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Graphite Decommissioning

Options for Graphite Treatment, Recycling, or Disposal, including a discussion of Safety-Related Issues

Technical Report

Graphite Decommissioning

Options for Graphite Treatment, Recycling, or Disposal, including a discussion of Safety-Related Issues

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REPORT SUMMARY

Many of the international participants in the EPRI Decommissioning Technology Program use graphite as a moderator material in their gas cooled reactors. This report reviews the current options for the management and disposal of irradiated nuclear graphite following the decommissioning of these nuclear installations. It also discusses specific issues associated with the disposal of graphite, and outlines innovative options for recycling or reusing products formed from the irradiated material.

Background

Although there are some examples of successful graphite disposition (most notably at Fort St Vrain in the US), utilities elsewhere have not yet made much progress with graphite management. This is due to a combination of “SAFESTORE” policies, concerns relating to safety of handling and disposal, and absence of suitable disposal facilities. In most cases, utilities have simply left graphite moderators of retired reactors “in-situ” and deposited graphite fuel sleeves in silos that are not suitable environments for long-term disposal. However, several countries (including the UK and France) have changed their policies and now require appropriate disposition of reactors and their graphite moderators and components as soon as possible. The methodology for safely dismantling and disposing of graphite waste has therefore suddenly become an important topic.

Graphite has particular characteristics that make it a very special waste form. Some of these issues include the phenomenon of stored “Wigner energy,” which contributed to the Windscale reactor fire in 1957, the perceived possibilities of conventional fire and dust explosion, and the problems associated with isotope inventories of carbon-14 and chlorine-36. Disposal possibilities include conventional burial, oxidation to the gas phase and release as carbon dioxide (with radionuclide retention as appropriate), or recycling into new graphite or carbon products.

Objective

To review the current options for the management and disposal of irradiated nuclear graphite following the decommissioning of nuclear installations that used it as either moderator or fuel component.

Approach

The project team reviewed data from various international organizations, particularly those in France, Italy and the UK, concerning the storage, handling and disposal of graphite, including safety issues, Wigner Energy, and fire and explosive hazards. The researchers addressed the properties of irradiated graphite, oxidation characteristics and radioactivity, and discussed methodologies for dismantling graphite cores. The report also reviews processing and disposal options and includes appendices that cover several of these issues in detail.

Results

The report concludes as follows:

- Adequate information exists to enable the safe dismantling and processing of graphite moderators.
- Concerns about Wigner energy are limited to the minority of reactors in which the moderator operated at low temperature. Since the phenomenon is well understood, the industry can define appropriate precautions to avoid unacceptable energy release.
- The report addresses fire and explosion hazards of graphite. Although graphite is a form of carbon and therefore potentially combustible, it is relatively resistant to oxidation, which is of value when considering safe handling, processing and disposal. Operators can also prevent any risk of a dust explosion during decommissioning activities.
- The radionuclide inventory of irradiated graphite is unusual in comparison with other nuclear wastes. Cobalt-60 and tritium are the principal isotopes of short-term importance; carbon-14 and chlorine-36 are dominant in the longer term.
- The three main options for disposal of graphite are oxidation to the gas phase and release as carbon dioxide, direct burial, or recycling into new products for the nuclear industry. In each case, opportunities exist for pre-processing to concentrate or remove radionuclides to enhance the safety of the chosen option.
- The possibility of recycling graphite into new nuclear industry products is in its infancy. In due course, this possibility may become very important, particularly if the industry proposes construction of new graphite-moderated reactors.
- It is unlikely that one single solution to graphite management will be appropriate everywhere since there are issues that may lead to the adoption of diverse solutions in different countries and for different reactors.

EPRI Perspective

The graphite moderators of retired gas-cooled nuclear reactors present a difficult challenge during demolition activities. As a result, utilities have not dismantled any moderators of CO2 cooled power reactors to date. The international participants in the EPRI Decommissioning Technology Program are now addressing the issues, and requested a review of available data. This comprehensive review provides valuable source material on the current state of knowledge, and points the way to further work on specific problem areas. Specifically, EPRI has initiated a detailed study of graphite dust explosions, and will address other topics later.

Keywords

Low level waste disposal
Graphite
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ABSTRACT

Although graphite is not a major waste form in LWR reactors it nevertheless represents a very significant problem in nuclear plant decommissioning for many of EPRI's international members. Graphite is used as a moderator material in many reactor types, particularly the gas cooled reactors in UK and France. It is also used for minor components such as fuel element sleeves. In all there are about 250,000 tonnes of graphite waste to be dealt with in decommissioning worldwide.

Although there are some examples of successful graphite disposition (most notably at Fort St Vrain in the US), not much progress has been yet been made with graphite management elsewhere. This is due to a combination of "SAFESTORE" policies, concerns relating to safety of handling and disposal and absence of suitable disposal facilities. In most cases graphite moderators of retired reactors have simply been left "in-situ" whilst graphite fuel sleeves have been deposited in silos which are not suitable environments for long-term disposal. However, several countries (including the UK and France) have changed their policies and now wish to see reactors and their graphite moderators and components appropriately dispositioned as soon as possible. The methodology and safety of dismantling, and waste disposition of graphite have thus rather suddenly become important topics.

Graphite has particular characteristics that make it a very special waste form. The phenomenon of stored "Wigner energy", which contributed to the Windscale reactor fire in 1957, the perceived possibilities of conventional fire and dust explosion, and the problems associated with isotope inventories of carbon-14 and chlorine-36, are some of the issues. For disposal there are the possibilities of conventional burial, oxidation to the gas phase and release as carbon dioxide (with radionuclide retention as appropriate) or recycling into new graphite or carbon products. In particular, new high-temperature reactors will require graphite, which should ideally be manufactured with a proportion of recycled waste graphite if possible.

This report discusses all the issues relating to handling and disposal of graphite in depth. It concludes as follows:

1. Adequate information exists to enable graphite moderators to be safely dismantled and processed.
2. Concerns about Wigner energy are limited to the minority of reactors in which the moderator operated at low temperature. The phenomenon is well understood, and appropriate precautions can be defined to avoid unacceptable energy release.

3. Fire and explosion hazards of graphite have been thoroughly considered in this report. Although graphite is a form of carbon and therefore potentially combustible, it is nevertheless relatively rather resistant to oxidation, which is of value when considering the safety of handling, processing and disposal. Any risk of a dust explosion during decommissioning activities can also be prevented.
4. The radionuclide inventory of irradiated graphite is unusual in comparison with other nuclear wastes. The principal isotopes of short-term importance are cobalt-60 and tritium; in the longer term carbon-14 and chlorine-36 are dominant.
5. The three main options for disposal of graphite are oxidation to the gas phase and release as carbon dioxide, direct burial or recycling into new products for the nuclear industry. In each case opportunities exist for pre-processing to concentrate or remove radionuclides and thereby enhance the safety of the chosen option.
6. The possibility of recycling of graphite into new nuclear industry products is in its infancy. In due course this possibility may become very important, particularly if it is proposed to construct new graphite moderated reactors.
7. It is unlikely that one single solution to graphite management will be appropriate everywhere. There are issues which may lead to different solutions being adopted in different countries and for different reactors.

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1

INTRODUCTION

The objective of this report is to review the current options for the management and disposal of irradiated nuclear graphite following the decommissioning of nuclear installations in which it has been employed as either moderator or fuel components. All currently identified options will be considered without prejudice to any particular national or international policy for radwaste treatment but with particular attention paid to safety-related issues associated with these options. Such options include innovative measures for re-cycling or re-use of products formed from the irradiated material. It is also desirable to learn from the present history of the nuclear industry how the specification of future nuclear graphites and the design of the structures in which they are used can contribute to the simplicity of the eventual decommissioning of next-generation plant.

Whilst recognising that a number of national governments have strategies for the disposal of radioactive wastes in general, that there are international programmes and guidelines (*e.g.* IAEA[1]), and that a number of international treaties have effectively limited certain disposal options, the authors believe that it is now appropriate – at least in the specific context of nuclear graphite – to present a comprehensive review of the technologies currently available (in 2005) in the belief that the results of an objective technical assessment of all possibilities should be made available to assist the subsequent political and consultative processes which accompany the final national and international decisions.

The majority of irradiated graphite wastes will originate from the United Kingdom, France, and the countries of the former Soviet Union. The United States also had a significant programme of early production reactors, and there are lesser quantities of irradiated nuclear graphite in a number of countries which include China, Germany, Spain, Italy, Japan and North Korea. For reactors built in the late 1940s and the 1950s, little or no thought was given to the ultimate destiny of the reactor components, and there was little improvement in this position over the next twenty years. The issues for dealing with a cumulative total in the region of 250,000 tonnes of such material are only now being properly addressed.

As the major world producer of irradiated graphite[2], it is useful to consider the position in the United Kingdom. Having suffered considerable delays in identifying an acceptable repository site for the disposal of general intermediate and high-level wastes (ILW and HLW), the government recently set up both a new Nuclear Decommissioning Authority (NDA) with responsibility for achieving decommissioning of civil nuclear installations, and a special

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[1] Definitions, including acronyms, are collected in Appendix 1.

[2] 91,300 tonnes of which 83,000 tonnes derives from the commercial power programme, according to UK NIREX figure published in 2001 at a UK/Russian graphite symposium held at Sosnovy Bor, Russia: this covers all projected UK active graphite waste production up to the year 2170 but does not appear to include quantities from weapons moulds and similar sources.

Committee on Radioactive Waste Management (CoRWM) with a three-year remit to consider all options for UK radwaste disposal. An interim view from CoRWM favours the pre-existing radwaste policies of interim surface storage and deep-repository disposal, but there does not appear to have been any significant attempt to consider individual waste streams with different physical or chemical characteristics. UK NIREX, previously responsible for preparing the way for a UK repository and also for advising the nuclear organisation on waste-packaging and transport requirements based upon this waste destiny, has recently become independent of the UK nuclear industry and will continue in this role of preparing for a phased disposal concept and preparing an inventory of radioactive waste within the UK, and "adhering to government policy at all times" [1]. France is now considering a separate repository for graphite, but this dedicated facility will not be available until 2013 at the earliest.

The last comprehensive review of options for the management of graphite wastes is believed to be a European review in 1984, funded by the then 'Commission of the European Communities', which took as its basis the disposal of graphite from the United Kingdom 'Magnox' and 'AGR' reactor programmes [2]. This review did not make a specific recommendation, but concluded that both sea dumping or deep-repository disposal (either inland in clay or at a coastal site in shale) would lead to acceptably-low potential doses to the individual, whilst incineration was not regarded as a desirable alternative, largely through the management of the arisings of gaseous ^{14}C, unless the large volume reduction was an over-riding factor.

Ref [2] considered the graphite-disposal issues almost exclusively in terms of the radioactivity content and the potential for release of isotopes through leaching and other processes. In re-examining the range of options for graphite disposal which are apparently available in 2005, it is helpful to consider the whole of the nuclear-graphite lifecycle from its 'design' and manufacture through its operational history and behaviour to any 'safe-storage' period planned with the graphite held within the reactor pressure vessel after final shutdown ahead of final dismantling and disposal. Each part of the lifecycle potentially impacts upon the waste-graphite disposal or re-utilisation, and the past experience in this area is of potential value to the present designers of new HTR and VHTR systems.

The issue was re-examined briefly during an IAEA Technical Committee meeting in 1999 on Nuclear Graphite Waste Management. A paper by one of the present authors (AJW) sought to open a debate upon whether the continuing indecision about the fate of nuclear wastes presented a crisis or an opportunity in terms of graphite wastes [3]. This issue was further developed, with an emphasis on the importance of an objective evaluation of true ('objective') risk rather than 'subjective' risk on the part of politicians and the public, in [4].

This present paper now offers a comprehensive review of options based upon these principles and taking into consideration all options, potential processes and theoretical proposals for the treatment and/or disposal of waste nuclear graphite. An analysis of safety-related issues, both in regard to dismantling operations and to subsequent disposal options, is also included.

Short sections on graphite manufacturing, utilisation issues and irradiation behaviour are therefore presented ahead of the main areas of concern, namely the properties of graphite (and graphite dusts) which are perceived to be of importance during the safe storage, dismantling and disposal of graphite-reactor cores, and the detailed accounts of alternatives to encapsulation and deep burial.

It is demonstrated that the existing graphite-moderated reactors present no specific hazard for dismantling as a consequence of graphite properties, other than for some very specific exceptions which are identified and separately discussed. These exceptions relate to reactors in which serious incidents have occurred or in which the graphite has been irradiated at very low temperature with the consequent accumulation of significant amounts of Wigner energy. The otherwise generally benign state of the graphite during dismantling also extends to any dusts generated during the process, even when high-temperature cutting equipment is used in the vicinity (provided appropriate precautions are taken).

Numerous options then exist for the removal and ultimate destiny of the graphite, which the authors consider should be included for consideration in subsequent national and international debates. It is extremely important to apply a rigorous objective risk assessment using appropriate scientific and technical criteria in order to define the appropriate options to be put forward for public consultation and final governmental decisions.

2

NUCLEAR GRAPHITE MANUFACTURE

The most important feature of nuclear graphite manufacture which contributes to the ease of decommissioning and disposal is the chemical purity, with respect to isotopes which become activated. The generation of isotopes with short half lives (up to around twenty years) can lead to immediate problems for dismantling in terms of accessibility and personal radiation doses; isotopes with much longer half lives must be considered in terms of ultimate disposal options.

With the benefit of hindsight, the British and French graphites (at least) were not sufficiently purified. A particular irony is that the graphite for the second generation of British reactors (AGRs) was given a revised specification which allowed an *increase* in impurity cobalt and which has resulted in severe difficulties in handling even the quite small quantities of graphite present in containers of monitoring samples because of the induced ^{60}Co activity. ^{60}Co will thus present problems for any early dismantling of these cores.

A second problem has arisen through the use of either chlorine gas or freons in the purification process to remove certain metallic impurities as their volatile chlorides, leading to residual ^{35}Cl contamination. This isotope has an extremely long half life, and this means that the graphite must have multiple safety barriers against diffusion and leaching if it is subjected to repository disposal.

