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Collation of Data/Information from other Work Packages

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Executive summary

The CARBOWASTE Work Package 1 Integrated Waste Management Approach is intended to establish an integrated waste management approach for the most significant sources of irradiated carbonaceous waste, identifying the most appropriate options for dealing with this kind of legacy waste. The outputs will enable comprehensive roadmaps to be developed based upon the most acceptable technical choices for each member state involved with the project. This work package comprises seven tasks and this report addresses one aspect of the final Task 1.7: Synthesis.

The specific task within Task 1.7: Synthesis addressed here is the collation of information, data and analysis from Work Packages 2-5 in a manner that readers can easily appreciate, so that methodologies can be derived for their appropriate options.

The outputs from Work Packages 2-5 are considerable and it would be inappropriate to reproduce them in any detail. The purpose of this report is to provide a break-down of the CARBOWASTE work package structure and to summarise the key findings. Readers requiring more detailed information should refer to work package summary reports and then to specific deliverable reports. It should also be noted that this collation of data focuses on work package outputs that directly impact on the final Synthesis report. The final section of this report offers an overview of the broad achievements and key messages of the CARBOWASTE project.

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1 Introduction

The CARBOWASTE Work Package 1 (WP1) Integrated Waste Management Approach is intended to establish an integrated waste management approach for the most significant sources of irradiated carbonaceous waste, identifying the most appropriate options for dealing with this kind of legacy waste. The outputs will enable comprehensive roadmaps to be developed based upon the most acceptable technical choices for each member state involved with the project. This work package comprises seven tasks and this report addresses one aspect of the final Task 1.7: Synthesis.

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2 Work Package 2: Retrieval & Segregation

Every reactor is of different assembly characteristics and operational conditions of graphite and other carbonaceous material will vary from reactor to reactor. The integration of the graphite fixing and support in the core as well as measuring devices will create diverse 'gangue' material which is mixed with the extracted waste and need to be separated into different waste streams for treatment or disposal. This fact will impact the removal techniques and environmental conditions will be challenging. The main objectives of the first four tasks are stated as:

- Planning retrieval stage to prepare i-graphite in a form to facilitate waste management (wet or dry);
- Proposing techniques for segregating 'gangue' material from carbonaceous waste;
- Evaluating impact of timing and (dose drops) and *in-situ* conditioning; and
- Demonstrate modelling feasibilities and techniques.

Regarding the challenge to find a solution for managing the large quantities of graphite coming from spent High Temperature Reactor (HTR) fuel, the head end operations appear as a fundamental step. The objectives of a further two tasks are stated as:

- Development of versatile processes to separate coated particles (CP) from moderator;
- High integrity fraction of CP to limit cross contamination between CP and moderator graphite; and
- Separating coatings from the fuel kernel and conditioning of coatings for treatment and disposal.

2.1 Task 2.1: Radiological, reactor design and graphite mechanical integrity considerations

The primary output of this task has been the compilation of a Data Pack, which has focused on retrieval and segregation of irradiated graphite from nuclear reactors with reference also made to operational graphite waste. The predominant reactor configurations considered were Magnox, RBMK and UNGG, recognising that there are other configurations. The Data Pack was used to develop a strategy for WP2 Tasks 2.2 and 2.3, suggesting constraints to the study, identifying source data and gaps, suggesting a proposed goal for the retrieval and segregation toolbox compartment, developing a workshop agenda for completing delivery of WP2, developing further criteria and issues and introducing a strategy for modelling.

The strategic information presented as part of the Data Pack was largely based on UK experience of removing graphite from two reactors (GLEEP and WAGR) and also more limited information pertaining to Bugey decommissioning.

2.2 Task 2.2: Examination of retrieval options

Retrieval and segregation has been considered in the context of decommissioning commercial reactors in less than 25 years or up to 75 years after shutdown. Retrieval and segregation of i-graphite stored in an unconditioned state was also reviewed. WP1 provided input to the study including specific country information, graphite data, reactor systems, past retrieval experience, a roadmap and upper level evaluation of retrieval criteria. The Data Pack produced under Task 2.1 was used as an input to a WP2 workshop to consider retrieval options.

There are many requirements to achieve optimum retrieval and segregation: (i) the pre-requisites of good nuclear practice, the route map and the project management process, (ii) the definition of the preliminary waste route and its integration with the integrated waste management process, (iii) a staged approach to selecting the methods and tools. A generic retrieval and segregation process has been defined that can be broadly applied to any reactor system. The parameters and inputs needed to select each of the process steps have been developed. It was established that in-air or underwater retrieval and segregation are likely to be the dominant working environments and criteria have been presented for their evaluation.

Planned methods for decommissioning Magnox, UNGG and RBMK reactors have been considered and challenges and alternative approaches identified. The result of the analysis has led to a generic upper level work breakdown structure and a number of checklists to aid solution engineering. To proceed to a solution, the preliminary waste route must be defined that fits the integrated waste management strategy for the total i-graphite management based upon specific reactor design and condition knowledge. To fully manage risk, it is important to control contamination, protect the work force against radiation and achieve good visibility of the operational workface. These parameters affect the choice of working environment (in-air or underwater); but there is no single solution and tooling selection must be on a case by case basis. Tooling suggestions are noted based on prior experience.

In a separate study, the development and testing of specialist tooling for removal and handling of graphite bricks stored within Latina reactor core has been undertaken. Different types of tools were devised and tested on unirradiated material in order to investigate reliability, functional ranges, operational limits and possible directions for further optimisation. Further work would be needed to test the validity of these finding to irradiated components.

2.3 Task 2.3: Segregation of graphite from non graphite components

There are no CARBOWASTE outputs that explicitly address segregation of graphite from non graphite components. The WP2 summary report offers the following points on segregation options for the graphite itself:

- Selective removal of i-graphite from different parts of the core taking account of variations of activity within the core. It is generally understood that maximum radioactivity levels are in those blocks nearest to the centre of the core.
- Sort graphite outside in an extension to or outside of the reactor containment prior to dispatch; this is then a function of the *Preliminary Waste Route.*

- Segregation by splitting of individual graphite blocks into parts of different specific radioactivity; it has been reported that the radioactivity level within individual moderator blocks decreases with distance from the fuel channels.
- Volume reduce the graphite prior to dispatch to suit an alternative waste route or to fit into waste disposal containers.
- Undertake a modification of reactor operation during its final months before shut down that allows the cooling medium to encourage the removal of C-14.
- Undertake any of the processes identified by Work Packages 3, 4 and 5 in-situ to encourage removal of H-3, C-14 or Cl-36 from the i-graphite before it is retrieved; this has never been applied in practice.

2.4 Task 2.4: Diagnostic and modelling activities

The following types of modelling were identified as of potential benefit to CARBOWASTE, specifically with respect to supporting retrieval and segregation needs. It is considered that these would provide useful tools for the CARBOWASTE toolbox.

1. Nuclear Physics Modelling - Modelling of the in core behaviour based on inventory and irradiation history to predict post irradiation inventory and its distribution.
2. Chemical / Molecular Modelling - Modelling the structure of the graphite, giving consideration to factors such as chemical oxidation and graphite voidage and Wigner energy.
3. Structural Modelling - Modelling of the stresses in reactor and used to consider structural issues, for example thermal and oxidation impact on structure, in core stresses, locking of bricks, understanding importance of condition of bricks to retrieval.
4. Mass Balance / Flow Sheet - Modelling of the overall mass balance and inventory of the reactor system; particularly to consider the origin of C-14.
5. Operational Research / Production Engineering – Modelling of the processes such as retrieval operations to consider potential throughput of unit operations.
6. Visualisation – This is a generic group of models, but could be used for through core mapping, 3D / Virtual Reality (mock up) and could allow the results of the other modelling techniques to be presented and understood.
7. Environmental – Modelling of discharge dispersion or dust generation.
8. Heat Transfer / Computational Fluid Dynamics - Evaluate the performance of specific unit operations or systems, in terms of heat transfer and fluid flow.

A WP2 workshop was held in Gateshead, UK in July 2009 with the following purpose: to review existing Magnox, RBMK and UNGG issues and then to develop a generic process for retrieval and segregation, to relate to the Multi Criteria Decision Analysis (MCDA) analysis in the context of WP1 task 1.6 and to support development of best practice and to facilitate specification of diagnostic and modelling requirements, task 2.3. This confirmed that these areas were all relevant to CARBOWASTE. However, to focus attention on areas of priority for retrieval and segregation and where further development was considered necessary, the following specific areas were recommended for further study:

1. Mass balance modelling (including nuclear physics for inventory);
2. Structural modelling;

3. Operational research modelling; and
4. Visualisation.

Separately, a review was undertaken of UK modelling techniques currently used in the assessment and prediction of reactor graphite core condition. Although the review has focused on commercial nuclear plant, some of the models described may be applicable to other facilities containing irradiated graphite. The findings are summarised below.

- The dosimetry and reactor physics models provide inputs to most of the other models discussed. The requirement to run these models depends upon the intended application of the other models. Dosimetry and reactor physics calculations carried out in support of operation of the plant up to end of generation will generally suffice. However, for activation modelling, specific outputs may be required, noting that loss of graphite mass over life through oxidation feeds back into these calculations.
- Activation modelling could be a key tool for users in assessing the range and activity of radionuclides in waste graphite, provided radionuclide precursors are understood and their concentrations over the operating life of the plant can be quantified. Such modelling would need validation against measured radionuclide fingerprints. Activation modelling might support classification and segregation of waste graphite.
- Radiolytic oxidation modelling is important for determining graphite properties and may also be important for the assessment of radionuclide mass balances from the activation modelling. Prediction of graphite properties could be important during core disassembly and subsequent handling of core components. As noted above, activation modelling might support classification and segregation of waste graphite. General trends in weight loss due to radiolytic oxidation across cores may be derived from published measurements made over the operating lifetimes of the cores. Assessment of the mechanical performance of core components under specific decommissioning methods (such as drill and tap or vacuum lifting) might need more detailed distributions of weight loss. This could entail running oxidation models or could be based upon interpretation of reported distributions and trends in weight loss.
- Material properties modelling could be important during core disassembly and subsequent handling of core components. General trends in properties due to radiolytic oxidation and irradiation damage across cores may be found from published measurements made over the operating lifetimes of the cores. Assessment of the mechanical performance of core components under specific decommissioning methods (such as drill and tap or vacuum lifting) might need more detailed distributions of mechanical and physical (such as porosity) properties.
- Models of individual core components use dosimetry, oxidation and material properties outputs together with plant operating conditions, to predict component shapes and their internal stress states. This provides information on the potential for interaction between components and on the likelihood of cracking. Depending upon the reactor and core component under consideration, geometry changes and stresses may be small compared with loads applied during disassembly and handling. However, such models provide a means of quantifying such effects and running new cases or assessing model results from existing operational safety cases, which could support decommissioning activities.
- Models of whole core performance are designed to predict behaviour during transient conditions (start-up, shutdown), faults (temperature transients during events such as loss of boiler feed) and external perturbations such as earthquakes. Such assessments are highly

complex and their suitability for supporting graphite waste management activities may be limited. A potential application may be assessment of the potential for core "lock-up" due to irradiation-induced dimensional change and hence the ease or otherwise with which a large assembly of components could be taken apart. Mock-up rigs to support computational models provide visualisation but are of limited value.

2.5 Task 2.5: Conditioning of HTR-waste

Both pebbles and compact type fuels have been addressed in this task. Data from the former HTR reprocessing plant (JUPITER) at Forschungszentrum Jülich (FZJ) has been retrieved. Exploratory experiments have been carried out with specific processes with the objective of collecting data to allow assessment of the scaling up of laboratory processes towards an industrial scale as well as secondary waste streams.

