic rocks (rocks that changed into another kind of rock as a result of heating and pressure by adjacent igneous material) in form of small flat particles (flakes) of different sizes: from fine (50 µm diameter, 1 µm thick) to large (800 µm diameter, 150 µm thick). Due to the high degree of crystalline perfection of their structure graphite flakes have the values of the density, electrical conductivity and thermal conductivity close to the theoretical maximum. Flake graphite possesses excellent compacting properties (low spring-back). Flake graphite contains 90-95% of carbon. Suppliers of flake graphite are China, Brazil, Canada, Norway, Madagascar, Ukraine, and Zimbabwe.

4.1.4.2 *Vein graphite (crystalline lump graphite)*

This occurs as filling fissure (cracks in rocks) in veins in metamorphic or igneous (formed from molten magma or lava) rocks. Vein graphite may have various forms and dimensions from fine powder to lumps of 10 cm size. Vein graphite structure has high crystallinity, which provides excellent electrical conductivity of the material. A supplier of vein graphite is Sri Lanka.

4.1.4.3 Microcrystalline (cryptocrystalline) graphite

Microcrystalline graphite (commercially called “amorphous”) occurs in metamorphic anthracite coal beds or in carbonaceous sedimentary rocks in form of extremely fine crystalline grains. Suppliers of microcrystalline (“amorphous”) graphite are China, Mexico, Korea, and Zimbabwe.

4.1.5 Secondary Synthetic Graphite Scrap

This is recovered from machining operations of graphite parts, graphite scrap, defective and broken graphite details. Secondary synthetic graphite has lower crystallinity and lower purity than primary product.

The potential exists to incorporate some of the graphite from the reactors in place of the secondary synthetic graphite as a raw material for production of new graphite. The main issue to consider here would be the activity contained in the graphite

4.2 Powder Preparation

This is a 3 stage process (shown in Fig 2 below) which consists of:

- Pulverising of raw materials; ground in crushers and ball mills
- Conditioning / Screening of the resulting power to the required PSD (particle size distribution).
- Blending with a 'binder' such as coal tar pitch, petroleum or synthetic pitch.

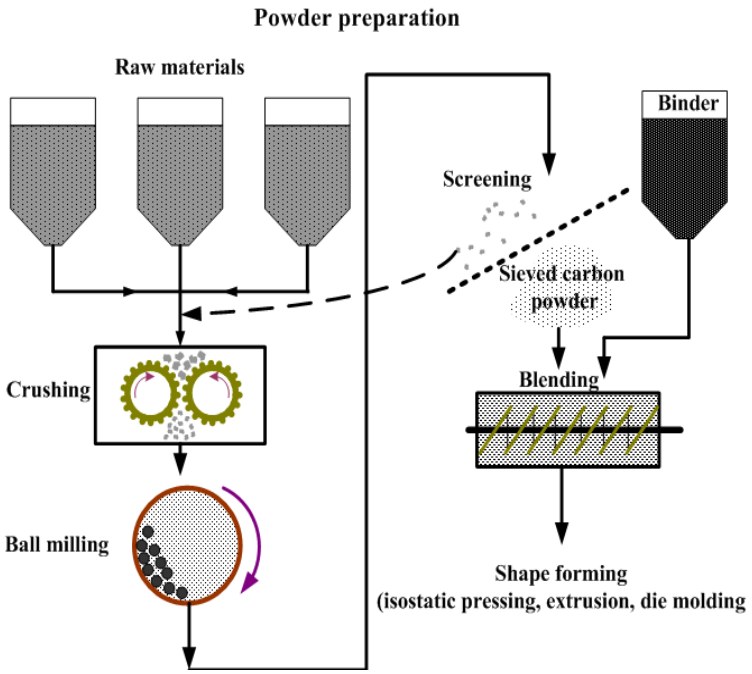

Fig 2 – Diagram showing the stages of Powder Preparation for Graphite [19]

4.3 Shape Forming

Once the carbon powder has been mixed with the binder it is compacted using one of the following shape forming techniques:

4.3.1 Extrusion

This is the shaping of the powder mixture by forcing it through a die with an opening (see Fig 4). Extrusion results in a long product (rods, bars, long plates, pipes) of regular cross-section, which may be cut into pieces of required length. Extrusion uses a rather "plastic", so called "green mix". It consists of granular particles and fine powder with pitch binder. Extruded graphite materials are isotropic (properties in the extrusion direction differ from the properties in other directions).