There is now a much greater understanding of the importance of particular isotopes in decommissioning and disposal terms which should, hopefully, lead to great improvements in this area for the manufacture of new graphites for HTR. In addition to improvements on specification, magnesium fluoride rather than chlorinated compounds can be employed in the final purification stage.

A separate issue relevant to dismantling is dimensional stability of large graphite structures under the influence of fast-neutron damage. Any significant distortions, cracking, or jamming of components in the reactor cores can lead to severe problems for dismantling. In this respect, the choice of source pitch and coke and the manufacturing process has a strong influence on irradiation behaviour. The earliest graphites were manufactured from pitch coke (“needle coke”) and pitches derived from the oil industry, using an extrusion process to produce the crude blocks before they were baked. This resulted in variation in properties along the extrusion axis and perpendicular to it (‘anisotropy’). If the density of the blocks was not high enough, they were re-impregnated with pitch under pressure and re-baked. The final graphitisation process, at temperatures up to 2800ºC, was accompanied by purification with chlorine-containing gases.

To produce a theoretically more dimensionally stable product, a moulding process was employed. The UK AGR graphite was manufactured in this way, using coke derived from natural gilsonite mineral obtained from the USA. The most recent graphites, especially those from Japan, employ isostatic pressing using a rubber moulding bag or a vibration moulding technique, and this is intended to give the best performance under irradiation.

Grain size in the finished product is also important in determining dimensional stability, impact resistance and internal strength, and careful choice and blending of coke and milled filler material (‘flour’), which may be re-ground graphite, is also an important factor.

A full description of the manufacturing processes is not relevant here, except to emphasise the importance of considering the final behaviour and characteristics of the graphite when deployed in the reactors. Further information on manufacturing processes can be found in [5] and elsewhere.

In all decommissioning scenarios, it is important to recognise the physical nature of nuclear graphites. Even the highest-density material is porous, and a significant proportion of that porosity is open to the coolant circuit in gas-cooled reactors or to cover gases in systems such as RBMKs. A typical open-pore volume (as a percentage of the bulk volume of the graphite) would lie in the range 10-21%, depending upon the grade. In consequence, deposition of activated materials can occur both upon the geometrical surfaces of graphite components and on internal pore surfaces, especially where there are permeable gas flows through the graphite blocks due to pressure differentials.

The issue of chemical purity is also extremely important. Control of boron content is of obvious importance for a nuclear material, but other impurities which are capable of activation by neutrons to radioisotopes with significantly long half lives clearly need to be subject to strict concentration limits if problems during decommissioning are to be avoided. Sections 8, 9.2 and 9.10 examine some of these issues in detail.

It is appropriate to conclude this section with a cautionary note. In the early days of the nuclear-power industry, quality control was not of the highest standard, and decommissioning of the older plant may produce some unexpected issues, including unanticipated material in the graphite.

3

UTILISATION OF GRAPHITE IN NUCLEAR PLANT AND OPERATIONS

The most obvious source of irradiated graphite is from reactor moderators and reflectors. The highest irradiation, and therefore the highest potential activation of impurity isotopes, will be found in the former, although local movement of contaminants such as metal oxides from component corrosion may result in additional deposition of activity in all regions, as noted above. Highly irradiated regions may also have suffered significant radiation damage from fast-neutron exposure (Section 4) resulting in component distortion and/or mechanical failure, leading to potential difficulties in dismantling.

Reflector regions will usually be less radioactive, as the slow-neutron flux is much less and there is less potential for movement of adventitious contamination. Different grades of graphite may be present compared with the moderator: these will usually be of a lower grade, possibly lower density, but less prone to irradiation damage because of the much lower flux. Some water-moderated materials testing reactors (MTRs) have graphite reflectors – *e.g.* DIDO/PLUTO designs at Harwell (UK) and Jülich (Germany).

Sources of moderator and reflector graphites for disposal from gas-cooled reactors include Magnox and AGR systems in the UK, the French UNGG reactors, single British-designed Magnox reactors in Italy and Japan, and early production reactors which employed air cooling, such as BEPO and the Windscale Piles (UK), the Brookhaven reactor (USA), etc. The principal water-tubed reactors with large-scale graphite moderators and reflectors include the Hanford reactors (USA), the RBMKs in the countries of the former Soviet Union, and their precursor production reactors and development plants (e.g. Krasnoyarsk, Beloyarsk, Chelyabinsk etc); there are also related designs in other countries such as China.

The more limited number of HTRs currently decommissioning are a special case because of their moderator and fuel configurations. These may either be of the fuel-block design, such as Fort St. Vrain in the USA (already successfully dismantled), the current Japanese HTTR project, and the ‘Dragon’ reactor (OECD partnership, located in the UK), in which there is a matrix of fuel compacts (containing individual fuel particles) within ‘removable’ fuel blocks, or of the pebble-bed design developed in Germany in which 60-mm-diameter fuel balls are used to form an integrated moderator. The current Chinese HTR-10 development reactor follows this principle. The latest HTR designs from the PBMR Co. in South Africa also utilise this concept but with a central interlocking graphite cylinder to even out heat distribution across the core. Each system presents a unique situation for eventual dismantling; systems have been developed to ‘strip’ graphite from fuel balls and will thus generate new types of graphite-based waste stream for subsequent treatment.

An important feature of this whole group of graphite moderators and reflectors is the wide range of irradiation conditions and different exposures to adventitious circuit contamination. In addition there are additional contamination sources where significant fuel failures have occurred, leading to fission-product contamination. This means that it is often the case that the comparison of radioactivity inventories from different reactors is often rather pointless, and that each plant (even within a group of ostensibly similar reactors) may have individual characteristics which need to be taken into account in decommissioning and disposing of the graphite.

There are also many sources of graphite components which are additional to the moderator and reflector. These may consist of ‘thermal columns’ in various MTRs and research reactors, channel sleeves, sometimes inserted to repair damaged channels after they have been re-bored (e.g. a Magnox reactor at Chapelcross (UK) and some Russian reactors), or fuel components such as central graphite rods (French UNGG reactors, with the exception of Chinon), outer circumferential fuel sleeves (many examples *e.g.* UNGGs, UK AGRs, selected Magnox designs such as Tokai (Japan), Hunterston ‘A’ (UK)) and side locating struts (*e.g.* Berkeley, UK). Often these graphite fuel-element components have been stripped from their fuel elements on site after discharge, and consigned to silos where they may remain mixed with other metallic components.

A final minor source of contaminated graphite arises from the moulds used for forming components of nuclear weapons. This material has not been irradiated as such but it is potentially contaminated with (mainly) alpha emitters and therefore must be treated as classified waste.

It is thus seen that there exists a diverse range of graphite radwaste with a wide range of potential radioactive content, some of which will be integral with the material arising from activation of impurities and some of which will be associated with surfaces and with internal porosity, arising from the transport within reactor circuits of material which has then been activated in the core by the neutron flux. Whilst this diverse collection of graphite will undoubtedly require a number of different treatment solutions, the graphite itself is a unique waste stream within the general radwaste arising from the nuclear activities around the world. It is therefore quite logical to consider solutions for treatment and disposal of graphite wastes separately from those applied to other forms of radwaste.

4

GRAPHITE IRRADIATION BEHAVIOUR

The irradiation of the graphite within a reactor core can potentially lead to three types of change in the material which subsequently impact upon the dismantling and handling of the material during decommissioning:

1. Activation of impurities and transported materials leading to induced radioactivity;
2. Changes in physical and mechanical properties; *and*
3. Radiation chemistry effects.

These are now briefly outlined:

4.1 Production of Radioisotopes

This problem has already been mentioned. The activation process is largely, but not exclusively, brought about through interactions with slow neutrons and is thus unavoidable where suitable parent isotopes are present, in the form of impurities or transported materials. Isotopes with relatively short half-lives build up to a steady-state level during operation of the reactor and can then be expected to decay relatively quickly – the common impurity ^{60}Co for example having a half life of 5.27 years. Such isotopes present a short-term hazard for dismantling and their presence is a major part of the argument in favour of a period of 'safe storage' in the reactor vessel before major dismantling of the reactor structures is attempted.

The lesson for the future arising out of past experience is that the impurity specification for new graphite reactors in the future needs much more careful control than in the past, where the significance of the generation of activity which impinges both upon maintenance regimes and decommissioning issues has not received sufficient attention. Designers of new plant also need to consider the materials standards for other parts of the coolant circuit, to minimise corrosion and hence the potential transport of dusts which can deposit within the graphite and themselves become activated.

4.2 Irradiation Damage in Graphite

The interaction of fast neutrons with the graphite crystal structure leads to the displacement of carbon atoms and the creation of vacancies within the crystallites. The net result within an individual crystallite is an expansion in the *'c'* direction and a contraction in the perpendicular *'a'* directions, and these changes can be very large over the life dose of a reactor – often more than 30% expansion in the *'c'* direction, for example.

In a bulk graphite component, the crystallite directions are randomised or at least partially randomised and this, together with the presence of void spaces results in much smaller dimensional changes in structural components. The net behaviour is complex, especially in non-isotropic graphites where a tendency to partial alignment of crystallites can result in quite different behaviour in the directions perpendicular and parallel to extrusion, for example. This leads to the build up of differential stresses within the components, which are compounded by any flux gradients across the component. Whilst some of these stresses ‘creep’ out under irradiation, they return in reverse sense when the reactor is shut down and this can lead to component cracking in older plant, with consequent potential problems in decommissioning of jamming and or fragmentation of the components.

Changes also occur as a result of fast-neutron damage in other physical, mechanical and thermal properties of the graphite, but most of these are relevant only in power operation of the plant, although changes in heat capacity are of potential importance in dismantling situations where heat is applied.

The one property which is of great significance when it occurs is the accumulation of Wigner energy. The importance of this is directly related to the irradiation temperature of the graphite, being extremely significant in old plant operated with the graphite near or just above ambient temperature. A potentially large accumulation of energy can build up within the graphite which is capable of release if the graphite is subsequently heated to around 50K above its irradiation temperature. Although a total release demands very high temperatures, it is possible, if the accumulation is sufficiently large, that the potential rate of energy release (as a function of increasing temperature) can exceed the specific heat capacity of the graphite. Under these circumstances a self-sustaining release could occur under near-adiabatic conditions. This is the condition which resulted in the need for anneals of Wigner energy in the early US and UK production reactors, and which was the initiating event in the Windscale accident of 1957 [6].

In Magnox-type reactors, graphite temperatures lie in the range 180 - 360ºC and accumulation of Wigner energy is limited to the cooler regions and even here the total stored energy saturates at levels which ensure that release rates upon heating are comfortably below the specific heat capacity [7]. In AGRs and HTRs there is no significant issue: in RBMKs there are small regions where Wigner energy is of significance.

The understanding of Wigner-energy accumulation and release processes has recently been considerably improved through an improved understanding of the damage processes, derived both from sophisticated structural calculations which explore the relative energies of potential damage structures *e.g.* [8] and through innovative measurement techniques such as the combination of thermal annealing of irradiation damage in graphite with simultaneous X-ray-diffraction measurements, as performed recently on graphite removed from the thermal column of the ASTRA research reactor in Austria [9].

Thus, the potential problem of Wigner release during dismantling is now clearly understood to be limited to old low-temperature reactors but, even here, with the possible exception of Windscale Pile 1 where roughly 15 tonnes of damaged fuel remains within the fire-damaged region, appropriate precautions can be taken to ensure that the graphite cannot be heated sufficiently to initiate a release.

There was at one time concern that graphite cutting and grinding operations could raise its temperature significantly, particularly as the irradiation reduces its thermal conductivity very significantly. This is a special concern where large accumulations of Wigner energy are present. Accordingly, special tests have been conducted to study the temperature increases incurred in graphite by typical cutting and grinding operations, and such rises have been demonstrated to be quite insignificant: for example, grinding a hemispherical hole for the recovery of a trepanned sample in the Windscale Piles was shown to result in a local temperature rise limited to 3K [10].

Waste authorities have however raised questions about the potential for extremely low rates of energy release during the modest heating expected during grouting processes and the subsequent quasi-adiabatic conditions of storage in deep repositories in assemblies of concreted drums. These concerns have been expressed particularly in regard to graphite from reactors which have a significant accumulation of Wigner energy, such as the Windscale Piles [8]. Although such release rates can easily be shown to be extremely low and below anything which can be measured in conventional apparatus such as a differential scanning calorimeter, proving that very slow rises of temperature over hundreds of years due to random movements of displaced atoms and vacancies in the graphite crystallites will not occur in a quasi-adiabatic situation is not a trivial task. This issue is addressed in more detail in Section 9.

Incineration, and similar processes, are of course *assisted* by the presence of Wigner energy, and such methods of disposal remove all concerns about subsequent graphite storage behaviour.

4.3 Radiation-Chemistry Effects

There are two principal issues of radiation chemistry which affect decommissioning of graphite reactors. The first applies in systems cooled by oxidising gases – *i.e.* air, or carbon dioxide. Here, direct oxidation of graphite occurs under the influence of ionising radiations, principally gamma. As the degree of oxidation relates to gamma flux, there are significant variations in net oxidation around the cores and through individual components, this latter point arising because the oxidation occurs in-pore – wherever coolant gas is present. The oxidation is also proportional to gas pressure, such that the later reactor types – the newest Magnox reactors (UK and French UNGGs) and AGRs in the UK, for example, suffer the greatest oxidation, which has locally reached over 40% weight loss in some cases (see, *e.g.* [12]).

Such high weight losses in local regions of the core do present potential issues for handling the blocks upon dismantling because of a reduction in the strength of the components, although even these current weight losses do not reduce strength sufficiently to compromise current operational safety cases for the reactors concerned.

A second radiation-chemistry issue is specific to the carbon-dioxide-cooled reactors and is a greater issue in Magnox-type reactors than in AGRs. This is the production of reactive forms of carbon from the minor components of the coolant gas. It is principally the polymerisation of carbon monoxide (the product of graphite oxidation) and is deposited principally upon and within the graphite pores adjacent to fuel and interstitial channels in the reactor, although some is found throughout the pore structures. In AGRs, lesser amounts are formed from the methane which is deliberately added to the coolant as a corrosion inhibitor.