Previous experiments at FZJ on reactor graphites and matrix materials for HTR fuel elements were corroded in air at 673K. Significant differences were found in the chemical reactivity of the various materials. The reactivity of the matrix graphites was observed to pass through a particularly pronounced maximum for burn-ups of less than 6 wt%. The experiments were extended to include matrix spheres in a temperature range from 623 to 653K. In individual cases, the catalytic effectiveness of metals precipitated from saline solutions was also incorporated (caesium nitrate proved to be especially effective). Based upon these results, tests were performed with the aim of utilising the observed losses in strength of matrix spheres during corrosion to disintegration in air at low temperatures for the reprocessing of fuel elements. Disintegration of the elements was attempted with the least possible chemical burn-up in such a way that the coated particles were separated without being damaged and the remaining graphite dust could be processed into a weak- or medium-active product suitable for final disposal. This has the potential to lead to a simplification of the approach for the head end processes to separate coated particles from the graphite matrix. Results showed that it is possible to disintegrate matrix spheres with a burn-up below 30% in less than three days. Lower burn-ups (<20 %) may be possible with optimised procedures. By using caesium nitrate as the catalyst, the reaction temperatures can be limited to 670K (870K in the absence of a catalyst). The following conclusions were drawn:

- It is possible with only partial combustion of the matrix at low temperatures to loosen the graphite structure in such a way that the residual, unburnt graphite can be separated from the coated particles in powder form. Process-related damage to the TRISO particles can be practically ruled out. Particles coated solely with PyC will probably not be corroded due to their high chemical inertness in comparison to other matrix formulations. This will thus prevent fission products from entering the matrix material. The graphite powder itself remains weak or medium-active. The off-gas flow also retains its low activity and is considerably reduced in comparison to the previous combustion head end. Homogeneous pre-corrosion may be an adequate step to increase the efficiency of other segregation methods for the head end of HTR spent fuel reprocessing plants.

- Pulsed current fragmentation has been considered as a head-end phase during the reprocessing of fourth generation reactor fuels and HTR compacts. The generation of a high voltage pulse via electrical discharge was used to disintegrate inactive materials. After the fragmentation process, changes in and the distribution of sizes produced were assessed to

determine its success. The critical parameters were found to be pulse energy and the mass of the material to be processed. A method involving successive cycles of fragmentation/separation by screening can improve the fragmentation performance. The presence of TRISO particles promotes fragmentation.

2.6 Task 2.6: Removal of Coating Layers from TRISO Particles

In order to minimise HTR waste volumes, it is very important to be able to separate the fuel from the larger volume low level activity graphite. The separated TRISO particles can then be reprocessed for waste separation or disposed of in a geological repository. In addition, preparation of acid-graphite intercalation compounds (GICs) from the separated graphite may constitute a way to recycle this waste.

Two separation methods have been tested on HTR-type compact fuel with ZrO_2 TRISO particles: low (H_2SO_4+H_2O_2) and high (H_2SO_4+HNO_3) temperature acid treatments. In both cases the TRISO separation was complete but some TRISO layers oxidised at high temperature. At low temperature, the desegregation of graphite grains was facilitated by intercalation of sulphuric acid between the graphene layers. The acid-GIC obtained consisted of pure phases of high quality suggesting their potential for industrial recycling. The study showed:

- Clean separation of TRISO particles from the graphite matrix is possible at room temperature via acid treatment with a mixture of sulphuric acid and hydrogen peroxide. This treatment prevents damaging the particles, which constitutes the condition *sine qua non* for the success of the separation method applied to the spent TRISO fuel particles.
- Industrial recycling of the separated graphite via preparation of the graphite intercalated compounds may be an attractive way to recycle this waste for industrial and environmental applications considering the high quality of the GICs and exfoliated graphite obtained at room temperature.
- However, more research is necessary to test the method with irradiated compacts to study the effects of irradiation on the treatment process and on the behaviour of the volatile elements such as Cl-36 and C-14.

Removal of coating layers from TRISO particles by laser cutting has also been investigated. A Q-switched Nd:YAG laser system was employed for this process, based upon its successful deployment for the decontamination of metal surfaces. An initial study of surface decontamination with pulsed lasers comprised three parts:

1. The relationship between ablation rate and laser fluence was investigated after optimal processing conditions were determined.
2. Equipment was tested on the removal of a thin layer of metal from the surface of stainless steel (without contamination).
3. Laser cutting was trialled on a TRISO particle.

The Nd:YAG laser system was successfully used to cut a TRISO particle. The use of a fiber optic cable in conjunction with a focussing lens allowed the laser to cut or drill through the graphite material by only adjusting the focus of the beam to the depth of the cut. The addition of an automated X, Y, Z translation stage allowed the precise cutting of small objects. It was essential to

avoid strong heat absorption into the graphite material resulting from plasma formation at the high fluences. The laser system employed offers a feasible and efficient method for cutting through the TRISO particle layers in order to remove the UO_2 kernel.

3 Work Package 3: Characterisation & Modelling

The objectives of this work package are stated as:

- To validate analytical methods for inventory determination in irradiated graphite by a proficiency test applied to real graphite waste;
- To determine the type and location of impurities and radioactive isotopes in un-irradiated and irradiated nuclear graphite within the selected grades and sources;
- To determine the mechanism by which impurities / radioactive isotopes may be removed from nuclear graphite by various treatments;
- To determine the stability of radioactive isotopes in nuclear graphite before and after treatment; and
- To make inter-comparisons on irradiated and non-irradiated graphite samples.

The work has been broken down into five tasks and selected outputs from these tasks are summarised in the sections below. It is important to note that the summaries provided below do not reflect the considerable outputs from the tasks, but rather reflect their impact on WP1 MCDA and its input fields.

3.1 Task 3.1: Inter-Comparison Test and Sample Management

The purpose of this task was to distribute samples to different facilities for radionuclide inventory determination, based upon a range of methods. This would include both unirradiated and irradiated graphite sourced from a Materials Testing Reactor (MTR) (TRIGA reactor in Romania), a French UNGG reactor, a Lithuanian RBMK reactor and a UK Magnox reactor.

The output from this task provides additional information on the radionuclide inventories and the uncertainties in such determinations for selected sources of irradiated graphite. Such information may be useful for WP1 MCDA sensitivity analyses but it cannot inform WP1 on actual MCDA inputs. This task provides a valuable reference for radioanalytical determinations with guidelines for different methodologies. It has also led to the harmonisation of methods with experience interchange between specialist laboratories, which should enhance confidence in users and public opinion.

3.2 Task 3.2: Structural Changes from Irradiation and Treatment

Under this task, structures of graphite and carbon materials with and without irradiation were investigated using x-ray diffraction (XRD), Raman spectroscopy, confocal microscopy. The effects of simulated irradiation damage by implantation of a range of different atoms (C, N, D, Cl and Co) were also investigated using XRD. A study was also undertaken to assess the effects specimen form (powder or solid) on XRD. Materials used in these investigations included graphite and carbon-based materials from the German AVR (reflector, fuel pebble, insulation) and Dido reactor (reflector), an RBMK in Lithuania (moderator), a French UNGG reactor (moderator) and from the BEPO reactor (moderator) and a Magnox reactor (moderator) in the UK. In the case of XRD, the work showed peak broadening in irradiated material indicating damage to the structure and some reduction in crystallite size. Simulated irradiation damage was broadly consistent with in-service damage. These observations are supported by Raman spectroscopy. Confocal microscopy uses

lasers to build 3D surface profiles of graphite and the method was applied to BEPO graphite with different irradiations. Graphite specimens taken from the French Saint-Laurent UNGG reactor were subjected to a range of density, porosity and pore size distribution measurements and the results compared with those for unirradiated material.

In separate studies, unirradiated graphite from the same reactor was compared with highly oriented pyrolytic graphite (HOPG) by cross-linking several techniques including Raman microspectrometry, transmission electron microscopy, scanning electron microscopy and XRD. Spatial distribution analyses of Cl-36 were measured in Saint-Laurent UNGG graphite. Heterogeneous distributions were recorded for both unirradiated and irradiated graphite.

The outputs from this task are not likely to impact on WP1 waste management MCDA analysis. This task confirms and builds on existing knowledge of the behaviour of graphite under irradiation. It has shown that polycrystalline nuclear graphites are very different from graphite single crystals, effectively being highly graphitised carbon/carbon composites with multiscale organisation (which has been studied by XRD-Raman-TEM). Neutron irradiation leads to disorder, structural damage (changes in single crystal lattice parameters) and nanostructural damage. It has been suggested that the occurrence of strongly disordered nanoporous carbon may be able to trap contaminants such as C-14. Furthermore, such nanoporous carbon is highly reactive during gasification and may point to a new method for carboxygasification for nuclear waste decontamination for some graphites.

3.3 Task 3.3: Localisation of Impurities and Isotopes before & after Treatment

There are many types and sources of irradiated nuclear graphite waste and therefore it is unlikely a comprehensive database of empirical data for all this waste could ever be achieved. Therefore to gain an understanding of the location and stability of impurities / radioactive isotopes in irradiated graphite waste before and after various treatments, a range of scientific techniques have been employed to investigate where and how impurities / radioactive isotopes are located within virgin and irradiated nuclear graphite.

Activation processes and chemical reactions, focusing on H-3, C-14, Cl-36 and metallic radionuclides have been reviewed, and radiation damage and accumulation of Wigner energy in graphite is discussed.

The location of C-14 and its precursors in the matrix is of considerable interest. The relatively low concentration of C-14 in irradiated nuclear graphite prevents investigation by direct spectroscopic methods. Instead, attention has focused on chemically detectable precursors and the behaviour of the graphite to different chemical treatments (with the analysis of C-14 containing reaction products). The principal C-14 precursors are C-13 and N-14. C-13 is probably homogeneously distributed within the matrix owing to its natural occurrence in carbon. C-14 from N-14 will largely follow the distribution of nitrogen in nuclear graphite and will be concentrated at surfaces. There is also evidence for C-14 hotspots possibly arising from activation of N-14 in nitrogen-containing compounds of the binder material.

The predominant precursor for Cl-36 is Cl-35. This may be present in the raw materials at manufacture but is also added via purification during manufacture. There may also be contamination from air after manufacture and during storage and it may be present in low levels in reactor coolant gas. Chlorine is found to be heterogeneously distributed within the graphite and there is no evidence for correlation with metal impurities. In unirradiated graphite, it is present in

two chemical forms: approximately 70% is in organic form bonded with carbon in the matrix and approximately 30% in inorganic form as oxychlorine compounds.

Tritium arises from activation of Li-6 and B-10 impurities. There is evidence for hydrogen isotope migration in nuclear graphite, by molecular diffusion with entrapment at crystallite edges and between graphene layers. Its thermal behaviour has been investigated in WP4.

Radionuclide inventory data has been provided on untreated graphite from the MTRs at Jülich, the outer graphite layer of an AVR fuel pebble, a UNGG reactor in France, the Magnox reactor at Latina, the RBMK reactor at Ignalina, the TRIGA MTR in Romania, the RAPHAEL graphite irradiation programme at Petten and the BEPO experimental reactor in the UK. Characterisation methods included γ-spectrometry, liquid scintillation counting, x-ray tomography combined with radiography and autoradiography (for surface mapping). Radionuclide activities (Bq/g) have been reported for H-3, C-14, Cl-36, Cr-51, Mn-54, Fe-55, Co-60, Ni-63, Sr-90, Cs-134, Cs-137, Ba-133, Eu-152, Eu-154 and Eu-155. In the case of the RBMK graphite, predicted C-14 levels from activation modelling have been compared with measurements, indicating that the nitrogen concentration in the graphite must be ~8ppm to account for observations.

An assessment of methods for determining the activity of long-lived radionuclides in graphite has been undertaken. Specifically, determination of the activity of Ni-63 and actinides has been addressed. In the case of Ni-63, solid samples are mineralized in a microwave system. Samples of larger mass (>0.002 kg) are mineralized at a corresponding temperature in a muffle oven or by extraction, by heating with acids. The developed radioanalytical method is based on a group co-precipitation of iron and nickel radioisotopes and their stable elements on an inert carrier and their subsequent separation using anion-exchange chromatography. Selective Ni-63 separation is performed by extraction chromatography. The chemical yield is evaluated by atomic absorption spectrometry. The purified Ni-63 fraction is measured for its activity using liquid scintillation counting. The method for determining activities of Pu-238, Pu-239, Pu-240, Am-241, Cm-242, Cm-243 and Cm-244 in irradiated graphite samples (including other irradiated carbonaceous waste like structural material made of graphite or non-graphitised carbon bricks and fuel coatings samples) is based on the ashing and dissolution of matrix by aqua regia and radiochemical separation using extraction chromatography. Pu-242 and Am-243 isotopes are used for chemical yield determination. Other radionuclides are deposited on stain steel disks prior to measurement by alpha spectrometry.