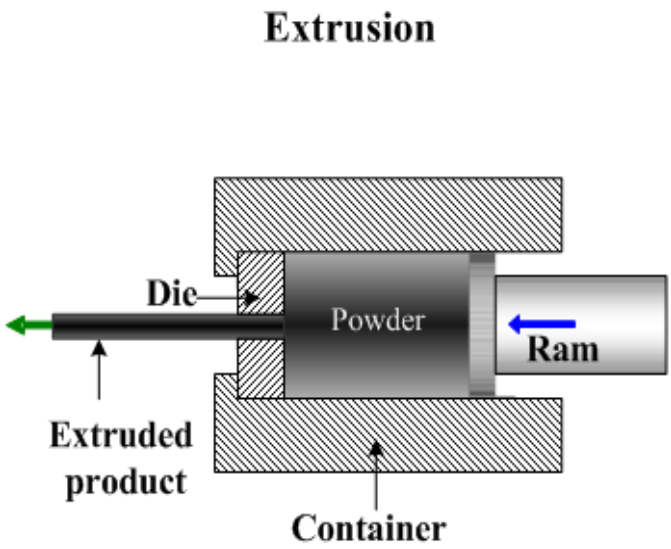

Figure 3 - Diagram showing the Process of Extrusion [19]

4.3.2 Die Molding (Pressing)

This is the powder compaction method involving uniaxial pressure applied to the powder placed in a die between two rigid punches(see Fig 5) Uniaxial die molding is effectively used for mass production of simple parts (alternative method is isostatic pressing).

The die molding process consists of:

i) **Die filling** – At this stage a controlled amount of powder in fed into the die cavity.

ii) **Compaction** – Upper punch moves down and presses the powder at room or elevated temperature with a predetermined pressure. The pressure varies between 10,000 psi to 120,000 psi (69 MPa to 830 MPa).

iii) **"Green" compact part ejection and removal** ("green" compact – shaped powder) – The pressing cycle repeats 400 to 5000 times/hour, depending on the press type, powder filling properties and the part size and geometry. Hydraulic and mechanical presses with load up to 750 tonnes are used for the powder die pressing.

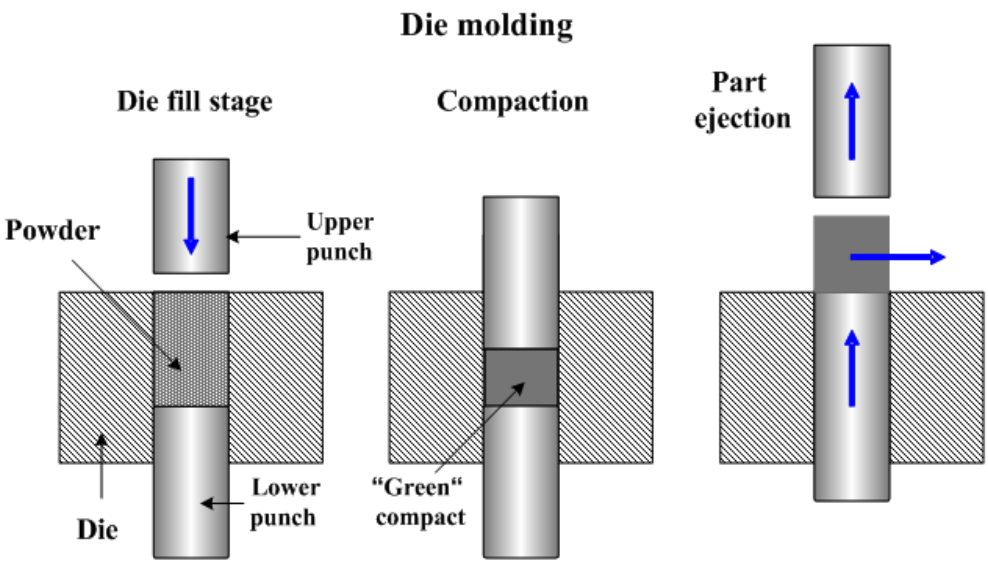

Figure 4 - Diagram showing the die molding process [19]

4.3.3 Cold Isostatic Pressing

Powder compaction method conducted at room temperature and involving applying pressure from multiple directions through a liquid medium surrounding the compacting part.(See Fig 3) A flexible (commonly polyurethane) mould immersed in a pressurised liquid medium (commonly water) is used in the cold isostatic pressing method. Materials with uniform anisotropic structure are prepared this way [19].