The significance of this material is its thermal reactivity in air, which is up to 10^3 times greater than that of the graphite. The quantities are generally small, although the distribution around the core is quite variable [7] and locally has been found to reach up to 3% by weight of the associated graphite in the worst case. Consequently, its presence needs to be taken into consideration in decommissioning where, for example, flame cutting of adjacent metallic structures is contemplated, and also where dusts may be generated. These issues are considered in more detail later.

5

SAFE STORAGE

An option initially favoured by the UK for its Magnox and AGR reactors was the retention of the graphite within the pressure vessels of the reactors for periods of up to 135 years [13, 14], inclusive of an initial ‘care and maintenance period’ of around 30 years during which dismantling of ancillary plant and structures would be completed. Monitoring of core temperature and humidity would also be undertaken during this initial period. The philosophy of the longer safe-storage period was that short-lived isotopes would decay and enable dismantling to be effected with much reduced personnel doses and much more easily than if it was commenced immediately.

The French and Italian operators of graphite-moderated reactors proposed similar strategies, but with different periods of safe storage, the shortest being 40 years. Regulators collectively noticed the different opinions on the appropriate timescale, and also public opinion strengthened against “leaving problems for future generations”; consequently, these strategies are now all under review.

In the UK, the Nuclear Decommissioning Authority, which newly has responsibility for decommissioning all closed civil nuclear plant, has recently announced that it is planning on a maximum period of 25 years for defuelling, decommissioning and release of Magnox-reactor sites for alternative use [15]. EdF in France is now thought also to be aiming for complete decommissioning within about 25 years. Authorities in Japan are understood to be considering complete decommissioning of the single Magnox reactor Tokai I within 17 years.

‘Safe storage’ presently remains an ‘option’, or part of an ‘option’, for the treatment of radioactive graphite wastes, and is therefore nominally assessed here.

Certain graphite reactors have already been left after closure for periods of more than 40 years, without specific efforts to achieve a ‘safe storage’ regime. These include the Hanford reactors in the USA and the Windscale Piles in the UK. Little data are available on the former, but the experience with the latter, despite concerns over Wigner energy and (in the case of Pile 1) damaged fuel and isotope cartridges remaining jammed in the core, has given confidence in the stability of the graphite over a long period of disuse after final operations ceased. The UK BEPO reactor has also been left undisturbed without incident since shutdown in 1968, except for the removal of a large four-inch diameter horizontal core from one side of the reactor block to the approximate centre of the core, for isotopic and Wigner-energy assays.

The industry has addressed and assessed a number of specific aspects of graphite storage within reactor vessels for potential risk and hazard, and these are enumerated below:

5.1 Wigner-Energy Release

Recent new measurements on graphite from the Windscale piles confirm the expectation that there is no significant difference in the quantity of Wigner energy (measured as rate of release per unit temperature rise) compared with samples removed shortly after the 1957 accident [10, 16]. This shows that a lengthy period at ambient temperature has not had any significant effect on Wigner energy, and this is entirely in accord with expectations given that a significant release rate is found to be initiated only when the graphite temperature is raised to about 50K above its irradiation temperature (which in the case of the Piles was in a range 30 - 130ºC). This applies even to samples where there was sufficient Wigner-energy content for a self-sustaining release to be possible, as evidenced by the rate-of-release curve for the small non-adiabatic sample used in the test exceeding the theoretical specific heat capacity [10]. The same situation is likely to apply to the Brookhaven reactor in the USA.

Thus, the graphite in Magnox, AGR and other reactors which have enjoyed much higher operating temperatures is much more secure, since (i) the temperatures achievable in safe storage conditions cannot remotely approach the irradiation temperature + ~50K and (ii) there is much less Wigner energy present in any case.

Temperature monitoring in stored Magnox cores (*e.g.* the Berkeley reactors, shut down in 1988 and 1989) confirm that there is no low-rate release leading to any measurable heating: core temperatures shift only a few degrees in an annual cycle, reflecting the changing seasons.

5.2 Thermal Oxidation of Graphite in Air

This subject is separately treated in the following Section, because of its importance in dismantling operations. The extensive knowledge of the oxidation kinetics confirms that there is no risk of any oxidation under safe-storage conditions. This also extends to dust-explosibility issues.

5.3 Generation of Nitric Acid From Air by Residual Radiation

Consideration was given to the possibility and extent of nitric acid formation from moist air in the Magnox reactors in the UK, primarily because of concerns about potential corrosion of steel components within the vessel (*A.J. Wickham, personal communication*). The perceived mechanism was radiolytic formation of the acid, but measurements in three different reactors in the periods immediately before and following removal of the reactor fuel showed that nitrate formation on steel surfaces, as determined from swab samples, was inconsequential, as was the gas-phase concentration in the air within the vessel.

The question of damage to the graphite through the formation of intercalation compounds was also raised. Generally speaking, such compounds, which insert species between the layer planes in the graphite crystallites, require very low temperature for formation as well as an extremely strong (chemically) oxidising environment, which is not available.

The only compound which has been considered worthy of further investigation is the so-called "graphite nitrate", which is discussed (along with intercalation compounds) in [17]. Diffusion of the acid species into the graphite structure is considered to be the rate-determining step.

Although severe conditions (nitric/sulphuric/perchloric acid mixture, or 'red fuming' (>96%) nitric acid) are generally necessary, formation of the nitrate compound from natural flake and pyrographite has been observed at 25ºC [18]. However, the quantities and concentration of any potential nitric acid formation at the commencement of the 'care and maintenance' period are simply far too low to make this a real possibility, and therefore no degradation of graphite from nitric acid is expected throughout the 'safe storage' period.

5.4 Graphite Property Changes

Fast-neutron irradiation during the period of reactor operation will have resulted in significant changes to many physical- and mechanical-property changes of the graphite. The most relevant changes from the point of core stability will have been reductions in strength (also contributed to in gas-cooled plant by graphite loss through oxidation), build-up of internal stresses and, particularly for fine-grained materials, embrittlement. In addition, some distortion of components may have occurred, and perhaps limited cracking in certain cases; there will also have been changes in thermal properties, most notably a significant reduction in thermal conductivity. However, one may assume that the reactor operating case to end of life was sufficiently robust to accommodate these changes.

Graphite core assemblies which have been irradiated to high fluence and degraded in such fashion are most prone to cracking and damage when the reactor is shut down, whether this be for maintenance or the final shutdown at end of life. This situation arises because irradiation creep tends to ameliorate the stress build up during operation, and the stresses reverse and intensify when the cooling takes place. Channel-monitoring programmes are implemented in operational reactors during the maintenance shutdowns to obtain assurance that the extent of any damage remains acceptable within the operational safety case for the next period at power.

At the final shutdown, therefore, there may be a small addition to any recorded damage within the core, which will probably not have been noted through examination – although it may have become apparent during the final removal of the reactor fuel. It is extremely improbable that this would compromise a safety case for a safe storage period when the operational safety case was accepted for the preceding period: there is no mechanism to further degrade any physical or mechanical properties once the reactor operation has ceased.

It is known that the atmosphere in which strength measurements are conducted has a significant effect on the result, and that the water content of the atmosphere is particularly important in this respect [19, 20]. Logsdail [20] noted that tests conducted in the typical reactor coolant gas CO_2 find graphite to be stronger than tests conducted in moist laboratory air, the normal environment for such tests. Thus, ironically, archive data on graphite strength may be inappropriate for the operational conditions under which they have been employed, whilst being entirely appropriate for the safe-storage circumstance.

Current safety cases for safe storage rest largely on seismic assessments, for which the measured sample data therefore remain appropriate. Friction and wear data on nuclear graphite are, however, very limited. The only other uncertainty which remains associated with the safe-storage safety case is the use of small-sample data for large-component assessment – see, for example, [21] - and even in today's operational reactor safety cases it is necessary to support predictions based upon small-sample data with mechanical tests on assemblies of components in order to satisfy the regulators of the validity of the case. The arguments required to support a safe-storage case are, of course, far less onerous than for an operational case.

5.5 Leaching of Activity From the Graphite

Leaching data on nuclear graphites are more fully assessed in Section 8. Here the concern is with 'naked' graphite (as opposed to grouted materials in repository disposal), and with attack by rain water or condensate water. Ingress of rain water requires a substantial failure of the pressure vessel and outer containment, and is extremely improbable except in a reactor which has no formal containment system, such as the early production piles in the UK, Russia and the USA. Whilst even this may appear improbable, we should note the poor state of the external buildings on some of the Hanford reactors, and also that the UK BEPO pile, assembled within an old aircraft hanger, suffered just such a water ingress at some time within the first seven years after its shutdown in 1968, presumably due to a leak in the hanger roof allowing water to impinge on to the essentially unprotected top of the reactor.

The leak was discovered in 1975 during the taking of a four-inch diameter core of material through the side of the pile through to the approximate centre line. The graphite recovered from a sequence of three core graphite blocks was found to be damp, and a very recent analysis of graphite from the core has confirmed that the water had washed material from the structural concrete of the reactor into the graphite stack (measured as natural boron contamination during the course of isotopic assay work, *A.J. Wickham, personal communication*).

It is therefore evident that a proper assessment of the risk of ingress of rainwater needs to be made in a safe-storage case. In regions with atmospheric industrial pollution, the pH of the rain may be as low as 4.4 - 4.6 [22], but this may be altered by interaction with concrete to give a substantially higher alkaline pH. Any condensate water within the vessel is likely to remain acidic.

Assessment of the potential for leaching requires a combination of the available leaching data (discussed later) with a risk assessment relating to water ingress and the leakage pathways for any contaminated water which does accumulate within the vessel.

5.6 Gas-Phase Activity Release

The principal isotopes of concern here are ^{3}H and ^{14}C.

Tritium is formed from lithium impurity in the graphite, and also from fission processes because of the ease with which it can escape from fuel containments. Some specialists consider the fission route to be the principal source of tritium, at least in Magnox reactors.

Gas-chemistry experiments in UK Magnox reactors have demonstrated that tritium held on graphite pore surfaces is transferred to gas-phase hydrogenous species with extreme ease [23, 24]. This implies that tritiated species initially adsorbed on the graphite surfaces will have exchanged tritium with atmospheric moisture and this tritium will have been lost very quickly after reactor operation ceased. Under safe-storage conditions, when moisture content of the air is not specifically controlled, this will represent a major increase in the concentration of hydrogenous species compared with operational conditions and also, most likely, with maintenance conditions where air-driers have usually been employed to limit the moisture ingress for reasons of metal oxidation.

In water-tube reactors, a slow loss of tritium to the cover gas would be expected, especially if that gas contains hydrogenous impurities. Upon establishment of safe-storage conditions, this gas can be presumed to be atmospheric air, and so the same situation prevails as for the gas-cooled plant.

Further releases will depend upon the solid-state diffusion of tritium within the graphite, which is much slower than the surface exchange rate but remains significant at (Magnox) reactor operating temperatures [25]. However, the high activation energy for the process (60.4 $\mathrm{kcal.mol^{-1}}$) implies a rapid reduction in the potential release rate with reducing temperature.

[16] provides data on the release of tritium from samples of Windscale Piles graphite as a range of temperatures into a 1% H_2 / Ar purge gas. As an example, 0.2% of the total tritium in the sample was released after 30 minutes at 300ºC, in this case representing 211 $\mathrm{Bq.g^{-1}}$. Calculations taking into account the relatively short half-life of tritium can be made to estimate the quantities of tritium likely to be released into the safe-storage environment: in the UK Magnox plant a ‘breathing’ arrangement, or major loss pathway, is engineered deliberately to enable monitoring of the tritium egress during the initial ‘care and maintenance’ period, to ensure that statutory release limits are not breached. Tritium egress in the later stage of safe storage will be much reduced anyway because of the decay.

The incidence of ^{14}C in nuclear graphites is documented in a recent review commissioned by UK NIREX [26]. In gas-cooled reactors, and in water-tube reactors where the graphite cover gas is nitrogen or air, the dominant route for formation of ^{14}C is *via* the reaction $^{14}\mathrm{N(n,p)}^{14}\mathrm{C}$, the nitrogen source being a combination of the original impurity nitrogen in the graphite (some of which may be as gas in the closed pores) together with that from the cover atmosphere. A second, significant pathway is *via* $^{13}\mathrm{C}(\mathrm{n},\gamma)^{14}\mathrm{C}$. Production from either ^{16}O or directly from ^{17}O *via* $^{16}\mathrm{O}(\mathrm{n},\gamma)^{17}\mathrm{O}(\mathrm{n},\alpha)^{14}\mathrm{C}$ is a minor, but non-trivial, route in coolants containing oxygen isotopes. The proportions vary from design to design, and the life-average nitrogen impurity content of coolant/cover gases obvious plays a role: for a UK AGR the proportions of the ^{14}C arisings after a lifetime operation and 50 years ‘cooling’ are calculated to be in the ratio 69.6% (from ^{14}N) : 30.4% (from ^{13}C) : 0.014% (oxygen sources). Although ^{13}C makes up approximately 1% of the graphite, its capture cross section at 0.0009 barns should be compared with that of ^{14}N (1.8 barns).

There is an important distinction between ^{14}C arising directly from ^{13}C or impurity nitrogen within the graphite, and that arising from the coolant. The former will be in graphitic form, with the ^{14}C incorporated into the lattice or remaining trapped within closed porosity. ^{14}C formed from the coolant or cover gas will be in the form of amorphous carbon or carbonaceous solids containing some proportion of hydrogen and oxygen, and will be present largely as deposits on the geometrical surfaces of the graphite and within the open porosity, the extent of the latter being to some extent dependent on the presence of permeable gas flows through the transport porosity during reactor operation. Thus, much more of this form of ^{14}C will be expected within the porosity in graphite from pressurised cores compared with water-tube reactors where there is very little, if any, pressure differential across graphite components.