Secondary Ion Mass Spectrometry (SIMS) has been used to identify C-14 and to distinguish it from N-14 in irradiated and unirradiated AVR fuel pebble graphite. The analysis of CN- ions suggests that this may be a bonding pathway for N-14 in the matrix during irradiation. Electron microscopy and x-ray fluorescence has also been employed to locate impurities in the graphite matrix. Frequently, elements can be detected as particles on the surfaces of pores. It is also important to note that the distribution of impurities and of radionuclides is inhomogeneous with no two samples from the same source showing identical results.

The outputs from this task are not likely to impact on WP1 waste management MCDA analysis. The source of graphite and its reactor environment will have a strong influence on the radionuclide inventory. Users need to ensure that the results they use are representative of the reactor type under consideration and its specific irradiation history. The speciation and location of radionuclides, if known with confidence, could influence waste treatment and will determine leaching behaviour and therefore packaging and storage options.

3.4 Task 3.4: Modelling the Behaviour of Impurities and Isotopes in Graphite

An understanding of the behaviour of impurities and the production of isotopes in irradiated graphite can be from activation modelling, based upon knowledge of the irradiation history of the material.

Activation modelling has been undertaken by the University of Manchester for graphite in a UK Magnox reactor, determining and quantifying the decay of the important isotopes including C-14, H-3 and Cl-36. Separately, the Lithuanian Energy Institute has studied the activation of ex-service graphite rings from RBMK graphite cores. A third study by the Institute for Nuclear Research in Romania (INR) of isotope accumulation in the graphite of the TRIGA materials testing reactor has also been undertaken. A fourth study of EDF graphite from the UNGG reactor types has been reported, focusing on the highest activity radionuclides C-14, Ni-63 and H-3, radionuclides affecting storage volumes (for example Cl-36), Co-60 (as a means of quantitative measurement of waste packages), Cs-137 which is an indicator of fission product release and Be-10 and Ca-41 which are soluble in underground water in a repository.

The UK study generated predictions of H-3, C-14 and Co-60 activities in Magnox reactor graphite at end of life which could be compared with experimental results from material trepanned from Wylfa Reactor 1. Differences between measurement and prediction were attributed to uncertainties in original impurity levels. It was also recognised that account needed to be taken of loss of material by radiolytic oxidation and the increase in impurity levels from material in the reactor gas circuits.

In the Lithuanian study, the significance of C-14 precursors (N-14 and C-13) has been assessed. For nitrogen impurity concentrations up to 10^{-4} % by weight, the resulting activity of C-14 is considerably lower than that from C-13 activation. When the nitrogen concentration reaches ~1.1×10^{-3} % by weight, the C-14 from nitrogen equals that from C-13 and the contribution from nitrogen becomes dominant beyond that. Back-fitting precursor concentrations to match measured radionuclide activities gave a reasonable correlation given the uncertainties in measuring impurity levels.

In the case of the TRIGA assessment, it is concluded that graphite undergoing long term irradiation cannot be released from regulatory control even after a long cooling time. The total activity and total clearance index values are due to the long lived isotopes produced by the graphite impurities during irradiation. The measured Eu impurity level in the graphite was found to be higher than the amount (2 ppb) considered in the activation calculations. Impurities could have non-uniform distributions in the graphite volume, as borne out by within-block analysis.

The French study also adopts the back-fitting approach for establishing realistic impurity levels for activation predictions. They observe that Cl-36 contents are low, reflected in a large observed variability of measurements. The main part of the Cl-36 activity in EDF waste graphite is found in sleeve material from Saint-Laurent stored in silos. They propose that graphite waste management of this material should be different from that for graphite from the piles. Comparing inventories across the UNGG fleet, the Bugey 1 core shows the highest radiological activities (with the exception of the Saint-Laurent sleeves), arising from the high neutron flux density for this reactor. In contrast, graphite from biological shields where fluxes are low is much less active and would lead to a different waste classification. The back-fitting approach has also been adopted for C-14 assessments, where it is observed that a knowledge of N-14 impurity levels in the graphite of an operating reactor is impossible to quantify; the release of radionuclides and their precursors through

radiolytic oxidation and thermal processes is almost certain to take place during reactor operation. Surveys of radionuclide content in irradiated graphite must be based upon sets of measurements owing to the large variability in local concentrations.

While the outputs from this task are not likely to have any direct impact on WP1 waste management MCDA analysis, activity inputs may be derived from predictions and these four studies highlight the associated uncertainties. The work highlights the potential for heterogeneous distribution of radionuclides through the different graphite components, providing the potential for segregation.

3.5 Task 3.5: Correlation with Existing Data on Graphite Wastes

The objective of this task is the compilation of a database that can inform inputs to modelling and treatment methods for decontamination. Fields to be included in the database are

- Analysis sample ID
- Reactor type
- Range of temperature
- Range of neutron flux
- Range of irradiation time
- Atmosphere during irradiation
- Isotope(s)
    - Specific activity
    - Specific activity
    - Overall uncertainty
    - Specific activity coverage factor
    - Specific activity confidence level
    - Specific activity date
    - Laboratory
    - Analysis procedure reference
- Weight losses during operation
- Structural data
- Chemical data

The outputs from this task are not likely to impact on the general approach to WP1 waste management MCDA analysis. The database currently represents a small fraction of the i-graphite inventory. Users need to ensure that the data they use are representative of the reactor type under consideration and its specific irradiation history.

4 Work Package 4: Treatment & Purification

This work package addresses decontamination of carbonaceous waste from graphite-moderated reactors with the following stated objectives:

- Understanding of incorporation and removal mechanisms of radionuclides in graphite;
- Development of a mechanistic model for impurity removal;
- Separation of radionuclides from carbonaceous waste by physical, chemical or biological treatment; and
- Technical feasibility and economic evaluation of developed treatment techniques on a laboratory scale.

Treatment as well as characterisation of contaminated graphite is a complex procedure raising specific issues on required precision and on safety. The latter is due to the existence of fine radioactive dust, which might spread due to its electrostatic properties. This increases the risk of contamination and incorporation. Therefore, special safety regulations must be considered especially when high temperatures and/or reactive gases are involved. Consequently, greater efforts are necessary to construct specific equipment to handle this material, in glove boxes or hot cells. In addition, the low concentration of Beta-emitting Cl-36 is difficult to measure. This especially applies for the investigation of the local distribution of Cl-36 and C-14 and under background irradiation.

Most of the treatment and decontamination processes covered by this work package are commonly used in nuclear technology but their efficacy for i-graphite is not well known. Therefore, a screening has been undertaken at the beginning of the project to identify the most efficient processes. Combinations of different purification methods may be necessary for optimisation.

The work has been broken down into four tasks and the outputs from these tasks are summarised in the sections below.

4.1 Task 4.1: Mechanistic Background of Impurity Removal

This task has built on analysis of data for the various grades of unirradiated and irradiated graphite obtained in WP3 in conjunction with data obtained for treated graphite in WP4. Some mechanistic understanding of impurity / isotope localisation before and after treatment is required to feed into the treatment options within WP4 and subsequent work packages. Techniques such as autoradiography and X-ray tomography have been highlighted for the analysis of impurity and isotopic location within irradiated graphite material. A meeting held in Manchester brought together experts in the fields of atomistic, experimental analysis and neutronics/activation modelling to discuss future collaboration in the development of a fuller understanding of the behaviour of C-14 formation and location.

Three main locations for radionuclides have been identified: homogeneous distribution, concentrated “hotspots” and as a film on pore surfaces and in near surface layers. In the case of C-14, if it is covalently bound within the structure, its chemical form is elemental. It can be removed by oxidation if exposed at a surface (the latter two locations). Apparent thermal release may be due to oxidation by impurities on the surface or in the system.

4.2 Task 4.2: Graphite Decontamination by Physical Treatment

Great care must be exercised in the interpretation of the findings from this task. The characteristics of the as-manufactured graphite, the irradiation conditions and the chemical environment during and after irradiation may all affect the outcome of physical treatments.

A study of the effects of temperature on the speciation of pristine chlorine in the Saint-Laurent A2 was undertaken using temperature programmed desorption in the temperature range 200–1000ºC and X-ray photoelectron spectroscopy. Chlorine is released as HCl and no Cl is detected. There are two chlorine chemical forms present in virgin graphite. They correspond respectively to: inorganic chlorine (around 30%, and probably chlorite (ClO_2^-) and chlorate (ClO_3^-) compounds; organic chlorine (around 70%, with aromatic carbon (C−Cl) bonds). These compounds have different thermal stabilities: the release of inorganic compounds increases with temperature whereas the organic chlorine remains more stable. These results are in broad agreement with historical studies on irradiated graphites where a rapid release of around 50% of the initial chlorine in Magnox and 30% in AGR reactors was measured. A further 40% of the remaining chlorine is released over the reactor lifetime. All these results support the existence of two chlorine chemical forms of different thermal stabilities. It is likely that during reactor operation the more labile fraction is rapidly released.

Implanted deuterium has been used to study the thermal behaviour of tritium in nuclear graphite. Implanted samples were annealed in vacuum or in argon at temperatures ranging from 600°C to 1200°C for durations varying from 30 minutes to 192 hours. Only a small fraction of deuterium is released at UNGG reactor temperatures (less than 10 at.% at 500°C). The release becomes significant for temperatures higher than 600°C and is almost totally completed for temperatures equal or higher than 1200°C. The release follows two stages: a rapid release occurs within a few hours followed by a much slower release during which the release of deuterium saturates. The initial stage might correspond to detrapping deuterium located at crystallites edges and its diffusion at the crystallite surfaces as well as its permeation through the open pores. Compared to this “loosely” bound deuterium, the total release of deuterium located inside the crystallites and chemisorbed to carbon atoms through sp2 or sp3 bonds requires temperatures above 1100°C. The study shows that at UNGG reactor temperatures that do not exceed around 500°C, there is no significant deuterium release in inert atmosphere or vacuum. The role of gas containing traces of hydrogen bearing molecules (isotopic exchange) potentially enhancing deuterium release is being investigated. Similar results have been obtained for the release of tritium, present as strongly adsorbed tritiated water, in oxygen containing functional groups and as hydrocarbons.

Work was carried out on unirradiated graphite show a release of almost half the inventory of chlorine. It is not clear whether this release can be achieved from irradiated graphite which has been operating at elevated temperatures. Scalability of this process to large components has not been tested.

Studies at FZJ have focused on the release of H-3 and C-14 by heat treatment in inert gas experiments. High fractional releases of H-3 in nitrogen at 1300°C were observed with small accompanying (<1%) sample mass losses. Experiments in argon showed no benefits from powdering the material. Only relatively low levels of C-14 are released when heated in an inert

atmosphere. The thermal process of release is potentially convoluted by the presence of adsorbed oxidants on the graphite surface and by impurities in the inert gas. Production of CO and CO_2 has been observed in such experiments with an accompanying mass loss from the graphite, ceasing presumably when oxidants have been consumed. A potential process for releasing C-14 has been proposed, involving roasting in an inert gas followed by cycling between replenishment of oxidants at low temperature followed by chemical reaction at elevated temperatures. Such a process might be applicable to graphite that has C-14 concentrated at surfaces. Thermal treatments with steam are currently being investigated but it is too soon to draw any conclusions on its potential.

In summary, studies relating to H-3 release indicate that in-reactor release is unlikely due to the high temperatures required. The temperatures necessary for heat treatment following dismantling of the core may be economically unattractive. Such a process would likely require an inert atmosphere to avoid excessive oxidation. It is not clear whether this limited study is generally applicable to H-3 release. C-14 release through heat treatment without oxidation is inconclusive. In the presence of oxidant impurities, small releases of C-14 have been observed. There is no knowledge of the contribution of thermal diffusion to the release of radionuclides through heat treatment. The relative contributions to the release of radionuclides by heat treatment from the surface or by thermal diffusion to the surface are not known.