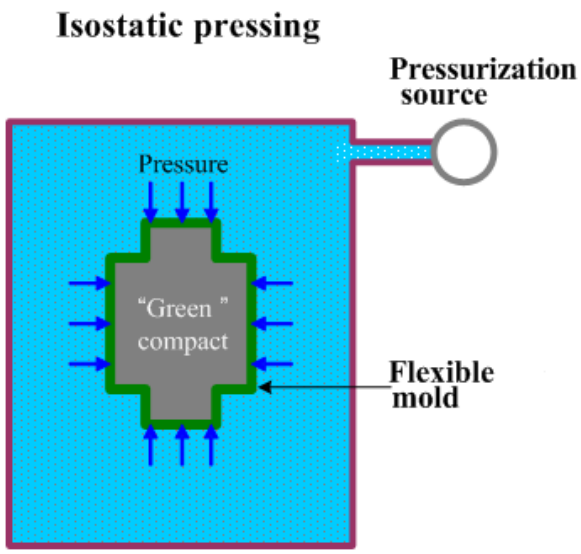

Figure 5 – Diagram showing the Process of Isostatic Pressing [19]

4.3.4 Vibration Molding

Vibrating is a discontinuous forming process for large dimension products. A mould is filled with the milled powder and a heavy metal plate is put on top of the mold, filled with green mix. Then the material is compacted by vibrating the mould for a certain period of time, to give the desired shape. The formed bodies show a higher degree of isotropy compared to extruded or die molder material [20].

4.4 Baking (Carbonisation)

The compacted parts ("green compacts") are heat treated (baked) in a baking furnace at 1000 – 1200°C in the absence of air. The baking process, which is sometimes called carbonisation, results in thermal decomposition (pyrolysis) of the binder into elementary carbon and volatile components. Carbon formed in carbonisation results in formation of pores, total relative volume of which (porosity) is determined by the binder quality.

The purpose of the baking process is to:

- change the binder pitch chemically by heating,
- converting it into a solid carbon mass
- which forms permanent carbon bonds between the coke particles.
- Thus a permanent solid rigid body is formed.

Baking furnaces are usually oil or gas-fired kilns, single-chamber furnaces or tunnel kilns. Small-dimensioned parts are also baked in electrically heated muffle, pit or push-rod furnaces. In ring furnaces and single chamber furnaces, it is possible to place the stock into steel containers (saggers), embed them in the packing material, and arrange these saggers in the chamber instead of placing pieces directly into the brick boxes of the furnace chamber. This handling is preferred in the case of shapes of different dimensions, as it allows a more advantageous usage of space. Also the loading and unloading procedures can be automated. Porosity is determined by the binder quality and in particular quantity.

4.5 Finishing and Surface Treatment

A carbon artifact contains open pores, which may make up approximately 25% of its volume. By filling these pores, the density, strength and conductivity of the artifacts can be increased to predetermined levels. Impregnating agents are usually pitch, resins and metals, which are brought into the formed bodies by a vacuum/pressure impregnating cycle. Pitch impregnated artefacts have to be re-baked in order to carbonise the pitch, whereas resin impregnated parts are either thermally cured and/or carbonised. The re-baking step also causes new pores to form, so that at least one more

impregnating operation is necessary. It should be stated however, that there are many examples of graphite's which have not been subjected to re-impregnation.

The potential exists for recycled graphite to be utilized, at least in part as a key constituent of the pitch or resin which is used as an impregnation agent for the process of finishing or surface treatment. It must be reiterated that, given the radiological inventory of the recycled graphite, the end use of such products finished in this way would be restricted to the nuclear industry.

4.6 Graphitisation

At this stage the shaped and baked parts are heat treated under exclusion of oxygen (air) at extremely high temperature (2500 – 3000°C). The graphitisation process results in crystallisation of amorphous precursor carbon, which transforms into crystalline graphite. During this high temperature treatment, the graphite is also purified since most of its impurities (binder residues, gases, oxides, sulphur) vapourise.

For many purposes, and certainly for nuclear graphites intended for moderator or reflector deployment, additional purification is necessary in order to reduce the boron content (the only element which is capable of displacing a carbon atom in the graphite lattice) and also for reducing heavy metal concentrations. Originally, chlorine gas was introduced into the graphitising bed through sparge pipes, and this was later displaced with freons. As both of these became recognized as environmentally inappropriate, it is usual now to employ magnesium fluoride, which has the additional benefit that no material capable of conversion to a radioactive isotope upon subsequent irradiation is introduced. This material is usually ad-mixed with the packing coke.

The strength and density of the graphite is dependant both on the grain size of the coke and its packing density determined by the granulometric composition. In addition the granulometric composition influences the thermal expansion co-efficient, elastic modulus, thermal and electrical conductivity, gas permeability and other properties.