Release characteristics of this ^{14}C will be considered in more detail in Sections 8 and 9. Under 'safe storage' conditions, negligible release through gas-phase mechanisms is expected. A temperature of more than 400ºC is needed to produce a significant oxidation rate in air for graphite. Whilst the deposited forms of carbon and carbonaceous compounds are up to 1000× more reactive, even these have a negligible rate below about 200ºC, and such a temperature is not attainable.

To confirm these points, there is direct evidence from the use of ^{14}C-labelled graphites and the production of ^{14}C-labelled deposits in research activities at the Berkeley Centre (formerly CEGB Berkeley Nuclear Laboratories, UK) and at UKAEA Harwell that no ^{14}C was released from either form under ambient air (*A.J. Wickham, personal communication*). Exchange of ^{14}C from bulk graphite to the gas phase is extremely difficult, as evidenced by the need for radio-frequency heating to over 2000ºC to 'label' graphite with ^{14}C in order to perform these tests [27].

Finally, the possibility of gas-phase activity release through biological processes during 'safe storage' has also been considered. A UK study on biological intrusion into a Magnox reactor under storage conditions, to which the present authors have had access, found no evidence for the possibility of bacteria utilising carbon directly and thus providing a release pathway for ^{14}C in waste products.

5.7 Particulate Release

Graphite may, in principle, release particulates from the solid graphite itself, from deposited carbonaceous material where it is present, or from deposited or entrained contaminants such as activated metal-corrosion products.

Carbonaceous deposits on irradiated graphite are generally closely adherent and are only likely to be released when the graphite itself is abraded. This implies that the possibility of particulate release of carbonaceous material would only exist during a seismic event, unless there was a severe temperature excursion resulting in expansion and movement of the blocks; not only is this extremely unlikely under 'safe storage' conditions, but thermal movement during operation has not been observed to generate significant dusts in graphite-moderated plant, and particulate emissions have not been an issue during operational life. Indeed, such friction and wear data as exist for graphite have tended to confirm that the coefficients of friction on graphite fall as sliding surfaces 'run in', and the lower temperatures in 'safe storage' tend to favour the retention of adsorbed gases, which also reduce the friction coefficient.

Attrition of graphite by biological attack is also considered to be extremely unlikely, and the current experience with UK Magnox reactors in 'care and maintenance' conditions confirms that particulate release should not be an issue.

The greatest potential risk of the release of particulate material comes from adventitious materials such as metal-corrosion products transported from other parts of the reactor circuit. Such cases need to be examined on an individual basis.

6

GRAPHITE OXIDATION CHARACTERISTICS

The potential exothermic oxidation of graphite and graphite dusts in air is a central feature of both operational and decommissioning safety cases for graphite-moderated reactors because there is an erroneous perception that it can represent an oxidation or 'fire' hazard, and the dusts an explosion hazard. This is despite the use of graphite as a high-temperature-resistant ceramic, its use in electrodes where temperatures reach thousands of degrees (including arc lamps), and even the use of graphite powder 'Graphex™' as a fire extinguishant in radioactive cave facilities.

Graphite has frequently been described as participating in fires, whereas the reality is that it is extremely difficult to burn – it is an almost perfect black-body radiator and has a high heat capacity (even after irradiation); despite this, notorious accidents such as Windscale and Chernobyl have been erroneously described as graphite 'fires'.

Nonetheless, combustion of graphite on a large scale is possible, and processes dependent upon it feature in the available options for disposal of irradiated graphite from nuclear plant. These processes rely upon and exploit the well-characterised chemical-oxidation behaviour of the material combined with good chemical engineering. It is however, exactly these possibilities (and the memory of the accidents) which have led regulators to become wary of graphite as a material, even to the extent of describing blocks from the dismantled and extremely-low-irradiated GLEEP reactor in the UK as a 'fire hazard' when they were being packed for removal from the hanger which houses the reactor. Special nervousness is reserved (with perhaps better justification) for graphite containing large amounts of Wigner energy and possible ignition promoters such as uranium hydride from failed fuel.

These latter issues are also clearly of important for any treatments and processing which might be proposed for blocks of graphite from such reactors (as discussed in Section 9).

It is therefore extremely important to document the true oxidation behaviour of nuclear graphite in this review. The subject is addressed under the following headings, with additional material reserved to appendices to this report:

- the established oxidation kinetics, including the effects of catalysts and their relevance and the criteria for establishing self-sustaining oxidation in air;
- oxidation in water and steam *(this is really only of interest for operational HTRs with impurities in the coolant gas, but a note is included here because of the possibility that some novel treatments or processing of recovered graphite blocks might involve aqueous processes, and also because certain utilities (for example EdF in France) are currently proposing to dismantle graphite reactors under water)*;

- the influence of higher-reactive carbonaceous dusts in systems irradiated in CO_2-based coolants;
- evidence from nuclear-industry test programmes;
- analysis of specific accidents against these criteria; *and*
- the flammability and explosibility of graphitic and carbonaceous dusts and the implications for dismantling activities.

6.1 The Oxidation Kinetics of Graphite in Air

Appendix 2 offers a comprehensive explanation of the oxidation characteristics of solid nuclear-grade graphite under all conditions likely to be encountered in decommissioning activities. Oxidation in air is immeasurably slow at ambient temperatures and becomes significant only around 350-400ºC. The rate is controlled by the kinetics of the reaction with oxygen at all surfaces of the graphite, including the entire open porosity into which air or oxygen can freely diffuse whilst the oxidation product, a mixture of CO_2 and CO, can diffuse out. The change of rate with temperature is represented by a simple Arrhenius equation.

As the temperature is increased, this simple kinetic rate increases (by a factor of around 7.8 over the range 400-450ºC, for example). Starvation of oxygen starts to become significant within the transport porosity, and the reaction rate fails to increase according to the kinetic predictions because of this ‘diffusion limitation’, with a consequent reduction in the oxidation of the deeper pores relative to the outer regions of the sample.

At even higher temperatures, the reaction becomes controlled by the available supply of oxygen, and under these circumstances the oxidation is largely confined to the geometrical surface of the sample.

These three conditions are known respectively as Modes I, II and III although there are no ‘step’ transitions between them, rather a slow conversion between modes as the temperature is increased. The proportion of CO in the product gases increases as the temperature rises and the higher modes are encountered.

This characteristic behaviour, and the associated oxidation rates, have been established over many years of observation.

Appendix 2 also includes observations about the effects of catalysts on the oxidation rate, concentrating on inorganic materials which may become associated with the graphite. Catalysis is not significant in Mode III and is of most importance in Mode I.

The data discussed may be applied to specific circumstances associated with a particular decommissioning activity or graphite treatment. In connection with dismantling activities, where regulators have been sensitive to the risk of graphite ‘combustion’, a set of criteria which must be *simultaneously* satisfied before self-sustained combustion of graphite in air, implying no continuous heat source applied, is possible [28]:

- a minimum temperature of 650ºC;3
- maintenance of this temperature either by heat of combustion or by some outside energy source;
- an adequate supply of air or oxygen;
- the gaseous oxidant source must flow at a rate capable of removing gaseous products but without excessive cooling of the graphite surface; and
- a suitable configuration of graphite and oxidant (note that a reactor channel was considered to be "suitable").

Appendix 2 also provides proposed detailed definitions for words commonly used (and mis-used) in the context of describing graphite oxidation, namely:

- oxidation;
- burning / fire;
- combustion;
- spontaneous ignition;
- ignition temperature;
- smouldering;
- incineration; and
- calcination

It is strongly recommended, for the avoidance of misunderstandings, that all technical arguments used to support dismantling and decommissioning activities should be phrased in terms of '*oxidation*' except where special circumstances apply.

6.2 The Oxidation of Graphite in Water or Steam

The reaction rate of graphite with water vapour is minimal below about 1000ºC unless a catalyst is present [29] even though it is favoured at lower gas pressure. No evidence is known to the present authors for significant reaction between carbon and water below 400ºC even when large quantities of potential catalysts are present. However, the formation of a surface-oxide complex has been proposed with studies in the range 25 - 200ºC in which extremely small yields of hydrogen were formed [30]. Ref [31], in the course of leaching experiments, offers oxidation data down to 200ºC, at which temperature the oxidation rate of Hanford graphite was estimated to be 10^{-8} g.cm^{-2}.day^{-1} (*i.e.* grams per square centimetre of exposed geometrical surface per day). Using an activation energy estimated at 12.8 kcal.mol^{-1}, the reaction rate at 100ºC, a temperature well in excess of 'safe storage' or dismantling conditions, can be shown to be $<10^{-10}$ g.cm^{-2}.day^{-1} and hence totally insignificant.

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[3] In the absence of a catalyst.

6.3 Reactive Carbonaceous Deposits

Graphite components which have been irradiated in a CO_2-based coolant are likely to have deposits of reactive carbon associated with them resulting from the polymerisation of CO together with a contribution from the radiolytic destruction of methane where it is present (principally AGRs plus some French reactors). Graphite monitoring programmes in the UK, described in [7], have found a wide variation in such deposit concentrations around the cores and values in some Magnox plant of up to 30,000 wppm (3% by weight of underlying graphite). Analysis of the curve representing the rapid removal of this material when samples are immersed in an oven at 450ºC show that that the reactivity of this material lies in the range 0.1 – 1.0 $g.g^{-1}.h^{-1}$, the higher values generally being associated with the cooler part of the graphite core – thus it is typically 100× more reactive than the underlying graphite. Thus its potential presence needs to be borne in mind, although it is unlikely to present a particular hazard during decommissioning even in the event of direct impingement of a cutting flame upon a deposit-covered surface: heat-transfer considerations mean that it will just result in a brief overall increase in reaction rate of the underlying graphite until it is consumed.

The implication of this material in relation to dusts is discussed in 6.6 (below) and in *Appendix 5* at Section A5.4.

6.4 Evidence From Nuclear Industry Test Programmes

The description given at the end of *Appendix 2,* of Schweitzer's experiment with an oxy-acetylene torch impinging on white hot Brookhaven-reactor graphite (the oxygen jet *cooled* the graphite rather than igniting it when the potentially-reducing acetylene supply was turned off), is perhaps the most graphic piece of evidence supporting the general contention that nuclear graphite cannot under normal circumstances present any kind of combustion hazard during reactor decommissioning or storage. It is perhaps relevant to quote verbatim from his paper [28], which is itself quoting from an unidentified earlier technical report by Woodruff and Bogert:

"There is a common perception taken from our experiences with coal and charcoal that when a mass of these fuels achieves a glowing red condition, a self-sustaining combustion is under way. Transferring the perception to graphite has led to repeated references to 'burning' graphite when, in fact, a self-sustaining reaction was not in progress. The test sequences described………..demonstrate how difficult it can be to achieve conditions for self-sustained combustion of graphite."

There exist a number of other experiences and studies which contribute further to this conclusion. These come from the USA, Italy, France and the UK. These are detailed in *Appendix 3.* This appendix also includes notes of some incidental observations relating to mobility of ^{3}H and ^{14}C which will be further elaborated in Sections 8 and 9.

6.5 Accident Analyses

Two major nuclear accidents – Windscale Pile 1 in September 1957 and Chernobyl unit 4 in April 1986 - have been repeatedly described either as being a 'graphite fire' or having a 'graphite fire' as an initiating or critical part of the event.

It should be evident from the foregoing that such a possibility is likely to be remote. *Appendix 4* presents a comprehensive and objective analysis of both of these incidents in the context of the understanding of graphite-oxidation behaviour.

It can be demonstrated from this analysis that there was, in all probability, no oxidation behaviour beyond that which would be predicted on the basis of the current understanding of the fundamental graphite oxidation mechanism which has been elucidated earlier in this report.

6.6 Flammability and Explosibility of Carbonaceous Dusts

In contrast to the situation with bulk graphite, graphitic dusts have been shown in recent studies to be 'weakly explosible' under the conditions of the standard 'ISO' explosibility test [32]. The presence of any more reactive carbonaceous deposits arising from irradiation of carbon monoxide in CO_2-cooled systems is an added complication. It is therefore necessary to make a proper assessment of the extent and nature of dusts within the areas of the core where any possibility of initiating an event can occur during dismantling procedures. In the UK, such a case has successfully been prepared for the authorisation of metal-cutting operations (and the subsequent removal of the graphite blocks) from the WAGR reactor at Sellafield [33].

It is important to recognise that the ISO standard specifies an apparatus containing a 10kJ pyrotechnic igniter. Without such an igniter, or with one of smaller energy, pure nuclear-grade graphite dusts appear unexplosible, and this is the situation reported in the previously-published standard reference [34].

Appendix 5 considers the available evidence on graphite dust explosibility[4] from recent test programmes in the UK, France and Italy, together with older research. This includes the effects of impurities arising from reactor operations. Impurities which are not themselves capable of oxidation, such as concrete dust or metal oxides arising from the corrosion of metallic reactor-circuit components during operation, will in general act as 'inerters' and thus diminish the potential risk [35 ,36], whilst SoGIN have demonstrated that irradiated circuit dusts collected from a cyclone after the full operational life of the Latina reactor are non-explosible in their ISO tests whereas unirradiated graphite dusts representative of Latina core graphite were weakly explosible (*M. Sturvi*, *personal communication*).

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[4] Strictly it is a deflagration rather than an explosion.

In order for a dust explosion to be possible, it is necessary to satisfy *simultaneously* all of the following criteria [34]:

- the dust must be combustible (the presence of volatile constituents is an important factor here);
- the dust must be airborne, implying either a need for a turbulent gas flow or for some physical disturbance which allows the dust to fall freely through an oxidising gas;
- the particle size must be optimised for flame propagation;
- the dust concentration must fall within the explosible range (i.e. neither too high nor too low);
- an ignition source of sufficient energy to initiate flame propagation must be in contact with the dust suspension (a high temperature surface may be sufficient for this, whilst a naked flame or electrical spark are obvious sources); and
- the atmosphere must contain sufficient oxygen to support combustion (this allows the possibility to provide an inert atmosphere local to the scene of any cutting operation if there is cause for concern about the reactivity of any adjacent materials).