4.3 Task 4.3: Graphite Decontamination by Chemical Treatment

Great care must be exercised in the interpretation of the findings from this task. The characteristics of the as-manufactured graphite, the irradiation conditions and the chemical environment during and after irradiation may all affect the outcome of chemical treatments.

A review has been undertaken of processes for removing metallic impurities during the manufacture of nuclear grade graphite. Purification processes involving halogen gas purges originally developed for the manufacture of spectroscopic grade graphite electrodes for chemical analysis were enhanced to cope with monolithic graphite blocks. The addition of chlorine gas at high temperatures is effective at removing most impurities commonly found in graphite, with the exception of boron which is more efficiently removed by fluorine gas. If the graphite is in monolithic form, purification would require an Acheson furnace with exhaust gas cleaning facility to condense the vapours leaving the material. In a powdered state, a vacuum graphitization furnace unit, which allows inlet of fluorine- or chlorine-containing gas would be viable.

The aqueous leaching of chlorine in nuclear graphite will mainly depend on the impregnation kinetics, the chemical form and distribution patterns of chlorine in graphite, and the diffusion of the soluble species through its pores. Historical Cl-36 leaching experiments on irradiated nuclear graphite from Saint Laurent reactor G2 show that around 80% of Cl-36 is released during the first month whereas a residual fraction is released with much slower kinetics. It is proposed that this behaviour points towards the existence of two distinct chlorine types as discussed in Task 4.2: a more labile fraction that is less bound to the graphite structure and another which is more stable, more strongly bound to graphite and/or present in the infrapores. The results of new tests undertaken under this task are in agreement with historical findings concerning the existence of two types of chlorine. These results point to the existence of an organic form of chlorine, strongly bound to graphite through C−Cl bonds resistant to leaching and an inorganic form, where chlorine is present as ClO^{2-} or ClO^{3-} compounds being far less resistant to leaching.

Chemical leaching tests have been made on BEPO and Magnox reactor graphites to determine the release rates and mobility of C-14 and H-3.

a. An acidic environment yielded the highest release activities for both radionuclides. No change in pH was observed in any of the leaching experiments.
b. C-14 is present in leachable and non-leachable forms. Intercalation with penetration of interlayer spaces within the graphite structure is thought to be the mechanism behind C-14 removal.
c. Hydrogen ion isotopic exchange is thought to be the mechanism behind H-3 release.
d. Steady state of release was achieved under all conditions by day 90. After this, very limited amounts of both H-3 and C-14 were released.

The chemical treatment process removing mobile and accessible H-3 and C-14 prior to decommissioning or repository storage shows that a significant portion of both radionuclides remains within the graphite structure. Even harsh oxidising and acidic environments have failed to remove more than 30% of the radionuclides. In terms of using this methodology as a pre treatment method the industrial and financial feasibility of these processes would need to be evaluated.

Ultrasound-assisted chemical decontamination using organic solvents has been investigated using material taken from the moderator of the Latina nuclear power plant. The method relies on an exfoliation process using organic solvents (i.e. a liquid-phase exfoliation-like process) to produce unfunctionalised and non-oxidised graphene layers in a stable homogeneous dispersion. The process, assisted by relatively low energy ultrasound, separates the individual layers in a more or less regular manner. In principle, the process removes interplanar interactions by dipole-induced/dipole interactions between graphene and organic solvents, resulting in a dispersion of the graphite in a workable medium. After separating the graphene dispersion from the organic solution containing contaminants, there is potential for the non-oxidised graphene/exfoliate powdered graphite to be re-cycled. The process, trialled for C-14 and Co-60, has shown relatively modest and highly variable removal efficiencies based on three different solvents (N,N-dimethylacetamide, N,N-dimethylformamide and N-methyl-2-pyrrolidone): ~1-28% removal of C-14 and ~0.1-9% Co-60. It is speculated that improved results for targeted radionuclides could be achieved by more selective solvents.

Soxhlet extraction, a distillation-based solid-liquid extraction method, has been investigated as a potential process for decontaminating radioactive reactor graphite samples, with a view to eliminating the need for final storage. Solvents used in this study were water, various organic solvents and inorganic or organic acids in different concentrations. The process was trialled on graphite originating from the FZJ research reactor Merlin and AVR high temperature reactor. The lower activity Merlin graphite contained the following radionuclides: H-3, C-14, Co-60, Ba-133, Eu-152, Eu-154 and Eu-155. The AVR material contained the following radionuclides: H-3, C-14, Sr-90, Co-60, Ba-133, Cs-134, Cs-137, Eu-154 and Eu-155. The first series of tests performed on Merlin graphite showed that, with the exception of the acids, all of the solvents used only removed very small amounts of the radioactive inventory. The best results were obtained with the acids with the higher concentrations. Extracting agents used for the second series of tests on AVR graphite developed this finding, using 6 M hydrochloric acid, 7 M nitric acid, 6 M acetic acid and 4 M sulphuric acid. The results from both series of tests showed that the methods used were not very effective in decontaminating reactor graphite. Compared to the other nuclides, tritium and C-14 in

particular, which contribute the highest level of activity in the samples, showed the poorest decontamination efficiencies. Using strong acids, all of the other radionuclides, with the exception of Ba-133, were comparatively easy to remove from the graphite. However, they were still not removed to a sufficient extent, as both the treated Merlin reactor graphite as well as the graphite from the AVR were still contaminated to such an extent after an intermediate storage period of 40 years that both of them would have to be disposed of in a final storage facility. Further tests would be needed to clarify to what extent a smaller grain size (and therefore a larger reaction surface) might have on decontamination efficiencies. The effects of fluence on decontamination might merit further investigation. Also the extent to which consecutive extractions with different acids could lead to better results could also be investigated.

An investigation has been undertaken of the chemical removal of Co-60, Eu-152 and Eu-154 from the graphite irradiated in the TRIGA reactor using different acids at various concentrations. Removal efficiencies using hydrochloric and sulphuric acids ranged between 70 and 90%, with the most efficient removals achieved for Co-60.

A number of other potential decontamination processes have been reviewed:

a. Chemicals can decontaminate graphite by selectively removing the surface layer and by destroying the binder material. Based upon studies using mineral acids, alkaline solutions, dissolved oxidising agents, organic washing detergents or such combinations, two possibilities for decontamination of the surface layer of graphite material were identified. A mild combination solution destroys the binder material and dissolves a minimal amount of graphite resulting in the removal of surface material. A more aggressive approach using electrochemical technology not only destroys the binder material, but also dissolves graphite surface material, resulting in the removal of the surface graphite layer as a decontamination step.
b. The use of molten salt technology to decontaminate graphite by removing the outer layer was investigated. The initial study was based on using a salt mixture at 350C. During the initial dissolving phase, no dissolution of the graphite surface was observed. Decontamination would therefore have been minimal. However, by adding a chemical to the molten salt, the structure of the graphite layer dissolves.
c. It may be possible to decontaminate graphite surfaces using electrochemical technology. The influence of different electrolytes on the decontamination time and volume reduction of generated secondary waste would require further investigation.
d. Decontamination by means of a high temperature plasma leading to controlled combustion of the outer layers of graphite offers a potential approach.
e. The use of blasting technology to decontaminate graphite surface by removing surface material in a suitable blasting confinement is currently being evaluated.
f. Laser technologies may provide an approach for surface decontamination and in particular the selective removal of the graphite layer surrounding the kernel of coated particles.
g. The use of spark erosion technology to remove the graphite surface layer may provide a possible decontamination technique.

The studies undertaken indicate that significant Cl-36 removal may be achieved through aqueous leaching. The impact of this effect is twofold: potentially as a treatment process the Cl-36 inventory could be reduced prior to disposal; however, such a process may also occur within the repository following resaturation.

Other radionuclides can only be removed in harsh environments and to a limited effect. This is a positive effect for untreated waste in a repository.

4.4 Task 4.4: Graphite Decontamination by Microbiological Treatment

Graphite decontamination by microbiological treatment is a promising alternative for C-14 separation as microbes incorporate C-14 from the surface of the graphite crystallites. The microbiological process makes use of the fact that a fraction of the total C-14 is produced by activation of N-14 and O-17 and adsorbed at the surface of the crystallites and pores.

It has been shown that microbes can process (consume) $Na_{14}C_2H_3O_2$ salt. This conclusion is supported by the shift of C-14 content from liquid to solid phase (bacterial biomass) and/or gaseous phase (bioreactor off-gas). This finding suggests that bacterial remediation of irradiated graphite may provide a means of C-14 removal. Experiments with, and analysis of, irradiated graphite would be necessary to determine the chemical form of C-14 and the viability of bacterial processing of that chemical in the radioactive environment. The actual chemical form(s) of C-14 in irradiated graphite may be a determining factor in the ultimate feasibility of such an application and a process based upon microbiological treatment is currently in a very early state of development.

An important outcome of this task is the identification of microbiological activity during the storage and disposal of irradiated graphite as a credible path for enhancement of the release of C-14.

5 Work Package 5: Graphite Reuse and Recycle

The objectives of this work package are stated as:

- To review existing graphite waste management methods and graphite manufacturing technology to establish any existing experience relevant to the development of recycle pathways.
- To identify new product production pathways and make new products from recycled i-graphite materials.
- To establish methods for separating C-14 for recycle and to match the resulting separated product to the market needs.
- To evaluate products from recycling activities for fitness for purpose.

The work has been broken down into four tasks and selected outputs from these tasks are summarised in the sections below.

5.1 Task 5.1: Review Existing Experience Relevant to Recycling

An extensive desk based review has been undertaken to consider:

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

Conventional graphite management is limited to two general approaches: encapsulation of the graphite waste for long term storage within a suitable repository environment and incineration with discharge of the resultant gas to atmosphere. The primary issues associated with long term storage of graphite relate to its radionuclide inventory (specifically certain key labile radionuclides with long half-lives such as C-14 and Cl-36), and the large volumes of graphitic wastes. The potential benefits of graphite decontamination include the potential to reduce the radionuclide to enable its reuse or its potential down classification (e.g. ILW to LLW) to enable reduced management requirements for its long term storage. Decontamination also provides the opportunity to derive valuable radioisotopes from the irradiated graphite (e.g. C-14), which have potential marketable end uses such as tracers for the radiopharmaceutical industry.

Decontamination processes are critical for removing a substantial proportion of the radionuclide inventory, simplifying the inclusion of carbonaceous materials within an industrial recycling process. They also dictate the form and properties of the recycled end product, and define the form and nature of the waste streams produced. These processes include graphite gasification (steam

reforming or oxidation with capture of volatile radionuclides and collection of residues), decontamination by 'roasting' (partial decontamination by selective removal of surface-located radionuclides), carbon re-deposition following gasification (effectively reversal of gasification producing products with residual activity suitable for reuse in the nuclear industry), chemical decontamination (unproven for large volumes but with the potential for reducing the radionuclide inventory), intercalation/exfoliation (increasing accessible surface area for radionuclide removal by another process) and direct reuse (shuffling components within a reactor to maximise useful life or use expended component as raw material for a new component). In the case of direct reuse, this option has been shown to be viable although of limited application due to carry-over of radionuclides. An intermediate reuse option considered was the production of carbon black. However, this product cannot replace coke due to its poor graphitisability and thermal properties. Other options include manufacture of silicon carbide and recycling carbon as high molecular weight aromatic hydrocarbons for use in pitch formulations.

5.2 Tasks 5.2 (Identification and Making of New Products), 5.3 (separation & Recycle of Radiocarbon) and 5.4 (Products Evaluation)

It is convenient to summarise the outputs from these tasks in the same way as that adopted in the WP5 summary report, namely to evaluate products together with describing the recycle/reuse process.

Graphite recycle to nuclear grade graphite

Pilot scale candidate products of nuclear grade graphite, which included a proportion of simulant recycled material (carbon black) were investigated. The purpose of the work was to understand whether the inclusion of recycled materials within new nuclear grade graphite (for use in moderator or fuel) would be achievable, and the end product still be viable for its intended purpose.