During the graphitisation phase, the lattice order increases and produces smaller inter-layer distances which is a slight contraction called the graphitisation-shrinkage and is approximately 3 to 5% and results in a slight rise in the material density. Of more significance is what happens when the graphite cools, since extreme micro-cracking known as Mrozowski cracks are introduce which turn out to be of fundamental importance in the subsequent irradiation (shrinkage/expansion) behavior of the material

Changes in material properties as a result of graphitisation:

- Crystal development
- Impurities vaporise
- Becomes a better electrical and thermal conductor

The diagram below shows the direct relationship between the temperatures exerted during the graphitisation process and the materials lattice structure.

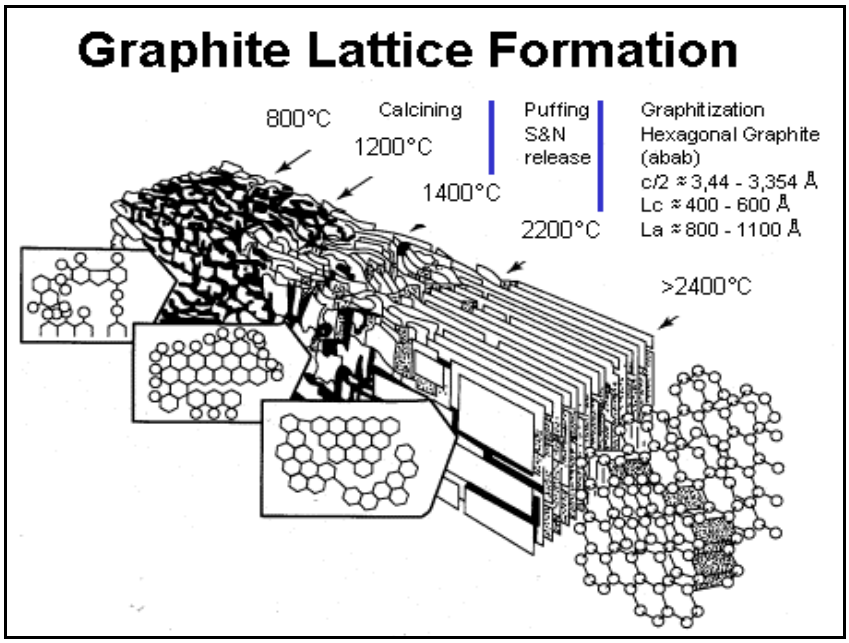

Figure 6 - Relationship between Graphite Lattice Formation and Temperature [20]

Graphitisation furnaces utilise heat generated by either electric current passing through the graphitising material (Acheson and Castner Types) or induction heating. The various furnace types used commercially are discussed over the following pages.

4.6.1 Acheson Furnace`

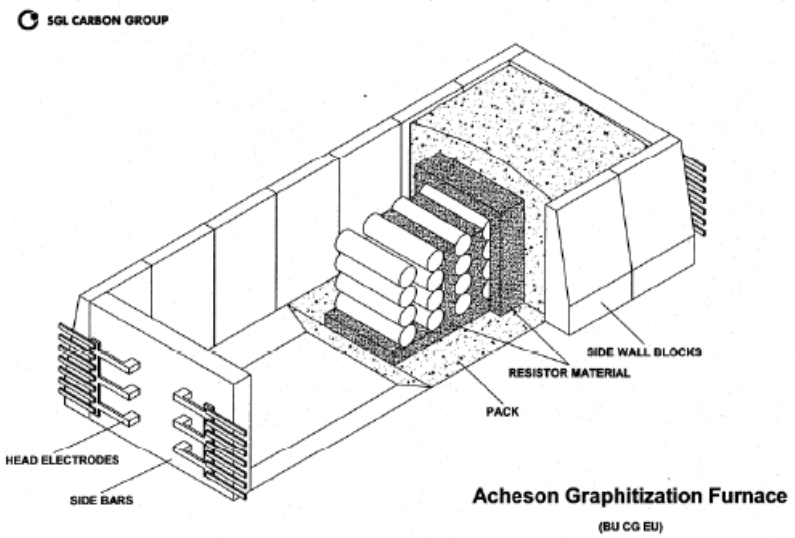

Figure 7 - Diagram showing an Acheson Graphitisation Furnace [20]

The stock is arranges in blocks within a horizontal bed, usually perpendicular to the axis of the furnace. The space between the segments is filled with a resistor material consisting of a coke/graphite granular mixture. The current is supplied to the load by two water cooled head electrodes at the narrow sides of the furnace, which is thermally insulated by a mixture of coke, sand, carbon black and/or sawdust, thus protecting the material against oxidation. As the electrical resistance of the furnace decreases with an increasing degree of graphitisation, the power to the head electrodes is controlled and adjusted by transformers.