All of these conditions must be satisfied simultaneously. An additional requirement, if a disruptive explosion is to result, is that the dust suspension must be in a confined space which inhibits the relief of the pressure rise resulting from the ignition. Specialist laboratories (for example, the Leeds University Energy and Resources Research Institute, UK) have developed arrays of connected enclosures for sophisticated analysis of the propagation of pressure pulses in model systems and assessment of their potential for causing specific damage.

In assessing the overall risk, secondary effects must be borne in mind. A pressure pulse arising from the ignition of a small amount of dust local to a cutting operation could cause dusts elsewhere to be elevated and thus enable them to contribute to a secondary explosion. Thus, any risk assessment must consider the full picture of the geometry and potential interactions, and not just the criteria noted above.

Appendix 5 details both the results of conventional and historical tests together with innovative work, particularly from the UK and France, which investigated specific geometrical arrangements and situations which represent in a highly pessimistic manner conditions which might be encountered during decommissioning activities. In each case, the results are highly supportive of the view that, properly managed, carbonaceous dusts within reactor vessels will not present any obstacle to safe decommissioning of the reactors.

More reactive amorphous carbon dusts and deposits may be present in reactors operated in a CO_2 coolant, and these are also considered in the Appendix.

Overall, several work programmes have confirmed that, whilst nuclear-grade graphite dust is considered to be weakly explosible in the standard ISO test, in practical situations (and *especially* in the presence of impurities), it is essentially self-extinguishing and extremely unlikely to present a hazard. It is also relatively easy to ensure that the conditions simultaneously necessary for the initiation of a dust explosion can be avoided in any practical decommissioning situation.

The essentially benign behaviour of graphite powder can be illustrated by a valuable example, taken directly from the nuclear industry. In the form of the commercial powder "Graphex™", graphite dust in bags was used as a fire suppressant in the nuclear industry in active cells and cave lines and, in the authors' experience at the Berkeley Centre, UK, has been successfully deployed more than once in this form directly on to burning Magnox following a hydride ignition in a failed fuel element during post-irradiation examination work.

6.7 Summary

In this Section, the oxidation behaviour of solid graphite and graphite dusts has been reviewed. It is shown that perceived risks of graphite 'fires' in any practical decommissioning/dismantling situation are entirely unfounded, that graphite even in extreme situations cannot 'burn' directly at any reasonably accessible temperature, but that it will oxidise at temperatures above around 400ºC in air in a manner which is well understood. It has also been shown that the behaviour of graphite dusts, should they be encountered, is likely to be relatively benign and also that the conditions which must be avoided in order to prevent any risk of a dust explosion are well understood and can be 'engineered' into a decommissioning programme.

On this basis, it is concluded that the dismantling of graphite-moderated reactors can be undertaken with no risk of incidents arising from the presence of graphite and graphite dusts. Special cases, such as the UK Windscale Pile 1 with its fire-damaged fuel elements and isotope cartridges together with high accumulations of Wigner energy, obviously demand special consideration in terms both of procedures and safety case, but here too the basic understanding of graphite behaviour can be applied to ensure that a viable and safe route is available.

7
METHODOLOGIES OF DISMANTLING GRAPHITE CORES

7.1 Dismantling the Graphite Stack

A range of technical options exists for the physical removal of graphite from reactors, and the appropriate choice will depend on the specific reactor design (especially the presence or otherwise of a pressure vessel) and on the condition of the graphite within the stack – in particular with regard to its residual strength and to its content of radioisotopes. Radioisotopes arise within graphite both from activation of original impurity atoms and also by transport of materials from other parts of the reactor circuit which then become activated. Where fuel failures have occurred, and in some reactors a very significant spread of fuel materials is present, then this additional hazard needs careful consideration.

Any use of mechanical equipment which rests upon the top of the stack in order to effect its dismantling requires confirmation of the mechanical properties of the reactor following its irradiation. For most commercial reactors, regularly sampling will have taken place to provide information on the changes in relevant properties such as compressive and tensile strength. Reactors irradiated in oxidising coolants may have experienced high levels of radiolytic weight loss – for example, the Bugey reactor in France had regions exceeding 40% weight loss when it ceased operation in 1994 [37]. Other reactors are known to have significant cracking of graphite components. In each case, a specific structural analysis needs to be completed to determine the mechanical adequacy of the graphite for the proposed dismantling methodologies. SoGIN in Italy appears to be the furthest advanced in this area, having established a programme developing and testing specialist equipment for graphite handling in its single Magnox plant at Latina (*A. Harrabalos, personal communication*).

Ref [38] describes the equipment under consideration for dismantling the Tokai I Magnox reactor in Japan. Here, after reviewing the requirements for a machine capable of removing single blocks, it was decided to develop the design further with the objective of removing up to seven blocks at one time. [39] describes the subsequent successful retrieval of graphite by a simple grab which opens out in the fuel channel to grip the graphite surface. It was found to be unnecessary to machine grooves or take other measures to retrieve the graphite by this means. German engineers are giving consideration to numerous methodologies for cutting the graphite within the reactor vessels [40].

For the Magnox and UNGG reactors, principally in the UK and France, differences of opinion continue to exist on the best ultimate dismantling methodology, and the affected utilities have taken advantage of original decisions to have long periods of ‘safe storage’ in order to delay addressing the issue. However, current circumstances and increasing public and political pressures are changing the scene. EdF in France strongly favours dismantling most of the UNGG plant under water, a policy previously proposed by CEA for the G2 and G3 plants under its direct control at Marcoule, although it has not been clearly established that the pressure vessels in these earlier plants can withstand the water pressure. In the UK, the Nuclear Decommissioning Authority has not yet declared a favoured methodology for the Magnox reactors, and this decision will probably await the outcome of the CoRWM debate on the subsequent handling of waste forms [15].

There is no specific plan either as yet for the UK AGRs, which are all still in commercial operation at the date of this report. It is almost certain that the same principles will be employed as are decided for the Magnox plant.

The other major group of graphite reactors, the RBMK's, also have formally an unresolved situation regarding dismantling, although a repository in Siberia is a strong possibility as an ultimate destiny for the graphite.

7.2 Dismantling Experience

Only a very small number of graphite-moderated reactors have so far been fully dismantled. These include the experimental HTR reactor Fort. St. Vrain in the USA, the early GLEEP stack at Harwell, UK, and the Windscale prototype AGR in the UK.

GLEEP is a special case in that the total irradiation was so small, and the consequent activation of impurities so equally small, that the stack was effectively dismantled by hand using only basic protective coveralls and gloves [41]. The subsequent treatment of the graphite in an industrial incinerator to mobilise a significant proportion of the ^{3}H and ^{14}C content will be described later in Section 9.10.

Fort St. Vrain presents the best-documented example to date of the dismantling operations and the restoration of the surroundings to "brown-field" status [42] and was the world's first full successful decommissioning of a commercial nuclear power plant. In this HTR design the fuel was present as compacts within graphite fuel blocks, necessitating the simultaneous handling of graphite and fuel.

In the 'prismatic-fuel' HTR design, removal and replacement of graphite fuel blocks is routine as part of maintaining the reactivity, and dedicated facilities were available to receive fuel blocks from which they could be put into a specially constructed spent-fuel storage facility – this being necessary because the original plan to remove them to a secure government nuclear site in Idaho was vetoed by the Idaho Governor. It is intended eventually to remove all of the fuel blocks either to a dedicated waste facility or to the Hanford site: at the time of the decommissioning (early 1990's) there was no intent to separate the fuel from the graphite blocks.

The reflector blocks from Fort St. Vrain – more than 5000 individual graphite components – were removed, along with other pressure-vessel internals, after cutting access through the concrete top head section (4.5 metres thick) and flooding the pressure vessel with water to minimise radiation dose to the operators. A rotating service platform was inserted in order to transfer the graphite to a transfer basket which was raised into a 'shield bell' and the contents transferred to shipment flasks for disposal as low-level waste (LLW).

Currently, a scheme proposal is in place within the European Union which aims to investigate thoroughly all aspects of the handling of irradiated nuclear graphite blocks and graphite-containing fuel components such as HTR compacts. The viability of separation processes, and the possible re-cycling or re-use of the bulk of the graphite material within the nuclear industry, will be investigated fully both on a technical basis and in terms of environmental and economic impact. Subject to funding approval[5], this work is proposed to be conducted in the period 2006 – 2010 and will involve major organisations throughout the European Union.

In the Windscale prototype AGR, where the graphite-sleeved fuel was removed to storage at an earlier stage, leaving only graphite moderator and reflector blocks to be dealt with in the absence of fissile materials, water flooding was also considered but was deemed to be unnecessary – partially on the basis that no suitable water-treatment plant was available and that the potential environmental risk through water spillage in a location with a high water table was assessed as greater than operating in air. The dismantling operation in air was completely successful [43] – a closed environment being maintained as the graphite blocks were removed through the penetrated vessel. Here, the blocks have been placed in storage boxes within a specially constructed surface facility, designated as 'interim' storage until an appropriate route for final disposal is available.

Wherever temporary storage boxes are employed for graphite, care needs to be taken to ensure that an electrochemical cell is not set up through the inadvertent inclusion of moisture or subsequent external corrosion of the boxes allowing water ingress. Such a cell would lead to a rapid degradation of the containment and a possible activity release.

This dilemma illustrated by the WAGR situation whereby the graphite blocks, having been removed safely from the reactor, have been placed into interim surface storage pending a decision about their final disposal, shows the lack of preparedness for the decommissioning of graphite reactors – and others – despite of lead time of more than 50 years since the construction of the first plants in the US, the UK and Russia. The lack of foresight in design, materials specification, construction, and operational procedures have all led in different ways to specific difficulties with subsequent treatment and disposal of the reactor materials, including of course the graphite. A major motivation for the EU work proposal referred to earlier is the certainty that any new build of reactors – graphite or otherwise – will require an identified waste-management route *in advance of construction* for all major waste streams, in order to secure licensing. And of course, the lack of a repository facility for ILW (the nature of most existing irradiated reactor graphite) in the countries which require one is sufficient justification for the investigation (or in some cases re-investigation) of other options for disposal of irradiated graphite.

One major factor in determining the appropriate course of action is the radioactivity content, and the degree to which the radioactive material is fixed within the graphite matrix or is present as loose contamination. The main considerations in respect of the presence of different radioisotopes are considered in Section 8.

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[5] The proposal has been submitted under the EU Sixth Framework Programme (Euratom), under the acronym 'GCR-MINWASTE'

7.3 Reactors With Special Situations

It is the very early reactors, essentially the plutonium production reactors, which present unique problems. Russian plant at Krasnoyarsk, Tomsk and Chelyabinsk were of a crude design, cooled by water and without pressure vessels [44]. Many fuel failures have occurred over the years, and similar problems also befell the two reactors at Beloyarsk which were the forerunners of the RBMK designs although utilising an experimental fuel design in which the coolant passed through the fuel assemblies rather than in separate water tubes through the graphite. In addition to having extremely contaminated material to deal with, including high levels of α activity, the Russian authorities decided that some of the these shut-down reactors should have their cores sealed using epoxy-type resin material. Whilst expedient in the short term to minimise the mobility of radioactive isotopes, this new combination of graphite and resin will present unique disposal issues in the future [45].

The UK Windscale Piles also present a unique problem, especially Pile 1 which experienced the 1957 fire. Reference is made in detail in *Appendix 4* to the high Wigner energy content of any graphite reactor operated at low temperatures, as plutonium producers generally are, and to the contamination by fuel and the oxidation of graphite which occurred during the Windscale accident [46,47] and the details are not repeated here. Dismantling under water has been mooted in the past, but there is no containment vessel as such and the Pile construction is not sufficiently watertight to prevent further radioactive contamination of the ground which would contravene current UK Environment Agency requirements. Instead, work to assess and minimise the hazards of dismantling in air continues, but the procedure to be employed has not yet been agreed.

The Brookhaven Graphite Research Reactor (BGRR) is currently being surveyed and sampled to obtain radioactivity data, and presumably Wigner energy data, prior to dismantling [48]. Of special interest is the significant distortion in the graphite in channels where there have been fuel failures. This is attributed to ‘overheating’, but it is not immediately obvious why the graphite should distort at temperatures well below the graphitisation temperature unless chemical reactions have taken place.

The Hanford (USA) reactors, which also contain graphite with significant Wigner energy and also experienced large amounts of irradiation damage because of the low irradiation temperature (distortions and cracking of graphite components), have until recently had no specific disposal plan except an intent to move entire intact reactors away from the immediate vicinity of the Columbia River flood plain to higher ground, before interment at shallow depth. However, current thinking *(B. Reid, PNNL, personal communication)* appears to favour a dismantling approach with appropriate handling and containment of the graphite blocks before burial on the Hanford reservation.

7.4 In Situ Removal of Graphite

The possibility of removing graphite by in-situ gasification has been raised [49]. In many cases reactors at the end of life have lost a considerable proportion of the moderator mass through gasification, and hence this offers the possibility of deliberately continuing the weight loss process until all the graphite is removed. To accomplish this the reactor gas circulation would be continued following the end of operation and fuel removal, using chemistry designed to gasify the remaining graphite. The possibility even exists of encouraging the local gasification of graphite in specific regions of the moderator by application of local heating in the circulating gas. This could be useful to overcome concerns about uncontrolled collapse of the graphite structure during the final stages of gasification.

7.5 Summary

It follows from this short resumé of the dismantling problems and options that there is no single – or simple – answer to the identification of a dismantling strategy for the graphite components in graphite-moderated reactors. Each design present a unique situation requiring its own specialised dismantling procedures and the development of dedicated remote-handling equipment, whilst individual reactors where specific incidents and situations exist require unique solutions.

One unique possibility for removal that could have value in specific situations in that of *in-situ* removal using a variant of the ‘steam-reforming’ process.