It is concluded from the results of trials that a maximum 5-10% of carbon black in the coke flour mix can be tolerated from process requirements and product properties point of view. The addition of carbon black as raw material had a significant impact on the binder demand, leading to products with higher porosity and structural defects. A significant and increasing deterioration of mechanical and thermal characteristics is observed with increasing amounts of carbon black in the formulation. Mechanical characteristics might still be improved through a secondary raw material preparation, i.e. producing a precursor from carbon black and pitch, baking and crushing the baked product for using it as raw material component for nuclear graphite production instead of plain carbon black. However, the thermal properties would only be marginally affected, keeping the addition limit for carbon black (and hence i-graphite decontaminated via the gasification route) still at around 10%.

Direct use of i-graphite or material from other decontamination routes was not considered due to the presence of critical radionuclides which constitute a particular issue when producing moderator/reflector graphite on an industrial scale of several hundred tons.

Graphite recycle to electrodes for waste vitrification

Manufacture of a recycled graphite via an innovative, fast processing technique to produce graphite electrodes for use in the nuclear industry for waste vitrification has been investigated. The study had

two objectives: defining the maximum fraction of carbon black or other recycled material that can be utilised in a "new" graphite artefact without compromising physical and mechanical properties and defining the ideal processing conditions to a fraction of carbon black and/or other recycled material.

The electrodes were fabricated using a mixture of petroleum coke, binder (coal tar) pitch and varying fractions of carbon black additive (as a surrogate for recycled graphite). The study demonstrated that carbon black loadings can easily be accomplished up to 5 parts per hundred of the dry fraction of the material. Higher loadings could probably be achieved by focusing on other methods to ensure more homogeneous mixtures prior to forming the artefact. The final properties of the manufactured graphite were within the 'acceptable' range for the purpose of vitrification of nuclear waste. Further development work could also be done to significantly strengthen this material and improve the other basic properties of the graphite.

Graphite recycle into silicon carbide

The production of silicon carbide (SiC), from graphite has been investigated with various potential end uses, including its use as a ceramic for embedding spent fuels. The preparation of porous SiC ceramics from stoichiometric mixtures of silicon and graphite was studied. Based upon tests with virgin graphite, it was concluded that pure SiC from graphite and silicon can be formed directly. However, the same procedure applied to irradiated graphite produced different results, leaving a small amount of free carbon present after the reaction process. The differing behaviours have not been explained.

The primary focus of this study is the development of a robust leach resistant material for use as a packing material for wastes under repository conditions. A series of leaching experiments were performed on irradiated graphite and SiC using three types of leachants: Q-brine, clay and pore water, at room temperature and at 90ºC. The measured activities of C-14 leached from irradiated graphite were much higher compared to the ones leached from the SiC made from the same graphite. The transformation of irradiated graphite into silicon carbide could be a way of decreasing C-14 release from the material. However, because of the limited amount of available irradiated graphite, tests were done with a very small amount of irradiated graphite compared to the silicon carbide and this could have some influence on leaching rates. Further testing would be necessary to confirm that silicon carbide prepared from irradiated graphite is a suitable product for reducing the release of C-14.

Graphite reuse for decontamination of waste streams

This study has investigated the use of irradiated graphite for the decontamination of both liquid and gaseous waste streams containing certain radionuclides, which include C-14, Cl-36 and I-129.

At nuclear installations, clothing decontamination is achieved with different detergents and the resulting effluent contains organic residues. In order to release this effluent to the environment, the organic contaminants must be removed. Irradiated graphite has been used as an adsorption medium to capture known soap detergents.

Research in the past has focused on improving processes for the removal and recovery of radionuclides from nuclear waste streams using ion exchange resins. Expensive resin material

becomes contaminated and has to be disposed of. By replacing the resin with irradiated graphite, contaminated material could be used to recover radionuclides from these waste streams. Adsorption coefficient values for Sr-89, Ag-110m and I-131 indicate that irradiated graphite can be used as an ion exchange medium. The treatment of graphite with silver nitrate may enhance the removal of radioactive iodine from waste streams based upon preliminary results of experiments to determine adsorption on the carbon nanotubes. Preliminary results of experiments to determine the adsorption of Cs-137 and Co-60 on graphite show the former not being absorbed but the latter being adsorbed at higher pH. C-14 was observed to leach out of the irradiated graphite posing a contamination risk. Experiments were also performed to study the adsorption of different radionuclides (Co-60, Cl-36, I-131 and Na-22) from a liquid waste stream (acid and alkaline) onto irradiated graphite. Only Co-60 in an alkaline medium was found to be adsorbed onto i-graphite. When the i-graphite was impregnated with Ag, the absorption of Cl-36 in acid solution increased.

The potential for using irradiated graphite to remove radionuclides from waste gas streams has been investigated, focussing on iodine and tritium. Testing has not advanced sufficiently to draw any conclusions.

These results show that considerably more testing would be necessary to characterise the adsorption behaviour of irradiated graphite before the viability of such applications could be assessed.

Direct reuse of graphite for various applications

Consideration was given to the reuse of graphite as electrodes to dissolve spent fuel. However, this potential application was abandoned due to the undesirability of contamination of the electrochemical system.

The reuse of irradiated graphite blocks as crucible material for radioactive waste treatment has been considered. Chemical etching technology was studied as a means for the manufacture of waste or molten salt containers (crucibles), avoiding contaminated dust generation. With a combination of mineral acids, it has been possible to create a smooth cavity inside a graphite structure without damaging the surface area (no cracks). Further work would be necessary to determine if any radionuclide transfer between the graphite and molten salt occurs.

Two further potential applications have been considered: the use of graphite blocks as disposal containers for solidified matrixes and the manufacture of nanotubes with DC plasma for radionuclide capture. In the latter case, adsorption of iodine has been shown to occur on commercially available single-walled nanotubes without any surface modification in a low pH (but decreasing significantly with the addition of the bipolar solvent). Adsorption of Cl-36 is also being investigated.

None of these direct reuse applications has been developed sufficiently to enable any assessment of their viability.

Isotope separation

There are three types of isotope separation technique:

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

Various methods exist for the separation of isotopes although not all of these have been or can be readily applied in the separation of C-14 from C-12. The isotope separation techniques described below are considered independently of each other. However, it may prove feasible to employee two techniques, the first to address the large volumes, and a second to focus on achieving a high purity C-14 product (for example).

Pressure Swing Adsorption (PSA) technology is an industry proven approach for the separation and purification of gases. PSA is potentially applicable to separate C-14 components of the outlet gas during the thermal treatment and gasification process of radioactive graphite by concentrating C-14 oxides and converting them into a solid form for disposal as an intermediate level waste. Based on previous work in Japan, it has been estimated that the Japanese PSA process will remove and concentrate at least 40% to 60% of the radioactive C-14. The PSA unit for separation ^{12}CO and ^{14}CO isotopes has only been demonstrated at lab-scale. More recent research and development studies and adsorption modelling indicate that up to 90% removal efficiency of ^{14}CO from ^{12}CO is possible using special adsorption media and column operations. Significant additional theoretical and laboratory work would be required to demonstrate the suitability of the process at an industrial scale with a mixed gas stream.

The gas centrifuge technique was specifically developed to separate the isotopes of U-235 from U-238, and was developed to replace the gaseous diffusion method of U-235 extraction. The gas centrifuge relies on the principles of centripetal force accelerating molecules based upon mass. Once started, a modern centrifuge can run for more than 10 years with no maintenance. An advantage of the centrifuge process is its low energy consumption. The feasibility of separating C-14 from C-12 by this method has been investigated, as a means of treating the potential off-gas produced through steam reformation. Aspects being considered include: quantitative estimate of the separative work needed as function of process gas and the degree of C-14 enrichment; rudimentary cascade design (number of stages) for a multi-isotope feed with isotopes C-12, C-13, and C-14; estimate of the enrichment cost based on the current market price for uranium enrichment; the additional cost for the preparation/conversion of the process gas has to be considered. Restrictions have been placed on the findings of this study.

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. This process takes place at almost ambient temperature, but involves boiling and cooling, which entails significant energy costs which could be limited by the use of an appropriate heat exchange system. The separation factor for C-14 with the amine carbamate exchange process is 1.02 (the same as with cryogenic distillation). However, distillation and gas liquid exchange cannot go further than separating C-13 and C-14 together from C-12; the reason for this is there will always be much more C-12 and C-13 than C-14. This shifts the process towards endlessly separating C-12 from C-13 with little impact on C-14. There are as yet no reports of any scale-up applications. One problem appears to be that the separation efficiency depends on

rapid transfer of carbon dioxide between the gas and liquid phases, and this transfer appears somewhat slow. Additionally, the theoretical plateau height is much higher with amine carbamate, than with cryogenic distillation, which leads to the requirement for larger columns.
It is important when considering the cost of this technique, to factor in the cost of the eventual dismantlement of the sizeable columns which is likely to generate thousands of tonnes of waste.

A US patent refers to the cryogenic distillation of carbon monoxide as a means of enriching C-14 in a single stage. Although simpler than the PSA technology, the very low temperatures required for this process are a drawback. Also, the initial ratio of C-14:C-12 considered in this patent is much higher than that expected from a graphite-incineration process (for example) and thus that the number of distillation stages required, and hence the cost, would be very high. The separation factor for C-14 with the cryogenic separation exchange process is 1.02. A development of this procedure achieves separation as the dioxide, using a re-circulating system on successive batches of resin until the C-14 in the dioxide builds up to a sufficient concentration using an adaption of the PSA technology. At this point, separation can be effected, again as the monoxide, using zinc as a reductant. 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.

A diffusion method has been considered for isotope separation. Two isotopes with the same energy will have different average velocities, but the lighter atoms (or the molecules containing them) will travel more quickly and be more likely to diffuse through a membrane. The difference in speeds is proportional to the square root of the mass ratio, so the amount of separation is small and many cascaded stages are needed to obtain high purity. Diffusion is unlikely to be a viable option for the separation of C-14 and C-12, as it has been superseded by isotope separation by the gas centrifuge technology which has lower energy requirements as well as the required plant having a significantly smaller footprint.

Carbon tetrafluoride distillation has been proposed as a potential means of separating carbon isotopes, analogous to the separation of boron isotopes by the distillation of boron trifluoride etherate. However, no investigation of this approach has yet been attempted.

Separation of Isotopes by Laser Excitation (SILEX) is a technology developed in the 1990s for isotope separation to produce enriched uranium using lasers. This technique potentially provides a means for the separation or enrichment of isotopes of other elements including carbon although such an application has yet to be investigated.

Little information is yet available on the economics of isotope separation as applied to radiocarbon, but it is likely that any isotope enrichment process will be relatively expensive and unlikely to be applicable to the majority of the graphite waste. However, isotope separation could be important for certain graphite wastes, or fractions thereof. For example, if a small C-14 rich fraction were released from graphite by heating (roasting), this fraction could undergo isotope separation to yield a pure C-14 product. The C-14 could potentially be sold to users of the isotope (such as producers of isotopically labelled chemicals), thereby displacing alternative production routes.

C-14 recycle and supply

The presence of the isotope C-14 is usually considered a problem in the management of irradiated graphite waste. However, the isotope is used in many applications of chemistry and medicine in quite significant quantities. In order to achieve such recycling, two developments would need to take place. First there needs to be an efficient means of separating the C-14 from the graphite, and second the resulting product needs to have the right characteristics of chemical form, isotopic purity and quantity for supply to the market. It also needs to have the right price.

The potential industrial recycle of C-14 over a number of years could use a significant proportion of the total i-graphite inventory, although it is most unlikely that most or all C-14 in irradiated graphite could be recycled. For example, one UK manufacturer of products annually uses approximately 0.3% of the inventory of UK's Magnox reactors. Although C-14 is produced for manufacturers by reactor irradiation of nitrogen species and hence is available to them in high isotopic purity, a lower specific activity (i.e. isotopic dilution) could be acceptable to manufacturers as input material for some applications.