Nowadays nearly all graphitising furnaces are DC-operated since powerful rectifiers are available. For fine-grained material, an uncontrolled release of decomposition products from the charge does not cause problems, so that the normal maximum temperature of 2800°C can be reached within a few days. Depending on the size of the furnace and its operation mode, one working cycle including cooling lasts two to three weeks.

4.6.2 Length Wise Graphitisation (Castner) Furnace

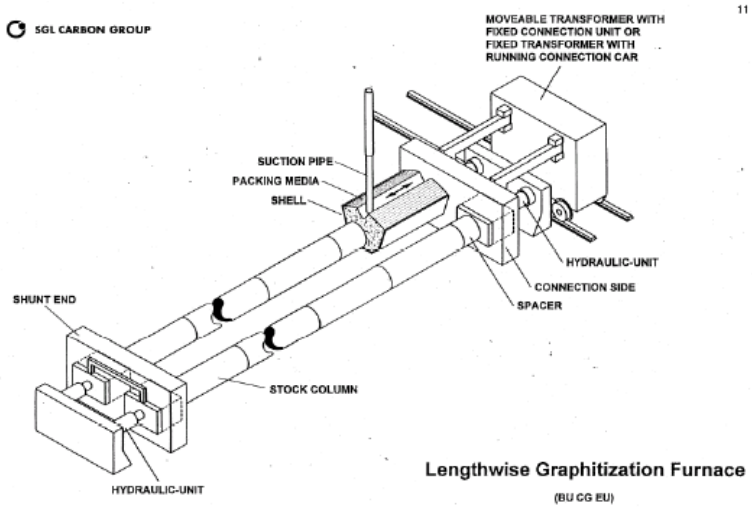

Figure 8 - Diagram showing the Length Wise Graphitisation (Castner) Furnace [20]

Lengthwise graphitisation (longitudinal array) was first described by Castner, and is characterised by the direct connection of the stock one to another in a row without a resistor material in between. The artefacts are clamped between the head electrodes of the furnace and heated by passing the current directly through the load. The contact area of the material to be graphitised has to fit well and therefore requires plane parallel machining and an adjustable clamping device in order to secure a constant, tight electrical contact for a low-contact resistance.

The installation against oxidation and high heat losses is the same as for Acheson furnaces. This graphitising method has the advantage of shorter heating periods, less power consumption, better control of process for electrode and smaller furnace dimensions.

4.6.3 Inductively Heated Furnaces

These are normally used for components which need to be graphitised with a very well controlled temperature profile in order to control internal differences in properties. Indirectly heated furnaces consist of a horizontal or vertical graphite tube of rectangular or cylindrical cross-section. The outside of these tubes is insulated with carbon black surrounded by a carbon felt jacket. The material is passed through the furnace, either continuously or at intervals. It is protected from oxidation by using water-cooled seals at the ends of the furnace and by applying a stream of inert gas. The main advantage of such furnaces is very close temperature control [20, 21].

4.7 Manufacturing Graphite in Radiological Conditions

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

5 Potential Recycled Products Used by Nuclear Industry

Due to the retention of a small amount of the graphite's radiological inventory (post processing), the opportunities for the use of recycled graphite are limited to the nuclear industry. The following sections consider the potential products which could be produced wholly or partly from recycled graphite.

5.1 Fuel and core products

Tristructural-isotropic (TRISO) fuel is a type of micro fuel particle utilised in high-temperature reactors. It consists of a fuel kernel composed of UOX (sometimes UC or UCO) in the centre, coated with four layers of three isotropic materials. The four layers are a porous buffer layer made of carbon, followed by a dense inner layer of pyrolytic carbon (PyC), followed by a ceramic layer of SiC to retain fission products at elevated temperatures and to give the TRISO particle more structural integrity, followed by a dense outer layer of PyC.(see Fig 9 below).