8
RADIOACTIVITY IN IRRADIATED GRAPHITE

8.1 General Principles

The radioactivity associated with reactor graphite arises both from the activation of the initial impurities and from subsequent contamination arising within the reactor circuit. For items such as fuel sleeves which may have been pond stored, the inventory may have been further modified by immersion in aqueous solutions.

The contamination may be as solid materials arising as corrosion products from reactor steel work and transported to the graphite core, becoming activated by the neutron flux. Alternatively, it may arise as a result of fuel-element failures or from gas-phase activation (e.g. ^{14}C arising from activation of $^{14}N_2$ in the cover gas or as a coolant impurity) followed by subsequent incorporation into the graphite or into carbonaceous materials deposited upon it.

The reactor atmosphere may also have influenced the final radioactive inventory in other ways, such as providing a pathway for the removal of ^{3}H (arising both from ^{6}Li in the graphite and from fission events in the fuel) by exchange with gaseous and absorbed compounds containing inactive hydrogen.

The initial impurities in different types of nuclear graphite differ significantly and, in components such as fuel sleeves removed from irradiation after relatively short periods compared with moderator blocks, radioactive inventories may be quite different. After longer irradiations, more isotopes reach equilibrium specific activities, and some with short half lives may even ‘burn out’ entirely. It is not practical to consider many graphites with different impurity contents and irradiation histories in this document, and so the topic of radioactive inventory, decay, and issues such as leaching potential are considered in more general terms.

It cannot be assumed that two reactors of similar design, even perhaps on the same site, will have identical characteristics in this respect. Specific operating histories have been found to influence transported materials strongly – events such as a disturbance to the normal pattern of coolant-gas circulation, or an ingress of water leading to enhanced release of corrosion products, are examples. Clearly, specific data on the graphite in a particular reactor which is to be decommissioned are invaluable in determining the appropriate requirements for graphite handling and its subsequent treatment. However, some example inventories from published information are given in *Appendix 6*. It is important when reviewing these data to consider the date of the analysis and the date at which irradiation ceased, in relation to the present day.

Ref [2], prepared by a UK team for the European Community's Research programme on Decommissioning of Nuclear Power Plants in 1984, presents a comprehensive analysis of the radioisotope issues using UK Magnox and AGRs as examples. The estimates of residual radioactivity and subsequent decay that they employ were, however, based upon the then-current presumption that the reactors would operate for 40 years at a 70% load factor and that this would be followed by ten years' 'storage' within the reactor vessels before the core graphite entered a final disposal route. Sleeve materials were not addressed in the study.

Whilst these assumptions are no longer appropriate, [2] provides a valuable basis for discussion. The work used Pile Grade 'A' graphite from the Magnox programme, and Gilsocarbon graphite produced by the former Anglo Great Lakes Co. for AGRs as reference graphites. This immediately presents a difficulty since it is now known that the impurity content of different batches of PGA (produced by two different manufacturers) and of gilsocarbon graphites in AGRs (three different manufacturers and various changes in the coking plant) resulted in large differences in some impurity concentrations (especially cobalt, leading to ^{60}Co, in the gilsocarbons). In fact, huge differences in ^{60}Co activity are evident in samples from the AGRs because, in addition to the manufacturing differences, some reactor boiler designs led to significant additional transport of steel-corrosion products into the graphite core, adding to the ^{60}Co problem.

This means that the conclusions of [2] in respect of relative isotopic contents do not explicitly apply even to one particular plant, but the general issues that they present are valid in all cases. Again, the value of specific assays from a plant prior to decommissioning cannot be overstated.

In general, in all cases for graphite-moderated plant, ^{14}C, ^{3}H and ^{36}Cl are the most significant isotopes likely to be present from impurity activation which need to be considered in terms of possible entry to the food chain, although the relative proportions will vary widely. It is the extremely long half-life of ^{36}Cl which determines a need to grout irradiated graphite in a cementatious matrix before it can be placed in a deep repository. Ironically, the chlorine was originally introduced as a means to purify the graphite at the graphitisation stage of manufacture, removing metallic elements as their volatile chlorides. This was superseded by the use of freons, now environmentally unacceptable, and magnesium fluoride is now the usual medium for modern graphite purification. ^{60}Co, ^{94}Nb, ^{152}Eu and ^{154}Eu are the most significant gamma-emitters leading to shielding and handling requirements during dismantling.

Uranium impurity in the graphite, although generally below 0.1 wppm, may give rise to fission products, as can traces of uranium on the external surfaces of fuel elements and also any fuel failures which have occurred during the reactor's operating history. Generally speaking, radioisotope yields of significant half life from these fissions are small compared with the direct activation products, with the exception of the gamma emitter ^{137}Cs. It is shown in [2] that up to 0.1 ppm uranium in the graphite, arising from fuel failures, does not affect the conclusion that the dominant isotopes will be ^{14}C and ^{36}Cl.

Other isotopes may also be of significance in specific disposal routes – for example, if they are especially prone to leaching from graphite in storage facilities, or in sea dumping, which was not excluded from the study at the time although subsequently vetoed by international agreement. Such isotopes include ^{133}Ba, ^{134}Cs and ^{108m}Ag. Where disposal methodologies are susceptible to possible leaching into groundwater or the marine environment, a further factor which must be taken into consideration is the ability of certain creatures (especially shellfish), plants and even local sediment beds to concentrate and retain certain isotopes, thus building up a greater potential hazard than is immediately evident from the basic concentrations of the isotopes in the leachate. Factors of up to 10^4 (quantity of isotope per tonne of material compared with quantity per m^3 of filtered water) are found for numerous isotopes in sediments whilst molluscs, particularly, concentrate heavy metal isotopes such as zinc, silver and cadmium [2].

A further part of the analysis should examine the specific nature of individual and collective doses arising from the disposed graphite. Some isotopes present an external irradiation hazard whilst others may present an inhalation or ingestion hazard, depending upon the local circumstances.

Overall, this tells us that a specific analysis of the initial isotope content of the graphite being disposed, the chosen disposal or treatment process, and the final physical state of the graphite/residues/containers in which it is disposed, is essential. Where a decision about options is being sought, this is a vital input parameter in an objective risk analysis.

8.2 Short-Lived Isotopes

The most significant short-lived isotopes arising in irradiated graphite are ^{3}H and ^{60}Co, with half lives of 12.3 years and 5.3 years respectively. The origins of both of these have already been indicated.

Tritium is a particular problem because of its ability to exchange readily with inactive hydrogen atoms in a variety of compounds which include atmospheric water vapour and which can find their way readily into biological systems. The problem of monitoring tritium releases from safe-stored reactors, where there are potentially numerous small pathways for escape of gases and vapours, was solved in a lateral way for the shut-down UK Magnox reactors by creating an easy route which would be certain to dominate the release, and then monitoring it to demonstrate that the resulting release was acceptable.

Tritium is created throughout the graphite from ^{6}Li, and diffuses at a slow rate [25, 50] to reach pore surfaces where it exchanges with adsorbed hydrogenous molecules. Adventitious tritium from fission events will also tend to become absorbed at the pore surfaces. Release in normal operation then occurs through exchange with hydrogenous molecules in the coolant (water in air-cooled systems, hydrogen, water and methane in CO_2-cooled systems), creating a quasi ‘steady state’. Transient higher release rates can be triggered particularly if an increase in the total hydrogenous burden of the coolant occurs due, for example, to a steam leak [23]. The system then slowly responds to the diffusion of tritium through the crystallites until a steady state is restored.

Particular care is thus required when handling irradiated graphite in quantity in the early period following reactor shutdown, especially when changes in the surrounding atmosphere occur, to ensure that personnel doses are minimised. However, after around 50 years, the tritium content will be negligible (~ ten half lives). It has also been observed in practice, in laboratories handling small graphite samples which are only recently removed from the reactor and are destined for monitoring tests, that tritium release has not been a significant problem in handling the material (*A.J. Wickham, personal communication*).

With this in mind, the requirements for graphite handling and shielding in the early years following shutdown, provided that loose contamination is not present, are effectively determined by the content of 60Co in the material. As already indicated, the actual contents of 60Co from different irradiated graphite sources vary widely, and specific monitoring of each installation is essential in determining the procedures needed. As an illustration of the range likely to be encountered, UK Pile Grade 'A' samples from Magnox samples could be freely handled in small quantities in the open laboratory after 30 years' irradiation whereas gilsocarbon samples from AGRs after much shorter irradiation periods needed steel or lead handling cells and remote manipulators, even for small masses of material (*A.J. Wickham, personal communication*).

8.3 Carbon-14

8.3.1 Production and Location

The presence of ^{14}C in irradiated graphite is of particular importance: its production is unavoidable, its perceived impact on the environment is high, although this is fiercely debated and probably inaccurate, and control of its releases is a major practical and economic factor in the various options for treating and disposing of graphite, including incineration options. ^{14}C is of course capable of entering and being retained in biological systems in almost any carbonaceous compound with which it can become associated, and the resulting beta decay presents the radiological hazard.

Most of the ^{14}C arising during irradiation comes from the activation of ^{14}N, even in systems which do not have either an air coolant or a cover gas containing nitrogen. The presence of quinoline-type compounds in the pitch used for the graphite manufacture is a significant source of inherent nitrogen impurity in graphite. A recent review [26] carried out for UK NIREX Ltd has examined in detail the origins and disposition of ^{14}C within graphites likely to enter the UK disposal routes (i.e. Magnox and AGRs, together with air-cooled reactors such as BEPO and GLEEP at Harwell and the Windscale Piles). The analysis is readily widened to cover other systems such as RBMK and early plutonium producers from Russia and the US.

The three principal routes for generation of ^{14}C in nuclear graphite are the following:

Reaction	Capture Cross-Section barns[6] (10^{-24} cm^2)	Abundance of Isotope in Natural Element (%)
$^{14}N(n,p)^{14}C$	1.8	99.63 ^{14}N in natural N
$^{13}C(n,\gamma)^{14}C$	0.0009	1.07 ^{13}C in natural C
$^{17}O(n,\alpha)^{14}C$[7]	0.235	0.04 ^{17}O in natural O

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[6] Figures for the most probable neutron velocity for neutrons in equilibrium with matter at 20.44ºC

[7] Also formed in a two-stage process from $^{16}O(n,\gamma)^{17}O(n,\alpha)$

Combination of these data with the available sources of these three elements within the graphite and reactor coolant allows the calculation of the relative importance of these pathways for UK AGR systems to be assessed (taking the average coolant concentrations over the operating life for oxygen-containing CO, CO_2 and H_2O and taking 50 wppm as an average concentration for impurity N_2 in graphite[8]). Assuming a standard operating lifetime of 30 years, the result finds the ratio 305:33:1 for production from ^{14}N:^{13}C:$^{16/17}O$ respectively. Whilst the nitrogen route dominates the production because of the very high cross-section for its activation, the ratio is extremely sensitive to the quantities of nitrogen assumed to be present.

In an air-cooled reactor, the proportion of nitrogen in the coolant is some 15,800× greater than in this calculation for a UK AGR – however, one needs to bear in mind that most of this ^{14}C formation will take place in the coolant, and that which deposits in solid form upon the graphite is also subject to continuous oxidation during the irradiation.

The RBMK system, with a high proportion of N_2 in the cover gas, where the other component is helium and is overall non-oxidising, is therefore expected to produce a much higher residual ^{14}C burden on and within its graphite compared with an air-cooled system at an equivalent irradiation, and this results in a major problem in dealing with the graphite [51 - 53]. Refs [51] and [52] provide useful information on the typical rates of loss to atmosphere of ^{14}C during normal operations at the Leningrad and Ignalina power plants respectively. It is also known from experience in the Canadian CANDU reactors which originally used nitrogen as an annulus cover gas that the irradiation produced the polymer paracyanogen $((C_2N_2)_n$ in which every carbon atom was ^{14}C [54], and thus compounds such as this are also potentially associated with the graphite and need to be taken into consideration. As both the monomer and the polymer are stable in air, they may also be present on the graphite of low-temperature air-cooled plant.

UNC Nuclear Industries have made a critical analysis of the ^{14}C inventory and potential release pathways for the graphite-water reactors at Hanford USA [55, 56], editing together for public release data from a number of previously classified sources. This includes observations of daily release rates from the operating reactors and makes the interesting comparison that the release rate from a 1200MWe plant was roughly comparable with the release of natural ^{14}C from a 200MWe wood-burning plant. The desirability of placing 'nuclear' activity releases into the context of the natural background and the accepted industrial/social environment is discussed in Section 11.2.

The UNC reports also provide a graphic illustration of the importance of the formation route of ^{14}C from $^{14}N_2$: at one time the Hanford reactors KW and KE were operating with a CO_2/He and a N_2/He cover gas respectively but at otherwise very comparable conditions: the daily release rates of ^{14}C, primarily as $^{14}CO_2$, were respectively $39 mCi.d^{-1}$ and $103 Ci.d^{-1}$ (1.44×10^9 and 3.81×10^{12} Bq respectively).

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[8] This estimate includes both impurity nitrogen compounds in solid form within the graphite and entrapped gas in 'closed' pores remaining from entrapped air during manufacture.

A similar conclusion may be drawn from an analysis of the Peach Bottom HTGR which was conducted in 1980 [57], which noted an ‘unexpected’ concentration of ^{14}C at the edges of graphite components and in the charcoal traps (intended to trap fission products) – the latter containing almost as much ^{14}C as the combined graphite fuel-element sleeves and spines. These authors appear not to have recognised the importance of ^{14}C from residual nitrogen in the coolant, although they do deduce that the Peach Bottom fuel particles contained a greater concentration of nitrogen than previous workers had assumed.

In both air-cooled and CO_2-cooled plant, a high proportion of the ^{14}C formed in the coolant comes from the ^{17}O (and indirect ^{16}O) route, and in CO_2-based systems this is the dominant route. The effectiveness of this contribution to the ^{14}C eventually found associated with the residual graphite depends both on the efficiency with which the aerosols forming in the coolant become adherent to the graphite surfaces and the extent to which they are re-oxidised through radiolytic reaction with CO_2. Factors such as gas velocity, permeable flow through transport porosity and so on, will all play a role in determining the eventual situation.