The possibility of recycling material directly from irradiated graphite (without isotope separation) has been examined. This would involve using 'roasting' techniques to produce a fraction with the highest possible specific activity of C-14, and selecting graphite with the highest possible C-14 activity for recycle. It is concluded that the gap is probably too large to bridge without some purification by isotope separation. The appropriate selection of graphite (and a 'roasted' fraction from it) would allow any isotope separation process to be conducted on a more economically beneficial small physical scale. However, more results from thermal treatment tests would be needed to determine achievable specific activities and the associated economics of recycle.

The studies have shown that large-scale application of these processes is generally not economically viable. Small-scale diversion of appropriate material through these processes is possible, but the impact on repository size for the remainder would be insignificant.

The SiC process has the potential to use graphite to replace grout or other encapsulants in immobilising other wastes. This is likely to be dependent on a significant qualification programme to determine suitable candidate wastes.

6 Work Package 6: Disposal Behaviour of Graphite & Carbonaceous Waste

The objectives of this work package were defined as follows:

- Determine the disposal properties of each primary or secondary waste product and waste packages; and
- Provide a "disposal point of view" on best practices for graphite/carbonaceous waste management.

6.1 Task 6.1: Disposal behaviour of i-graphite

Detailed knowledge has been generated on the behaviour of i-graphite under disposal conditions in case of direct disposal. The mobilisation of long-lived radionuclides like C-14 and Cl-36 is a key question for long term safety. The mobility of radionuclides under repository conditions prior to water access is an important concern. Access of water to the pore space in graphite as a first step for the release of radionuclides from graphite has been studied as well as corrosion of the graphite matrix and diffusion of radionuclides.

Review of leaching data on irradiated graphite

Work has been undertaken by EDF, Andra, CEA and the University of Manchester to understand C-14 and Cl-36 leaching behaviour under disposal conditions.

Overall, Cl-36 experiments were almost exclusively carried out on i-graphite samples from UNGG reactors whereas much more data are available for C-14 leaching under disposal conditions, mainly on Magnox and UNGG graphite samples. For both radionuclides, two stages have been evidenced for the leaching behaviour in disposal conditions:

- A first stage showing very rapid release kinetics (labile fraction); and
- A second stage showing slow release kinetics (non-labile fraction).

It has been shown for both radionuclides that water uptake kinetics through graphite pores is not a limiting factor that could explain the observed two stages. Unlike non-irradiated graphite where water impregnation is slow and low (saturation rates observed between 30% and 40% of the open porosity in samples after a period of 500 days), i-graphite is a hydrophilic material with fast water uptake kinetics and almost full saturation of open porosity. A possible relation between C-14 and Cl-36 releases and the graphite coke nature has been suggested. It has been found that the coke directly affects graphite radiological inventory but no clear correlation can be currently established with radionuclide leaching behaviour.

More specifically, a huge discrepancy on Cl-36 leach rates ranging from 10 to 90% of the Cl-36 inventory has been evidenced. These results confirmed previous results: Cl-36 leach rate depends on i-graphite operating temperature. High release rates are observed for samples that were irradiated at low temperatures whereas high irradiation temperatures lead to low release rates. The origin of this phenomenon is still unclear but it is believed that it could be related to two different Cl-36

chemical forms in i-graphite, leading to different release rates. The initial "spike" release – up to 80% of the total Cl-36 inventory – may correspond to Cl-36 atoms that are weakly bound to graphite or located in the graphite macroporosity. The evolution of the cumulative leached fraction and tests in diffusion cells indicate that such a release is a diffusion-driven process. The residual Cl-36 fraction is non labile and is released very slowly. It is assumed to be strongly bound to graphite and/or located in graphite infraporosity. Structural changes in i-graphite due to an annealing effect depending on operating temperature can also be put forward to explain these results.

C-14 leaching rate appears to be very low in disposal conditions when compared to Cl-36. It is always below 5% of the inventory; however, a sharp increase in C-14 release is observed under acidic conditions (HCl, H_2SO_4, H_3PO_4). Discrepancies are also observed between different graphite but no sizing parameter can be evidenced. At the beginning of the CARBOWASTE project it was assumed that C-14 arising from C-13 activation was located into the graphite matrix and was weakly mobile. In contrast C-14 arising from nitrogen activation was supposed to be mainly located at the surface of the graphite and so to be much more mobile. That assumption cannot be confirmed based on results on BEPO (air cooled reactor) samples and Wylfa (Magnox CO_2-cooled reactor) samples but cannot also be ruled out. More experiments are needed to answer.

It should be noted that slight differences are observed between results obtained on UK i-graphite (BEPO and Wylfa Magnox) and UNGG graphite. Whereas release rates obtained on BEPO and Magnox graphite can reach more than 1% (up to 5%) of the inventory, release rates experienced on UNGG graphite are always lower than 1%. Radiolytic corrosion that was observed to some extent in UNGG reactors could be at the origin of C-14 loss during operation leading to a mobile fraction of C-14 lower than in UK graphite.

Compilation of all the data collected to date on C-14 and Cl-36 leaching behaviour has produced a clearer picture of their expected release rate under disposal conditions, at least for the tested reactors. In contrast, there is still work to do regarding the understanding of their release behaviour and of their speciation which is of crucial importance for disposal performance assessments. More specifically, the key issue of C-14 speciation both in solution and in the gaseous phase has not been addressed.

Another key issue concerns the representativeness of leaching data. As shown in WP3 through i-graphite characterisation studies and i-graphite radiological inventory assessment, i-graphite is a heterogeneous material by itself and huge discrepancies have been observed between i-graphite depending on their operation conditions but also on their origin (coke used for graphite manufacturing). Such an issue is not only true from one reactor to another but also within the same reactor (e.g. Cl-36 leach rata variability depending on the irradiation temperature) and between pile samples and other i-graphite operational waste whose leaching behaviour has not been addressed within the CARBOWASTE project. These issues should be further investigated for disposal purposes but for treatment purposes as well.

There are still uncertainties on leaching results, and it is not expected that future works will significantly modify release models under disposal conditions. In this regard, conservative assumptions have to be made in particular for Cl-36 whose inventory is considered to be fully released upon contact with water. In France, this has led Andra to define a minimum clay thickness

of 50 metres for the design of a shallow disposal facility for graphite waste. This geological barrier should secure radionuclides migration and delay their discharge to the biosphere.

6.2 Task 6.2: Disposal behaviour of carbonaceous waste

The different treatment and recycle options will produce lower active graphite (if disposal is necessary this has been studied in task 6.1) or higher active secondary carbonaceous waste, whose disposal behaviour has been studied in this task.

Disposal Properties of Carbides as a waste form for C-14

Silicon carbide formed from irradiated graphite (in WP5) was studied under repository conditions. Three leachants were used (granite water, clay pore water and Q-brine), the leaching was done at room temperature and at 90ºC. The material was leached during a period of 160 days, with sampling every 40 days. Irradiated graphite was studied at the same conditions.

For the silicon carbide experiments, the measured activity of C-14 found in the leachant was in units of tens of Bq/g of silicon carbide. The leachant in Q-Brine was about two to three times higher active at the temperature of 90ºC than at room temperature. No significant influence of temperature on the leaching behaviour of the SiC powder in clay water was observed. In the granite water, higher activities were measured at room temperature.

The measured activities of C-14 leached from irradiated graphite are much higher comparing to the ones leached from the SiC made from this graphite. The measured activity of C-14 in the leachant was in hundreds to thousands of Bq/g of irradiated graphite. Also for graphite, the highest activity of C-14 was found in the Q-Brine leachant.

Based on the above, it seems that the transformation of irradiated graphite into SiC could be a way of decreasing the C-14 release from the material. Because of the limited amount of available irradiated graphite, the above-mentioned tests are done with a very small amount of irradiated graphite (0.02 g in 20ml leachant) compared to the SiC (0.4 g in 20 ml leachant). This could have an influence on the leaching rates. To confirm that SiC could be a suitable product formed from irradiated graphite concerning the lower C-14 release, more tests must be performed.

6.3 Task 6.3: Waste packages

Waste package designs should further improve disposal behaviour. Concrete is envisaged to be used as a waste package for i-graphite and a more resistant material such as SiC has been proposed for high level waste such as spent fuel.

Retention Properties of Cement for Cl-36

An important concern is the mobility of radionuclides in the waste package and its surroundings under repository conditions prior to and after water access. Graphite wastes usually contain the long-lived isotope C-14 and could also contain the very long-lived activation product Cl-36 arising from processes designed to remove heavy metal impurities during manufacture and/or sulphur

residual in the virgin material. Cl-36 is the major contributor to a potential dose resulting from disposal of i-graphite.

Concrete waste packages will be altered during the disposal due to leaching by natural water entering in the system. Retention properties of such a package depend on the mineralogical composition of the cement pastes, the alteration state of the material and the geochemical conditions of the water.

The present study aims at measuring the distribution ratio of Cl-36 in contact with a hydrated cement paste, under a controlled atmosphere, considering:

- Dependency with the alteration state of the cement paste;
- Kinetics of retention;
- Reversibility of retention; and
- Saturation effect arising from stable chloride already present in natural water.

The material studied is an Origny cement (CEM-V), which was mixed with water in 1997 (water to cement ratio = 0.38). The resulting CEM-V paste was kept in a portlandite ($Ca(OH)_2$) saturated solution over a four-year period to prevent carbonation and continue the hydration processes. In 2001, the samples were dried, crushed and sieved under a flow of argon. Several sieved fractions were then stored in HDPE vials in desiccators flushed with argon before closure.

A specific fraction of this powder has been used in the present study (100 - 200 µm). Fresh, deteriorated and degraded cement pastes were obtained by leaching different amounts of cement powder in closed batches under various conditions (solid to water ratio and composition of solution):

- fresh state: leaching of cement powder in artificial fresh cement pore water;
- deteriorated or degraded state: leaching of cement powder in degassed deionised water; and
- “natural” deteriorated state: leaching of cement powder in synthesised water representative of the pore water of a subsurface disposal site.

Experimental results show that the retention of Cl-36 is strongly reduced when chloride concentration increases, especially at degraded and deteriorated states. Based on these results, it appears important to be able to identify and quantify all chloride sources in a repository.

The retention isotherms give quite similar results for the deteriorated states, regardless of the solution used for leaching the initial cement paste (degassed water or synthesised “natural” water).

In conclusion, Cl-36 retention properties depend on the alteration state of the cement paste and also on the saturation effect generated by stable chloride ions provided by several sources in a repository (e.g. the “natural” water and the concrete itself).

Wet chemistry measurements show that distribution ratios (Rd) values slowly increase during the first 20 days of contact time, and then, whatever the case, Rd reaches a steady mean value. Rd values are relatively low. The maximum Rd value (35 $ml.g^{-1}$) was measured for the degraded state and at a low chloride concentration (4.8×10^{-5} $mol.l^{-1}$).

Rd values measured depend on the alteration state of the cement paste. Measurements at deteriorated states lead to the conclusion that the retention process is reversible. Isotherms show that Rd values for Cl-36 strongly depend on the stable chloride concentration in solution. At high chloride concentration, the saturation effect is observed (non-linear sorption isotherm). Such results highlight the importance to know and quantify all main sources of stable chloride in order to be able to carry out performance assessment.

UK Waste Packaging Conception for Irradiated Graphite

The UK has accumulated a legacy of higher activity radioactive waste from electricity generation, defence activities and other industrial, medical, agricultural and research activities. The UK Government has undertaken a wide-ranging consultation on the best means of dealing with these wastes and has concluded that geological disposal, preceded by safe and secure interim storage, is the way forward for their long-term management.

The Nuclear Decommissioning Authority (NDA) has been charged with implementing Government policy for the long-term management of higher activity radioactive waste by planning, building and operating a Geological Disposal Facility (GDF), which is an engineered facility for the disposal of radioactive waste. A GDF is likely to be located at a depth of between 200 m and 1000 m below ground, in a stable geology that provides long-term isolation of the wastes from the human environment.