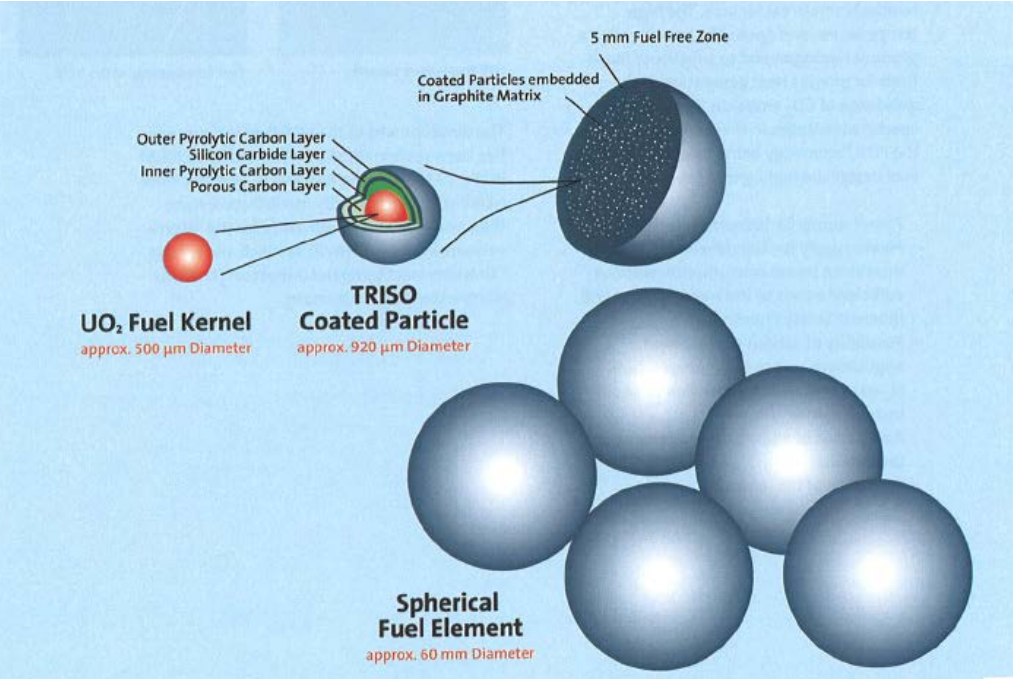

Figure 9 - Diagrammatic representation of the TRISO Fuel Particles [22]

TRISO fuel particles are designed not to crack due to the stresses from processes (such as differential thermal expansion or fission gas pressure) at temperatures beyond 1600°C, and therefore can contain the fuel in the worst of accident scenarios in a properly designed reactor. Two such reactor designs are the Pebble Bed Modular Reactor (PBMR), in which thousands of TRISO fuel particles are encased in a graphite fuel sphere commonly referred to as a pebble, and the prismatic-block gas-cooled reactor (such as the GT-MHR), in which the TRISO fuel particles are fabricated into compacts and placed in a graphite block matrix [22].

The potential exists to use recycled graphite (at least in part) in place of virgin graphite for the TRISO fuel particles. The flow chart below (Fig 10) highlights the production process of the TRISO fuel particles which is instigated with the supply of graphite. The radiological inventory of the recycled graphite would need careful consideration as to its potential affects on the fuel particles.

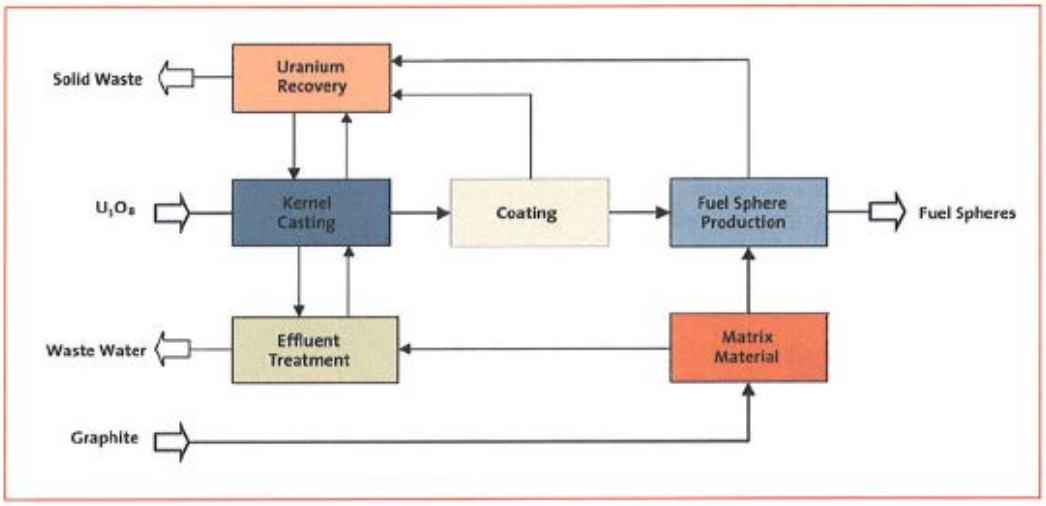

Figure 10 - Flow chart showing the production process of the TRISO Fuel Particles [22]