It will therefore be clear that measurements of the ^{14}C activity in graphite, and some understanding of the location and nature of the chemical form of adherent deposited ^{14}C, are essential in determining the available disposal options for the particular material. There is evidence that a high proportion of the ^{14}C arising in low-irradiated graphite from the air-cooled GLEEP pile in the UK could be mobilised (removed) by a period of around 3 hours at 1150ºC in an industrial incinerator, and that similar results were achieved on small samples of graphite from an HTR in a more controlled laboratory environment [41], implying that there is significant localisation on surfaces, and this is confirmed using Japanese data from secondary-ion mass spectrometry about the nitrogen distribution in unirradiated Pechiney graphite representative of the Tokai I Magnox reactor [58],: before these results were known, [26] concluded, from a detailed analysis of the graphite irradiation behaviour at the atomic level under fast-neutron bombardment, that most of the ^{14}C originating from impurities within the graphite itself would be strongly bound to the base graphite, and a French view on the irradiated UNGG material (also Pechiney) concurs (*L. Rahmani, personal communication*). Clearly this issue is deserving of further research work, and such studies are planned within the EU GCR-MINWASTE proposal discussed in Section 7.

A more detailed analysis of isotope mobilisation, including ^{14}C, appears in Section 9.6.

8.3.2 Discharges to Atmosphere

The next topic deserving of discussion is the perceived risk to the environment if discharges of ^{14}C-containing gases occur.

In the 1980s, the UK CEGB recognised the need to investigate disposal routes for the graphite in its Magnox reactors, and Nair undertook a study on their behalf on the environmental impact of incinerating the graphite [59]. The study recognised that release of $^{14}CO_2$ to the atmosphere would result in the incorporation of ^{14}C into plant tissue and would thus reach man both through the food chain as well as by direct inhalation.

The basis of the study was an assumption that one Magnox reactor graphite core would be incinerated per year, over a period of 20 years[9]. A very detailed analysis of global dispersion was undertaken, involving the tropospheric, oceanic (currents and sedimentaion) and terrestrial ecosystems, and use was made of atmospheric measurements on the dispersion of ^{14}C released into the atmosphere from atomic weapons testing. The 'baseline' for the study was the continuous natural formation of ^{14}C from atmospheric nitrogen through the action of cosmic rays, and it was against this unavoidable yield that the impact of irradiated graphite incineration was measured. Account was also taken of the so-called 'Suess Effect' [60] whereby the burning of fossil fuels slightly depletes the atmospheric ^{14}C ratio (w.r.t. ^{12}C) because they are depleted in ^{14}C through natural decay.

The absorption of atmospheric CO_2 in the deep oceans, the formation of carbonate sediments, and the exchange of $^{14}CO_2$ with existing ^{12}C carbonates in the sea water, implies that the effective half life of ^{14}C in the global ecosystem is much less than its radioactive half-life of 5760 years. Indeed, Morgan, of the USA Pacific North Western National Laboratory, has commented that a more realistic figure is 35 years [61].

The Nair study showed that the collective dose arising from the graphite incineration was at most 1.2×10^{-2} µSv, some three orders of magnitude smaller than the annual background from cosmic-ray production and six orders of magnitude smaller than the overall background radiation dose in the UK of about 1 $mSv.yr^{-1}$. Nair comments that it is debatable whether such low doses can sensibly be included in a collective dose assessment, given that they represent a mortality risk not exceeding 10^{-10} per year.

In the current debate about the alleged 'unsuitability' of incineration because of the release of ^{14}C, this important study relating the effects of deliberate ^{14}C releases by graphite incineration to the natural ^{14}C background seems to have been overlooked. It is important to recognise that the analysis concentrates on global collective doses, and does not examine the local personnel dose in the vicinity of an incineration plant. However, Dubourg has taken the argument further [62] and contends that the local dose to the most exposed group in the vicinity of a well-designed incinerator, using the 'ICRP 60' criteria, will be much lower than the allowable limit of 1 $mSv.yr^{-1}$ and should, in fact, be no more than about 4% of this limit.

Support for the trivial impact of carefully engineered releases of ^{14}C from graphite incineration options also comes from US research. Investigations into proposed incineration of HTR fuel compacts at Idaho National Laboratory has led to the conclusion that both ^{14}C and tritium could be released directly to atmosphere without concern [63], although the argument is slightly impaired here by the inclusion of yields from atomic weapons tests in the analysis alongside the results of cosmic-ray bombardment of $^{14}N_2$.

The true impact of the release of ^{14}C to the environment therefore becomes the key issue in regard to incineration methodologies, and is the driving force behind the consideration of (expensive) schemes to recover and concentrate the ^{14}C into smaller volumes of waste for disposal along with other radwaste in various ways which are discussed in Section 9.10. In this context we should note that UK NIREX consider the potential release of ^{14}C-containing methane

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[9] Strictly, the assumption was 1120 Ci ^{14}C contained within a mass of 2200 te graphite, released uniformly thoughout one year, for a period of 20 years.

from graphite in repositories as a potential hazard [64] and that Russian teams in collaboration with The University of Sheffield in the UK offer this as a supporting argument for their immobilisation process [65] which is discussed in detail in Section 9.8.

8.4 Chlorine-36

^{36}Cl - or more precisely, its potential for entering the environment through chemical reactions - is the principal reason why graphite wastes intended for a repository are deemed to require grouting with a cementatious material before being placed into storage containers. A comprehensive study was conducted by UK NIREX [66] to assess the chlorine inventory of wastes and this included a total of 458 assays of chemical chlorine content in graphite from various sources used in UK Magnox and AGR reactors, using neutron activation analysis. Losses under simulated irradiation (electron beam) and upon heating were also studied. Both of these processes resulted in significant losses of chlorine from the graphite.

Rahmani [67] has also demonstrated a significant movement of chlorine and chlorine isotopes into and out of graphite with time (or storage). A significant part of the ^{36}Cl content can be lost from small samples and powders, either through chemical reaction with atmospheric gases, diffusion or so-called ‘diffusion shock’ (in which is included the consequences of grinding up the sample). This was illustrated with data for Vandellos sleeve graphite:

0.013% ^{36}Cl lost in one year storage (silo) from a whole sleeve

10% lost in ten days from material ground to 1mm

80% lost in ten days from material ground to 100µm

These very recent results are not yet corroborated with data from other sources, but there is a clear suggestion that mobilisation of ^{36}Cl should be considered as well as that of ^{14}Cl and ^{3}H discussed in Section 8.3.1 and 9.6.

The migration of ^{36}Cl, and possibly other isotopes, might also be assisted by application of an electrical potential if the graphite is made cathodic by provision of a positively charged counter electrode. Chlorine is likely to be anionic (negatively charged) and will tend to migrate out of the pores and towards the counter electrode. Pressure variation and use of surface active agents might be employed to improve access of solution to the internal open pore structure

It is very clear that migration of ^{36}Cl can be very significant, and therefore a potential problem in waste disposal. The apparent mobility of the isotope may also be used to advantage in decontamination technologies ahead of possible re-use or recycling options for the material which are discussed in Section 9. These possibilities appear to merit further investigation.

8.5 Leaching of Radioactive Isotopes

Leaching of activity from graphite is an issue both in 'safe storage' and in any long-term storage arrangement, and is also pertinent to graphite debris such as fuel sleeves stored in silos. Consideration is limited to aqueous media, and any water which is likely to contact the graphite could be rain water (inleakage to surface temporary storage), condensate water, ground water penetrating a repository or, if sea dumping were re-considered, sea water.

The characteristics of each of these waters (pH, impurity content) will be different and, may be further modified as a consequence of penetration through immobilising media (such as cement grout), local corrosion of metallic flasks, etc. Thus, there are numerous options for the leachate chemistry which, in many practical circumstances, cannot be accurately predicted.

Immediate exchange of surface-bound ^{3}H with the water would be probable. The possibility of desorption of other isotopes associated with the geometrical and pore surfaces must be considered, but those which are chemically bound within the solid are unlikely to be leached until the carbon atoms themselves are leached: this may be by corrosion processes or by selective dissolution from other minor phases within the graphite.

Until recently, there have been only a limited number of studies on reactor-irradiated graphite and the results are not consistent. A study in the USA compared leaching of ^{14}C and ^{36}Cl from Hanford graphite and French Pechiney graphite in both de-ionised water and Hanford groundwater at pH 8.3 [68, 69]. After correction for a large difference in the specific surface area of the two materials[10], a much higher leach rate (per unit area exposed) was found for the French material – by two to four orders of magnitude in the early stages of leaching. Equilibrium leach rates were typically $1\text{-}2 \times 10^{-11}$ g.m^{-2}.d^{-1} (French graphite) and $2 \times 10^{-12} - 5 \times 10^{-13}$ g.m^{-2}.d^{-1} (Hanford) for ^{14}C and $2\text{-}50 \times 10^{-11}$ (French) and $2\text{-}7 \times 10^{-13}$ g.m^{-2}.d^{-1} (Hanford) for ^{36}Cl.

The mechanism which was believed to result in the leaching is a water-catalysed oxidation by dissolved oxygen to form CO_2 [70]. Eventually the leach rates of both ^{14}C and ^{36}Cl approached that of ^{12}C, as would be expected for this hypothesis: in one of the French samples there was insufficient oxygen present to oxidise the ^{12}C at the same rate as the ^{14}C, and there was evidence that the ^{14}C was then preferentially attacked.

Temperature effects were also studied, with an activation energy between 5.5 and 5.9 kcal.mol^{-1} for studies close to ambient temperature: a change of mechanism and a higher activation energy were suggested at higher temperatures.

Leaching tests were also carried out by CEA in France [71, 72] on a range of nuclides. The tests were conducted over 90 days with results also available after day 3, and are expressed as cumulative release fractions – unfortunately, as sample dimensions are not reported, direct comparison with other data is not possible. The order of leaching efficiency after 90 days, however, is ^{137}Cs>^{133}Ba>^{60}Co> ^{63}Ni>^{36}Cl>^{154}Eu>>^{14}C. The rate for ^{3}H was variable but between that of ^{60}Co and ^{14}C. This work also investigated the benefits in reducing leaching to be derived from impregnation with epoxy resin, bitumen and an epoxy/pitch material. The greatest benefit

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[10] The Hanford graphite is reported to have an extraordinarily large specific surface area of 5m^{2}.g^{-1}.

derived from the last of these and was stated to be due to the blocking off of all pores larger than 0.1 µm entrance diameter, and comparison with the un-impregnated samples of graphite taken from the Marcoule G2 reactor showed reductions in leach rates of between 10 - 100× after periods of 3 days and 90 days for ^{60}Co, ^{133}Ba, ^{137}Cs, ^{154}Eu, ^{3}H, ^{14}C, ^{63}Ni and ^{36}Cl.

A third series of tests were made in support of the EU study on graphite management modes issued in 1984 [2]. These used a third method of presentation, quoting results in cm.d^{-1} which derive[11] from an IAEA-approved method of study [73] which was modified by these authors to expose the entire surface area of the sample to the leachant. Again, comparison with the other work is difficult because of the different conditions. The initial samples (using small samples of irradiated Pile Grade 'A' graphite irradiated in a Magnox reactor for approximately 13 years to 16,000 MWd.te^{-1}) had a radionuclide inventory (in order of specific activity) of ^{3}H>^{14}C>^{55}Fe>^{60}Co>^{154}Eu>^{134}Cs>^{133}Ba>^{155}Eu>^{152}Eu>^{108m}Ag. ^{134}Cs in not included in theoretical inventories for irradiated graphite but has been detected in many samples: EdF have also recently confirmed that the observed radionuclide inventories do not match well the predictions (*L. Rahmani, personal communication*).

The samples were immersed in simulated groundwater or simulated sea water, the latter under pressure to simulate sea-bed conditions. Leaching of ^{3}H, ^{14}C, ^{133}Ba, ^{60}Co and ^{134}Cs occurred from all samples, but other isotopes leached were below the limit of detection. All leach rates fell off with time, in common with previous studies, except for ^{60}Co which rose steadily in each environment up to the full duration of the test, which was 150 days. The loss of activity of ^{3}H and ^{14}C over this period in each case was approximately 0.3% and 0.08% respectively.

The fundamental quantities required for radiological assessments of disposed graphite or for grouted disposal packages are the rates of release of specific nuclides as a function of time in an assumed scenario in which the basic packaging has been penetrated and access by water is possible. These data are highly specific to the graphite itself, to its irradiation history, its pre-treatment before disposal and its precise disposal conditions, and need to be extrapolated to very long times. The 'state of the art' in this area is very unsatisfactory, and suitable quantitative experiments whose results can be relied upon are difficult to devise.

Nevertheless, as part of the drive to obtain data to support the decommissioning of the French UNGG reactors, CEA are engaged on new leaching studies into pure water on material freshly obtained from the shut-down reactors. Partly being undertaken to underwrite the possibility of dismantling these plant under water, they will study the leaching of a number of isotopes, but principally ^{3}H, ^{14}C and ^{36}Cl from both powdered graphite and from solid samples. Some of the tests already completed have returned highly inconsistent results, for example with Eu isotopes. The water was replaced at each analysis, which took place at intervals of one to three months. The forthcoming tests will include samples trepanned from the channel wall arranged such that the sides of the cylindrical sample are encased in silicone rubber so that all isotopic transfer must occur from the ends. The samples will be partially immersed in water with the channel-wall end at the bottom and the more irregular broken-off end remaining in air. Analysis of the results will depend upon the extent of access of the water to the transport-pore structure, which for short-term immersion is generally extremely difficult since water does not 'wet' the graphite.

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[11] The strange units represent: (fraction of initial activity leached per day) × (volume/surface-area ratio of sample).

A number of computer codes have been developed for analysis of leaching potential in specific disposal geometries, for a range of materials which includes irradiated graphite. Such an example from the UK is described in [74]. This code relies upon good thermodynamic data for the compounds of the radioactive elements which are specified or measured in the inventory of the particular reactor graphite. In many instances, the chemical literature can provide reliable data: in other cases only estimated behaviour can be input, and in any cases an assumption of the nature of the leaching solution must be made.