The implementation of a GDF for higher activity radioactive wastes requires the NDA Radioactive Waste Management Directorate (RWMD) to demonstrate its confidence that such a facility would be safe, during both the operational period and after it has been sealed and closed. As part of that process, RWMD has developed the Disposal System Safety Case (DSSC), the prime purpose of which is to demonstrate that a GDF can be implemented in a safe manner and in such a way that would meet all regulatory requirements.

For many years RWMD, and the predecessor organisation Nirex, has produced specifications for packaged radioactive waste, including irradiated graphite. These specifications define generic standards and performance requirements for waste packages which will be compatible with the systems and safety cases for transport to and disposal in a GDF, therefore ensuring that packaged radioactive waste has characteristics that are compliant with the assumptions in the DSSC.

Currently generic specifications exist for two broad categories of waste, the *Generic Waste Package Specification* (GWPS), for waste packages containing Intermediate Level Waste (ILW) and Low Level Waste (LLW) (which includes irradiated graphite) and a specification for waste packages containing vitrified High Level Waste (HLW) and spent nuclear fuel.

The RWMD disposability assessment process exists to support UK Site Licence Companies (SLCs) that wish to condition and package higher activity wastes – including irradiated graphite - in a form that is compatible with plans for the implementation of a GDF. It is also used to support the ongoing development of the safety cases for geological disposal by the provision of information regarding the numbers and properties of the waste packages that will eventually require transport to and disposal in a GDF.

Through application of the disposability assessment process RWMD, together with the site operator and regulators, gain confidence that proposed waste packages will ultimately be compliant with requirements for transport and disposability. This may involve relevant parties together considering different packaging approaches and determining which combination of barriers (wasteform and waste container) best meet the needs for waste retrieval, processing, storage and ultimately, disposal. This is important as it gives confidence that packaging strategies, and ultimately investment decisions, are soundly based and will result in waste packages designed in line with transport and disposal requirements. Confidence in the developing DSSC is built up over time through a periodic review process by which the validity of disposability assessments are maintained by ensuring that they remain up to date and consistent with the DSSC as concepts for geological disposal evolve towards an operational GDF.

The main purposes of disposability assessments are therefore to:

- Give confidence to site operators (and waste owners) that the implementation of their proposals for waste packaging will result in waste packages that best meet the needs for processing and storage whilst being compliant with the eventual needs for transport to and disposal in a GDF;
- Provide confidence that the disposal concepts considered within the DSSC will be appropriate for the wastes they will be expected to cover; and
- Permit the identification of wastes that could challenge current disposal concepts and allow early consideration of what changes may be required to these concepts to permit the wastes to be accommodated.

In undertaking disposability assessments RWMD determines whether packaged wastes will have characteristics compliant with the safety case requirements for transport to, and operations at a GDF, and ultimately whether the wastes could be accommodated within a GDF post-closure safety case, i.e. that the packages are ‘disposable’. The main output of the assessment is an Assessment Report detailing the work undertaken and which may be accompanied by a Letter of Compliance (LoC); a statement to the effect that the waste package as described in the submission has been assessed and found to be compliant with transport and geological disposal as currently defined. Regulators’ guidance requires that waste packagers (Site Licensees) produce a Radioactive Waste Management Case (RWMC) which includes reasoned argument why packaged waste will be disposable – the disposability assessment and accompanying LoC will provide an important component of such a case.

Decisions on the long-term management of the large volume of irradiated graphite present in the UK waste inventory have not yet been made, noting that the reference position is geological disposal and that relevant waste packaging specifications have been developed. Four options for the management of UK graphite have been identified. NDA is undertaking a number of projects to further develop the understanding of these options. Future work will consider:

- Option 1 – **Geological Disposal** (reference position): The intention is to work with NDA RWMD’s “Upstream Optioneering” project to determine where there are opportunities to “optimise” the baseline option for the management of graphite.
- Option 2 – **Condition to Enable Disposal at the Low Level Waste Repository (LLWR):** NDA will work with LLWR Limited to better understand the potential capacity at LLWR

for graphite wastes in order to improve understanding of this option and enable it to be compared with other options for the management of graphite wastes.

- Option 3 – **Condition Graphite to Remove Contamination and Enable Free Release or Re-use**: Complete the active trials at the Studsvik facility and monitor the progress on international developments, for example research into pressure swing absorption.
- Option 4 – **Near Surface Disposal**: NDA will consider the outputs of the Hunterston A project and review the business case for continuation of the project. NDA will then also determine how this project will contribute to its understanding of near surface disposal of other graphite wastes.

6.4 Task 6.4: Assessment of waste performance

Performance of the waste disposal concept has been analysed (i) from the point of view of a near field/waste package model and (ii) from the point of view of an overall performance evaluation.

The following sections summarise assessment studies undertaken as part of CARBOWASTE for both surface disposal facilities (ENRESA and INR), and deep geological disposal facilities (NDA RWMD and LEI) in the context of respective national waste policy, national regulations and national graphite waste inventory. The approach taken in France to irradiated graphite is also considered. Conclusions are drawn, based on CARBOWASTE studies, of the disposability of irradiated graphite in surface disposal facilities and geological disposal facilities that are backed by participating national waste management programmes.

Spain: Summary of work by ENRESA – Spanish disposal concept and surface disposal analysis

The long term safety assessment of the disposal system, for radionuclide release, is directly linked with the concept of radionuclide retention properties of the different media considered, that oppose to the migration from the waste to the biosphere, analyzing the behaviour of the barriers applied (wasteform-condition material, container, cell, backfill, geosphere). On the other hand, for the scenario analysis of human intrusion after surveillance period of 300 years, the most important issue with regard to Waste Acceptance Criteria (WAC) is the activity content of the wastes.

Assessment scenarios considered are related to the construction of public buildings or residences with agriculture activities. Exposure, inhalation and ingestion pathways are assessed. The dose limits considered for the scenarios are 1 mSv/y and 0.1 mSv/y.

The concrete container is considered as a barrier. Transport properties analysis has been performed to quantify the effective diffusion coefficient, De, distribution coefficient, kd, permeability and hydraulic conductivity.

Waste packages also have to fulfil retention, specific leaching rates for wastes incorporated in cement, and diffusion values for those wastes conditioned using a mortar envelope. All these properties are required to be reported to the producers, and finally a quality control process is applied in order to verify the process complies with the WAC. In addition, the mortar that fills the gaps between packages is also supposed to meet the WAC requirement in relation to the retainable properties.

The most important issues for the Vandellos 1 irradiated graphite to be disposed in El Cabril are the C-14 activity content and the release of the labile fraction of C-14 and H-3 that are present along with the fixed fraction. The graphite matrix is itself a very stable material, and many leaching tests have concluded that the fixed H-3 and C-14 are quite stable in the irradiated graphite matrix over time.

Before putting the graphite inside any container it is treated by:

- Thermal decontamination under controlled non-oxidising atmosphere. This process will remove the labile fraction, which will be trapped in secondary waste. Additional C-14 and almost all H-3 are foreseen to be released.
- Impermeable Glass Matrix applied to the thermal decontaminated graphite. The final product is a very stable material, with a negligible or inexistent release rate of radionuclides.

Alpha emitters are low in the irradiated graphite, and strong gamma emitters (Co-60 mainly) are expected to be quite low after the period of surveillance (300 years). These considerations, along with the radionuclides discarded during thermal decontamination and the amount of irradiated graphite (3500 tonnes), make the doses produced by irradiated graphite in intruder scenarios equivalent or lower than the doses from other wastes.

Romania: Summary of work by INR - Romanian disposal concept and surface disposal analysis

The mass of nuclear irradiated graphite in Romania does not exceed 10 tonnes, coming partly from the thermal column of TRIGA reactor at INR site and partly from decommissioning of the VVRS reactor in Bucharest. The most important radioisotopes for long term activity of disposed irradiated graphite are C-14 and Cl-36.

The C-14 inventory estimated from combined graphite measurements and ORIGEN simulations in irradiated graphite from TRIGA reactor is 2.0×10^{10} Bq. For the Cl-36 inventory only, ORIGEN simulations are available that estimate it at 8.5×10^{9} Bq.

An optimal solution for the final disposal of irradiated graphite is sought and the most favoured option is currently disposal in a near surface repository, considering the low and intermediate level waste repository at Saligny site.

Performance assessment was accomplished with GoldSim software for irradiated graphite from the TRIGA reactor. The dose contribution was computed only for C-14 (gas and water pathway) and Cl-36 (water pathway). Two cases were considered: no engineered barriers - in order to obtain the most conservative dose value; and concrete as graphite encapsulation and disposal matrix. This ensures the safe isolation of the waste through the combination of the natural barrier (Saligny geology) with engineered barriers.

The dose assessment model proposed by INR is conceptual. The study assumes the independent disposal of 2.5 tonnes of irradiated graphite accounting for the TRIGA graphite inventory in a near surface facility having Saligny site characteristics. Only dose produced by C-14 and Cl-36 releases are assessed.

The current performance assessment of the near surface disposal does not take all the complex C-14 partitioning phases into account. Cl-36 behaves much simpler, being potentially released only in liquid phase and with no significant interaction with materials expected in a geological disposal facility. In the absence of dedicated studies to determine the leaching rate of C-14 and respectively Cl-36 from irradiated graphite of the TRIGA thermal column, the model uses fractional release rates of 1.7×10^2 1/yr for C-14 and 37 1/yr for Cl-36.

Two distinct cases were analysed:

- Case 1 assumes that both C-14 and Cl-36 are available for transport neglecting the concrete surrounding the irradiated graphite; and
- Case 2 considers 300 years of concrete barrier embedding irradiated graphite dispersed inside a disposal cell, 1 m high concrete liner as cell foundation and 0.60 m concrete walls around. To conform to the WAC for Cl-36, irradiated graphite disposal in a separate disposal cell is assumed.

In order to assess the impact on the annual individual dose, the model takes into account all contamination pathways: ingestion, inhalation and external exposure using the reference scenario corresponding to a residence farm built on the site after 300 years when the institutional surveillance ends.

The maximum total annual dose due to the C-14 summing all contamination pathways is estimated to an order of 1.0×10^{-2} mSv/year if no engineered barriers are considered and decreases to 1.0E-06 mSv/yr when cementitious barriers and sorption on cement are considered. The most important contribution to the dose is given by C-14 inhalation as $^{14}CO_2$, in both cases while external exposure contribution to the dose is negligible.

If no engineered barriers are considered (Case 1), the value for Cl-36 dose largely exceeds the accepted dose limit (1 mSv/year). If the graphite is dispersed in a cementitious matrix inside a disposal cell, the dose value becomes acceptable, the maximum having the order of 1.0×10^{-2} mSv/yr. For Cl-36 the most significant contribution to the dose is given by ingestion, in both cases.

In summary, C-14 does not represent a concern for surface disposal of irradiated graphite from the TRIGA reactor, neither as gas nor as solute. Cl-36 could be accommodated in a surface repository if appropriate disposal concept minimising the specific activity under the WAC limit is considered. Under these conditions, the dose constrain is fulfilled.

Lithuania: Summary of work by LEI - Study on geological disposal of graphite

The graphite reactor core elements from the Lithuanian nuclear power plant at the Ignalina site are from RBMK-1500 reactors. Two units of Ignalina NPP were equipped with RBMK type reactors consisting of graphite as a moderator and reflector. There is no final decision on the long-lived ILW disposal option or disposal container in Lithuania. The ILW (including irradiated graphite) are planned to be stored in the steel containers at interim storage facility until the final decision will be made. According to proposed generic repository concept for RBMK-1500 Spent Nuclear Fuel (SNF) disposal in the crystalline rocks in Lithuania, the long-lived ILW could be disposed at the same repository at a certain distance from SNF emplacement tunnels. Within this study, a cementitious grout (NRVB backfill) was assumed as proposed in the Nirex (UK) concept.

The main task for LEI was to study the differences between treatment and disposal options on the behaviour of RBMK-1500 graphite in crystalline rock. The source term was based on the analysis performed by LEI within CARBOWASTE WP3. The amount of graphite waste coming from the Ignalina NPP Unit 1 and Unit 2 has been taken into account (in total ~3800 tonnes).