5.2 Graphite Electrodes for Vitrification of Radioactive Waste

Vitrification is a proven technique in the disposal and long-term storage of nuclear waste or other hazardous wastes. Waste is mixed with glass-forming chemicals to form molten glass that then solidifies, immobilizing the waste. The final waste form resembles obsidian and is a non-leaching, durable material that effectively traps the waste inside. The potential exists to utilise recycled carbon/graphite for the production of the electrodes used for the process of vitrification of nuclear wastes.

Recycled carbon derived from the recycle of the reactor isostatically pressed fine-graphite grades are extremely cost effective electrode materials as they have, besides their electrical and thermal conductivity as fundamental requirements, also high mechanical strength, edge stability, surface quality and good machinability.

Discussions have been held with the graphite manufacturer GrafTech concerning the potential for electrode production. They did not rule out the idea of producing electrodes for waste vitrification from the simpler GrafTech “fast.process” route, and indicated that some of its proprietary electrode joining technology might be applied to these products. One of the key benefits of producing electrodes for recycled carbon is that they do not necessarily require graphitising prior to use. The graphitisation of the electrode occurs when the current is initially passed though it during its first use. [18]

5.3 Other graphite products

There are various graphite products which have the potential to be manufactured in part (at least) from recycled carbon/graphite. These components include:

- Nuclear fusion reactor plasma first wall materials used to confine high-temperature plasma generated in the nuclear fusion reactor, and to protect the vacuum vessel.
- Carbon Fibre Reinforced Carbon (CFRC) materials may serve as structural elements inside a High Temperature Reactor (HTR), wherever an extremely high strength is required, however to date these have been very limited in their use..
- Core bricks made of graphite for nuclear applications produced from isostatically pressed to extruded and vibration-moulded graphite grades developed to display highest strength, yet with reduced brittleness, highest isotropy as well as highest thermal conductivity.
- Hot Gas Duct Components that are inserted into the outlet pipe allow increasing the outlet temperature beyond the strength limits of metal pipe linings. Attributes such as heat resistance, gas tightness, chemical resistance and abrasion resistance are of key importance.
- Anodes for Uranium Hexafluoride Production are indispensable in any fluorine production process. The fluorine produced by electrolysis is needed in uranium hexafluoride production. Uranium hexafluoride is an important intermediate product in the nuclear fuel fabrication; it allows enrichment of the desired U235 material.
- Graphite protection for antennas within nuclear fusion reactors

Those products listed above have been produced by graphite manufacturers in the past for nuclear power generation, with the next generation nuclear power stations new products may be required which offer opportunities for graphite recycle. [20, 23, 24]

5.4 Carbon products

Activated carbon is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Due to its high degree of micro porosity, just one gram of activated carbon has a surface area of approximately 500 m^2. Gas purification filters with activated carbon are usually used in compressed air and gas purification to remove oil vapours, odours, and other hydrocarbons from the air. The most common designs use a 1 stage or 2 stage filtration principle where activated carbon is embedded inside the filter media. Activated carbon is also used in spacesuit Primary Life Support Systems.

Activation is the process of treating the carbon to open an enormous number of pores in the 1.2- to 20-nanometer-diameter range (gas-adsorbent carbon) or up to 100-nm-diameter range (decolorizing carbons). After activation, the carbon has the large surface area (500–1500 m^2/g) responsible for the adsorption phenomena. Carbons that have not been subjected previously to high temperatures are easiest to activate.

Activated carbon can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulfide (H_2S), ammonia (NH_3), formaldehyde (H_2CO), radioisotopes iodine-131 (131I) and mercury (Hg). This property is known as chemisorption.

The potential of utilising activated carbon for off-gas filters within the stations in order to remove radioactive isotopes such as iodine-131 is an attractive option, one which would be but one which would require significant work to prove viable.

5.5 Silicon carbide (SiC)

Silicon carbide (SiC) is a compound of silicon and carbon bonded together to form ceramics. Silicon carbide has a density of 3.2 g/cm^3, and its high sublimation temperature (approximately 2700°C) makes it useful for bearings and furnace parts. Silicon carbide does not melt at any known pressure. It is also highly inert chemically.

Silicon carbide can be used as a coating for graphite parts. SiC coatings are deposited from gaseous silicon and carbon compounds at high temperatures by utilising the Chemical vapor deposition process (CVD). The coefficient of thermal expansion of the graphite material must be matched to that of the SiC coating. The typical thickness of the SiC coating on graphite is 50-100um. Edges of graphite parts should be radiused before coating.

The coating renders the graphite with special properties, which include:

- High hardness figure
- Good thermal conductivity
- High oxidation resistance
- High purity

Another use of silicon carbide in the nuclear industry is as a layer of the Tristructural-isotropic (TRISO) coating for the nuclear fuel elements of high temperature gas cooled reactors or very high temperature reactors such as the Pebble Bed Reactor (discussed in more detail in Section 5.1 and Fig 9).

Silicon Carbide also has potential uses in both the production of waste containers and also as backfill material for void filling in waste storage facilities. This is due to the excellent chemical properties, reasonable mechanical properties and its ready availability [25].

5.6 Waste Additives

The concept of adding graphite as a waste additive has been researched by the Paul Scherrer Institute in Switzerland. The research rector DIORIT was decommissioned in 1993 and is now being dismantled. One of the materials to be conditioned is 45 tons of activated reactor graphite. A cost effective conditioning method was developed which involved crushing the graphite to a size of less than 6mm and then added to concrete and grout. The “graphite concrete” is then used as a matrix for embedding dismantled waste in containers in order to increase the packing fraction and therefore minimise the number of waste containers required. A significant cost saving (circa 55 SFr/kg to 17 SFr/kg graphite) was achieved [6, 26].

6 Recycling Carbon-14

One of the possibilities for the recycle of ^{14}C is to purify it for use as a medical radioisotope. ^{14}C is currently produced for GE Healthcare in the UK by the Petten High Flux Reactor (HFR), in the Netherlands through the process of irradiating aluminum nitride. The potential exists that this radioisotope could be produced from isotope separation of the steam reformed irradiated graphite.

For irradiated graphite to be a viable option as a source, the ^{14}C would need to be sufficiently purified by utilising isotope separation technologies such as Pressure Swing Adsorption (PSA). This option has yet to be considered in sufficient detail, and discussions with GE Healthcare to discuss the option further are in progress.

7 Conclusions

- The properties of graphite have been reviewed in as far as they affect the recycling of graphite. Although it is possible to recycle irradiated graphite directly, it is felt that this possibility may be unlikely because of the presence of gamma radioactivity.
- Gasification of graphite provides a route for the decontamination of graphite from all isotopes except ^{14}C. It also provides (through the Sabatier and Bosch reactions) a potential route to carbon black, which appears to be the intermediate of choice for the graphite manufacturers for the production of new products. Other types of intermediate have not been ruled out from further consideration at this stage.
- Recycling of graphite will involve the manufacture of materials under radiological conditions. Accordingly it is likely that recycled products will be limited to those which can be produced with simple processes.
- A number of potential products have been identified, which might be produced from recycled graphite. These include not only graphite products for reactors, but graphite for waste vitrification electrodes and other non-graphite products such as activated carbon filters and silicon carbide. Because of the radioactive inventory it is likely that all recycled products used will be for application in radioactively licensed facilities.
- ^{14}C is potentially a saleable product and could be produced from waste graphite (or fractions of it) by carbon isotope separation technology. Promising technologies for this application have been identified, but it is most unlikely that these would be applied to the full amount of graphite waste produced. Only small amounts are likely to be treated by isotope separation, on an appropriately small scale.

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9 Glossary

AGR	Advanced Gas-Cooled Reactor (UK)
CANDU	Canadian-invented, pressurized heavy water reactor
CFRC	Carbon Fibre Reinforced Carbon
CPC	Calcined Petroleum Coke
CVD	Chemical Vapour Deposition
GLEEP	Graphite Low Energy Experimental Pile
GTMHR	Gas Turbine–Modular Helium Reactor
HFR	High Flux Reactor (Petten)
HTR	High Temperature (helium cooled) Reactor
ILW	Intermediate Level Waste
LWGR	Light Water Graphite Moderated Reactor
PBMR	Pebble Bed Modular Reactor
PSA	Pressure Swing Absorption
PSD	Particle Size Distribution
PWR	Pressurised Water Reactor
PyC	Pyrolytic Carbon
RBMK	Reaktor Bolshoy Moshchnosti Kanalniy
RSA	Republic of South Africa
SiC	Silicon Carbide
TRISO	Tristructural Isotropic Fuel
VHTR	Very High Temperature Reactor
WAGR	Windscale Advanced Gas-Cooled Reactor