The release rate at which the radionuclide is being released by leaching in groundwater depends on the waste matrix itself and whether or not the waste form has been pre-treated. Leaching experiments of graphite indicate an initially higher release rate upon contact with repository water and a slower release rate at longer times. This corresponds to the different location and origin of C-14 within the waste and its availability to be released. The importance of the waste leaching rate was analysed within the context of different performance of engineered barriers considering three different cases each supplemented by a number of variants.

Modelling of the radionuclide migration within the near field was performed using the AMBER code (UK). The model for the radionuclide transport through the geological formations was developed with the TOUGH2 (USA) computer code. Modelling was undertaken for two options, one using the reference near field model (for non-encapsulated waste) and an alternative near field model (considering possible encapsulation).

Considering sorption, the impact of waste encapsulation is significant and leads to a decreased peak C-14 flux by up to approximately one order of magnitude in comparison to the non-encapsulated waste.

Modelling results of C-14 transport with no interaction in the near field showed that the differences in leaching rates do not lead to the same differences in the peak flux to the geosphere. Radionuclides released from graphite at rates of the order of 1.0×10^{-2} to 0.1 1/yr were released to the geosphere at a similar rate as in the case of instant release. If the radionuclides were released at lower rates (the order of 1.0×10^{-3}, 1.0×10^{-5} 1/yr) the flux to the geosphere becomes more dependent on the leaching rate. Due to transport and chemical interaction with backfill material (in terms of sorption and solubility), the C-14 flux to the geosphere was significantly decreased and the maximal fractional flux is in the range of 1.0×10^{12} to 1.0×10^{11} 1/yr.

Modelling results showed that the natural barrier system contributes to the significant delay of radionuclides even with conservative assumptions on engineered and natural barriers, with a significant decrease of the maximal peak flux rate by at least five orders of magnitude.

United Kingdom: Summary of work by NDA RWMD - UK study on geological disposal of graphite

Calculations in support of a study to examine the suitability of irradiated graphite wastes for geological disposal have been undertaken for the UK national inventory of irradiated graphite wastes, which comprises a significant volume of waste and a significant associated radionuclide inventory. Therefore conclusions that are drawn regarding the suitability of irradiated graphite wastes for geological disposal are relevant to large waste inventories, not only small quantities of irradiated graphite.

The analysis has demonstrated that it should be possible to safely dispose of irradiated graphite wastes in isolation (i.e. in vaults containing only packages of graphite wastes) in a wide range of

disposal systems (i.e. combination of disposal concept / Engineered Barrier System (EBS) and geosphere); including near-surface, shallow and deep geological disposal and a wide range of host rocks. Assessment calculations show that regulatory guidelines can be satisfied even given conservative assessment assumptions. A broader range of systems might be suitable given less conservative calculation assumptions. One particular issue that potentially requires careful management is the potential impacts associated with disruption of, or large scale intrusion into, near-surface facilities.

It may also be possible to safely dispose of irradiated graphite wastes in the same vaults as other ILW in a wide range of disposal systems. However, a broader range of processes become important, behaviour becomes more site / design specific and the important scenarios and behaviours may change as the system evolves. This makes it difficult to generically explore the suitability of graphite for geological disposal with other ILW.

Specific waste types of concern are those that give rise to bulk gas generation (i.e. metals, organics, strongly irradiating wastes) and that might lead to incorporation of C-14 in methane gas (i.e. organics), and therefore increase the potential for generation and transport of C-14 labelled gases. The potential for transport of C-14 labelled gases is particularly important for fractured host rocks and potentially for lower permeability host rocks where the concept includes an Engineered Gas Transport System (EGTS) to control the peak gas pressure.

Therefore, although it may not be necessary in all cases, there are advantages to disposing graphite wastes in isolation compared with co-disposal in the same vaults as other ILW. These include:

- simpler, more predictable behaviour;
- improved performance, e.g. transport in gas not likely to be an issue; and
- simplified safety arguments and safety case.

With increasing organic and metal (particularly reactive metal) waste inventories in the disposal vaults, the potential total bulk gas generation rate will also increase (given certain assumptions, in particular assuming sufficient water is available to support corrosion). This has the potential to significantly increase the mobility of C-14 via a number of complex processes.

In the UK, the majority of the graphite waste (by volume and radionuclide inventory) is classified as Shielded ILW (SILW). SILW contains relatively little quantities of organic and reactive metals, which are largely associated with Unshielded ILW (UILW) wastes. Further segregation of graphite from other SILW should be relatively straightforward and might offer performance benefits, for example through the ability to optimise the disposal concept for graphite wastes.

If transport of C-14 in gas is of concern for segregated graphite waste packages, e.g. potentially in a fractured host rock, it is likely that further performance benefits would be obtained from disposing graphite in concrete containers rather than steel containers, thereby reducing bulk gas generation to a very low level. This would also reduce the potential for reduction of inorganic C-14 to $^{14}CH_{4(g)}$ by autotrophic bacteria, using H_2 derived from anaerobic corrosion of steel, to a very low level. The potential significance of this process for isolated packages of graphite waste in steel containers is uncertain, although the available information and expert judgements indicate that it is unlikely to be significant.

Potential doses associated with human intrusion into a GDF containing graphite wastes are not insignificant. However doses associated with graphite wastes are likely to be lower than those associated with other waste types likely to be consigned to such a facility. This is because the dominant radionuclides for such scenarios (strong gamma emitters and alpha-emitters) are not present at significant concentrations in graphite. Therefore, external doses from examining borehole cores and associated situations are lower than for other ILW types.

Potential doses associated with human intrusion into untreated graphite wastes are significantly greater for an Surface Disposal Facility (SDF) where large scale excavation of solid material is possible. Similarly, large scale disruption of an SDF by natural processes and events could lead to significant doses to subsequent site occupiers, compared with regulatory guidelines. In both cases doses are due to uptake via the food chain. Therefore for an SDF, were untreated graphite wastes to be disposed, the significant potential for large scale human intrusion and the fate of exposed material could be important considerations in determining the acceptability of the concept.

For deep geological disposal, natural disruptive events are very unlikely to significantly enhance the potential dose from graphite wastes. An event could potentially result in a more conductive groundwater pathway to the surface. However, the key radionuclide in graphite wastes for such a pathway, Cl-36, is sufficiently long-lived and mobile that, for many host rocks, an enhanced pathway is unlikely to significantly affect the peak dose or risk, just the time at which it may arise.

French Irradiated Graphite Management Scenarios

In France, i-graphite accounts for ~23,000 tonnes of IL-LL waste, and mainly arises from former UNGG reactors (graphite moderated reactors, fuelled with natural uranium and cooled with CO_2) that were operated in France from 1956 to 1994.

Initially, French i-graphite was planned to be disposed in a dedicated disposal located between 50 to 200 metres underground. Such a scenario was notably based on the i-graphite content in Cl-36 which required a significant clay thickness in order to mitigate Cl-36 flow rate.

Since 2010 recent developments in graphite waste treatment and progress in radiological characterisation led Andra and waste owners to consider alternative management scenarios based on potential treatment and sorting, making it possible to open different disposal options. The following scenarios are thus being investigated from the perspectives of safety, cost and project risks:

- Separate management (sorting) of graphite sleeves and piles based on their different radiological inventory. In particular, Cl-36 inventory is currently assessed to be far lower in graphite piles than in graphite sleeves whereas piles represent the main part of French i-graphite tonnage (~18,000 tonnes). In this scenario, piles would be co-disposed with radium-bearing waste in a shallow disposal facility while remaining graphite waste, including sleeves, would be disposed with IL-LL waste 500 meters underground in the French deep disposal, Cigéo.
- Selective decontamination of graphite by means of thermal/chemical processes in order to make i-graphite inventory acceptable for shallow disposal. Partially decontaminated graphite would then be co-disposed with radium bearing waste in a shallow disposal facility while extracted radionuclides would be trapped, conditioned and disposed at Cigéo together with ILW-LL. If decontamination rates are high enough, partially decontaminated graphite could

alternatively be gasified into carbon dioxide. Residual ashes would then be disposed at Cigéo.
- A specific repository for the entire graphite waste inventory or alternatively direct disposal at Cigéo together with IL-LL waste.

The shallow disposal option consists of a repository implementation within a low permeability clay formation at a depth of about 15 metres provided the host formation is outcropping.

Within the framework of the Planning act of 28 June 2006, the geological repository, otherwise known as the Industrial Centre for Geological Disposal (Cigéo) is designed for HLW and intermediate level long-lived (IL-LLW) waste. It will be implemented in the Meuse / Haute Marne districts in the North-East of France. The underground repository cells are built at a depth around 500 meters below ground level within a thick clay rock layer. The disposal concept relies on the remarkable properties (retention capability, low permeability and homogeneity of the formation) of the clay rock which delays and mitigates the migration of the radionuclides contained in HLW and ILW-LL.

No overall performance analysis of the French case has been pursued within CARBOWASTE. Instead, a detailed modelling of waste performance has been performed.

Various alternatives of packaging concepts for graphite wastes based on CEMI and CEM V concrete were studied according to the origin of the graphite elements. Models were developed to describe both the degradation of the cement barrier and the transport of radionuclides across this barrier.

The goal of model development is to provide a chemical retention term to the source term model for C-14 release. Focus is on chemical/transport interactions of Cl-36 and C-14 on waste package level. Two models were developed:

- Diffu-Ca model from CEA, which considers cement degradation associated porosity increase and Cl-36 release; and
- SUBATECH model which avoids porosity increase due to the formation of carbonate minerals in clay water environments and describes C-14 release.

The Diffu-Ca model describes diffusion of radionuclides; this migration being influenced by the evolution of materials. It is assumed that the radionuclides (here Cl-36) are only transported by diffusion.

Cl-36 is released earliest when we consider degradation due to decalcification with early fractures and that the maximum reported activity flow is the most important with the calculations considering degradation with early fractures.

The case considering graphite waste package with degradation of cementitious materials and early fractures has the worst performance but is the most realistic one.

Full carbonation of the cement is calculated to take well beyond 100,000 years. While no interaction of organic C-14 with the cement is considered along the transport path, co-precipitation (isotopic exchange of C-14/C-12) is calculated to occur during carbonation of the cement. This

leads to accumulation of C-14 in calcite and a strong reduction of inorganic C-14 release. The retention of C-14 decreases slightly with time but even after 10,000 years more than 99.5% of released inorganic C-14 is retained in the calcite. All retention of inorganic C-14 is calculated to occur in the few centimetres of carbonated cement at the interface to the clay rock. The results show that cement is a very effective chemical barrier against inorganic C-14 release.

7 Key Outcomes from Project

- Graphite is a complex inhomogeneous material. Analytical methods need to be harmonised. Extensive sampling is necessary to achieve successful characterisation. Generalisations about its behaviour during irradiation and its final condition should be avoided. Source of material and irradiation history are key factors which will determine the ultimate condition of the material and the options for its management.
- Methods for the dismantlement of graphite cores are not limited to individual component extraction. The physical form of the retrieved graphite will be influenced by treatment and disposal options. Furthermore, packaging and ultimate disposal of the material at a deep geological repository or at a special site are not the only long term options.
- Notwithstanding the key determining factors of graphite source and irradiation history, data on the characterisation of graphite and on its treatment and leaching behaviour generated by different organisations with material from different reactors/facilities need to be pooled as a single database.
- Depending upon the radionuclide content of the specific graphite, decontamination by heat treatment presents itself as a credible option.
- The project has highlighted the potential for recycle and reuse of irradiated graphite as well as identifying new treatment and disposal concepts.
- The European collaboration on harmonising methods for performing leaching experiments and pooling data has provided a more complete and rational understanding of radionuclide mobility.
- CARBOWASTE does not define a single “best” way to manage graphite. This is not the objective of the project. Its objective is to improve scientific understanding and to identify graphite waste management options that meet the user’s criteria.
- It has created a European-wide collaboration on this specialist topic, which has now expanded to global cooperation through the International Atomic Energy Agency (IAEA).
- It has achieved better understanding through combining results and findings from different groups.
- It has started to make a practical difference to national plans and actions in managing graphite.
- CARBOWASTE is been an excellent example of knowledge transfer to the “next generation”.