Even when such a calculation can be made, the data must be interpreted appropriately for the physical nature of the store, site or repository from which the assumed leaching is occurring, in order to model correctly the leakage pathways back to the biosphere. In many cases, these will be isotope-specific. They include natural processes such as movements in the water table and connection to springs and streams, growing crops, grazing livestock, sea currents and sedimentation, the movement and feeding of fish and the (probably unpredictable) activities of man in the future.

With these uncertainties, together with the rather poor state of knowledge of leaching behaviour from graphite in general, there is at least a small argument in favour of consideration of routes other than long-term repository or dumping, unless there are mitigating factors[12]. Containing and dealing with the problem in the short term must now be seriously considered.

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[12] Such a mitigating factor could be 'dilution and dispersion', such as using remote deep ocean trenches for sea dumping, as an alternative to 'concentrate and contain' which demands supervision and provision against issues such as inadvertent leaching.

9

PROCESSING AND DISPOSAL OPTIONS

9.1 Introduction

Internationally, most current plans for graphite disposition consider burial in some form as the favored option. However, graphite is a special radioactive waste, and it is important to consider alternative potential options for processing and disposal of graphite, in order to ensure that a proper safety, economic and environmental basis exists for the options eventually chosen. The burial of the full world inventory of graphite would entail a very significant cost burden, and would require substantial scientific effort to underwrite its safety.

9.2 Conventional Burial Options

9.2.1 Land Disposal

Whatever delay has taken place prior to reactor dismantling and graphite disposal, long-lived radioisotopes capable of entering the environment will remain associated with the graphite. It is therefore a pre-requisite for land disposal that external containment will be required. This provides a barrier to release of activity during transport, handling and storage, and usually for a long period of time after disposal. The current UK perspective of containment is provided in Section 9.2.3.

Two types of land burial are possible: (i) shallow burial in a site with a defined “lifetime”, usually of a few hundred years; and (ii) deep burial in stable geological formations with a lifetime measured in thousands of years. In the UK and several other nations, only the former is presently available. UK NIREX are responsible for developing cases for transportation of materials to such a site, the acceptable radiological contents of wastes, the suitability of packaging and also, in principle, the provision of a site. However, their original proposal to provide a deep repository site by around 2010 [75], described at the time as the ‘final solution’ for UK radioactive waste disposal, has not been realised and, as mentioned in the Introduction, the present status is a thorough review of disposal options through the CoRWM committee plus a new Nuclear Decommissioning Agency responsible for all decommissioning activity. As a result, where graphite plant has been dismantled (*i.e.* the WAGR)[13], a temporary surface store has been built with the graphite sealed into steel ‘temporary storage boxes’ until a permanent disposal strategy has been agreed. It is worth noting here that in the view of some experts, any disposal strategy which requires the construction of new ‘temporary’ waste-storage facilities is an *inappropriate* strategy [76].

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[13] The special case of the low-activity stack GLEEP [33] is discussed in several places within this report.

Ref [2] discusses the logistics of land burial in detail. Standard waste drums (for example 200 or 600 litres) may be suitable for fragmentary waste such as fuel-elements struts and crumbled sleeves, and the smaller drums are already used in the UK for the small quantities of graphite produced from the graphite-monitoring programme which is sent, loosely packed and associated with other general low-active waste, to a shallow disposal site at Drigg in Cumbria. However, the use of small drums would be inefficient for large graphite blocks in large quantities, and custom-designed storage 'boxes' with a concrete lining to provide the necessary shielding are deemed to be more suitable for transporting such material to a repository. The shielding requirement is dependent upon the elapsed time since reactor shutdown, and can be greatly reduced if a 'safestore' period has taken place. Boxes could be individually designed to accommodate convenient numbers of particular blocks of specific dimensions from any particular reactor, with the void space minimised.

However, neither these transport boxes nor quantities of smaller drums would necessarily be suitable for the actual burial: it would, for example, be desirable to fill any remaining void space to provide additional mechanical stability and to further reduce the risks of leaching in the far future through ingress of groundwaters. The additional infilling is also likely to be needed to allow the stacked packages in the repository to bear the overburden stresses (in shallow burial) or the geostatic stresses which might arise in geological timescales: for this reason an external grouting process would be expected between the containers to provide a fully monolithic package.

Ref [2] also includes comprehensive calculations of collective dose commitment for the various land-disposal options, including the effect of the nature of the rock in the deep disposal site (and whether it is coastal or inland[14]) and, for the shallow repository, the consequences of farming or building activities. As an example of the issues raised by shallow burial, the ANDRA facility for stabilised drum disposal of low-level wastes at Centre de L'Aube in North-East France will eventually be covered by new sub-soil to a depth of tens of metres: grass and small shrubs will be planted but the mound will be kept permanently clear of trees because of the risk of penetration of the concrete caissons and their contents by tree root systems.

Section 11.2 reviews the political and societal issues which are perceived to be of importance relating to land disposal of graphite, in the context of promoting the case for an objective risk assessment of the whole range of options presented within Section 9. Other technical aspects which may be relevant in the considerations for land disposal are that the regulatory authorities may well impose restrictions such as a lower limit on the thermal conductivity of the graphite in order to avoid local overheating from decay heat. This should not be a problem for graphite from Magnox reactors, AGRs or HTRs, but it could present perceived problems for dealing with the graphite from early plant with low irradiation temperatures where the residual Wigner energy content is high or where significant fuel products remain dispersed within the graphite.

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[14] In the long-team leaching pathways context, most of the UK would be deemed as 'coastal'.

9.2.2 Sea Dumping

At the time that Ref [2] was prepared, sea dumping was considered by many to be the preferable option for ultimate disposal of most nuclear wastes other than high-level wastes, reliant on the reasonably long-term survival of containment barriers, deposition of the containers long distances from inhabited land in deep ocean trenches and reliance in the event of containment failure on the ‘dilute and disperse’ option to demonstrate that the risks to land-borne life and sea life on continental shelves is minimal. The analysis of this latter includes the aspects of dilution, targeted dispersion through ocean currents, and incorporation into ocean sediments.

The public perception of sea dumping in Europe is undoubtedly coloured by the history of inappropriate dumping by the UK in the Irish Sea, similar activities by the French, and Russian ‘disposal’ of submarine reactors in shallow waters on its northern coast. The French and UK governments have both retained an option to resume the practice after 15-25 years when debating the London Convention on Sea Dumping and the 1992 OSPAR agreement (the Oslo-Paris accord “Convention for the Protection of the Marine Environment of the North-East Atlantic”) which effectively binds its signatories to a zero-activity-release philosophy by 2020, as there are still strongly-held opinions that sea dumping can be the best environmental option for the disposal of bulky low-level wastes (which could include some graphite), as well as for general tritiated wastes. There is however a widely held assumption that a world-wide ban on sea dumping will be imposed despite scientific arguments in its favour. Significant sea dumping of wastes has nonetheless continued, notably by the countries of the former Soviet Union in Arctic waters along its northern coast.

In general, similar principles will apply to the design of suitable containment boxes for sea disposal of graphite as apply for land disposal: physical pressure at depth could be as high as any forces imposed through land movements. Additionally, issues of corrosion need to be addressed in order to preserve the containment barriers for the longest possible amount of time. Greater shielding would be needed to prior storage and transport than for the material once disposed, leading to the concept of a container designed specifically for the ‘buffer storage’ and transport phase.

Suggestions have been voiced that disposal of waste in subduction zones, whereby the material is returned over geological time to the core of the earth, is the most desirable type of location for sea dumping [4, 77]; however, some geologists have separately given the view that the high level of seismic instability in such zones makes them completely ***un***suited to disposal of radioactive wastes *(A. Maltman, University of Aberystwyth UK, personal communication: see also bulletin board at http://radlab.nl/radsafe/archives/0106).*

9.2.3 Stabilisation and Packaging

The development of suitable packages for direct disposal of radioactive graphite wastes will be dependent upon the overall requirements of the disposal system within which such packages are intended to be managed. A number of generic criteria will be applicable for each disposal facility regardless of the waste type – *e.g.* container size and weight, package surface dose rate and temperature, heat output and surface contamination, package radioactivity release under normal and accident conditions of handling, transport and disposal. In addition, for graphite wastes, the materials properties will be highly relevant.

A separate issue is whether the package is to be regarded as ‘temporary’ or ‘permanent’. A current German philosophy is to retain wastes as ‘recoverable’ from shallow repositories so that future advances in treatment technologies can be applied. This will generally mean that stabilisation will *not* be applied, leaving the packages potentially at statistically higher risk of activity release within the stores.

We confine the discussion here to the nature of the ‘grouting’ or cementatious materials which could be used for grouting (reserving the issue of using cements partially made from waste graphite products to a later Sub-Section). A great deal of work has been done is this regard in the UK in connection with waste graphite fragments arising from AGR fuel sleeves. Eight potential matrices were identified initially, of which three – cement, polymer-modifed cement and polymers – were identified as most promising and were therefore further evaluated [78]. Each was ranked in terms of effectiveness, safety of use, efficiency and cost both in terms of its own handling and preparation, and as a stabilising product, in the four stages of waste handling (storage, transport, handling and emplacement, disposal and processing). The testing programme included mechanical strength, dimensional stability, chemical properties (including fire hazards during preparation), radiation stability using accelerated alpha- and gamma-irradiation testing to simulate 100-year doses, thermal conductivity, thermal stability, and impact performance. As a result, the basic cement matrix was deemed the most suitable for this particular application. The formulation used is three parts of blast-furnace slag to one part of Portland cement.

For all potential storage boxes with the various shapes and sizes of graphite components within, the suitability of this particular matrix material would need to be re-confirmed and structural analysis of the containers conducted to confirm their structural integrity over long periods with all likely forces applied to them. Care must be taken to ensure that graphite items do not ‘float’ in the matrix during preparation: UK industry experience is that flotation only occurs if the mix is vibrated [2]. The combination of matrix and graphite waste requires also a leaching assessment, which may differ according to the final disposal route being intended.

9.3 Preparative Treatments

Preparative treatments fall into three categories: processes to separate graphite from other contaminants, processes designed to inhibit leaching from graphite components during subsequent storage or repository disposal, and those intended as a preliminary to some other form of processing for re-use or recycling.

9.3.1 Separation of Graphite From Other Materials

This issue arises primarily with wastes from silos where admixture with metallic materials, generally from fuel sleeves, has taken place. Obvious methodologies such as magnetic separation or mechanical separation are not discussed further here. The use of laser incineration, where prior separation is unnecessary, is covered in Section 9.4.

A UK patent application [79] was made in 1993 for a process involving electrolytic treatment in an aqueous oxidising electrolyte – the methodology was derived for admixtures of graphite with uranium which arise from metallic nuclear fuel forming. For this purpose the electrolyte is a strong acid mixture, to dissolve up uranium, which becomes dissociated from the graphite as a result of 'disintegration' of the latter under the influence of a direct current. The patent search indicated a 'lack of novelty' in several elements of the application, suggesting that these general methods with variants may be applicable for contaminated graphite in certain circumstances.

9.3.2 Conditioning for Disposal

The principal activity in this field has taken place in France with CEA [71, 72], utilising both bitumens and epoxy-resin systems. Such systems had already been investigated and put into use for sealing the radioactivity on other types of radioactive waste, and the processing for graphite was developed from experience with other porous materials such as concrete and limestone where the performance is enhanced through impregnation with thermosetting resins. It was considered that both potential sealants would be very compatible with graphite, as a pitch-based product – in the epoxy-resin system, the polyamine hardener is itself derived from pitch.

The investigations were made on graphite samples taken from a drilled core some 2.5 m in length drilled from 'power measurement chamber thimble' of the French G2 reactor at Marcoule, and initial investigations were also made with two different grades of unirradiated nuclear graphite, of which some samples were thermally oxidised to increase the open-pore volume.

The first tests examined the ease of water penetration into the graphite over periods up to 1000 hours. We have commented previously that water uptake in the short term is inhibited by the surface tension characteristics of the graphite: however, after long periods, penetration of up to 17% of the open porosity was found for G2 graphite and higher values for other grades. This observation is very important for analysis of the situations both of under-water dismantling of graphite-moderated reactors and if should water should reach unprotected graphite in a future repository.

The resin impregnation was effected under vacuum, with subsequent curing of the former at 150ºC; the bitumen process involved the application of first vacuum and then pressure to the heated graphite using a direct-distilled bitumen (coded "80/100") selected for its fluidity. Finally, an industrial material described as 'epoxy-pitch', with specific water-resistant properties and also a low exothermicity on curing which mitigated against any long-term concerns about heat generation in the impregnated systems once disposed of to a repository.

The leaching data have already been described: Shore hardness data for the epoxy-pitch resin was very satisfactory (75-85 at 20ºC and >50 at 30ºC) whereas no value could be obtained for the bitumen. Creep rates and compression strength of the resultant graphite matrices with epoxy-pitch were also found to be very satisfactory for storage. However, at the time of writing, no definitive decision appears to have been taken in France about the need for this pre-conditioning of graphite waste, or indeed about the final disposal route to be taken: CEA has however determined that the CEA reactors at Marcoule will only be decommissioned after the experience gained from disposal of EdF commercial reactors has been analysed.

In addition to the use of cementations grouts, CIEMAT in Spain have considered the use of metallic coatings for graphite waste (principally graphite sleeves from Vandellos), through a research programme conducted in association with The University of Alicante (mentioned in [80]). The latest available information suggests that this possibility has not been followed up.

9.3.3 Preparative Treatments Prior to Re-processing

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

The two techniques of chemical decontamination and selective isotope removal are covered below in Sections 9.5 and 9.6.

The principal additional preparative treatment necessary will be size reduction. Graphite poses some problems in size reduction because of its properties as a lubricant and the potential for formation of dust (relevant safety issues are covered elsewhere in this report). However, size reduction by conventional apparatus has been achieved without reported difficulty in preparation for incineration [81], and as a means of increasing packing for burial [39], although this reference does not say how the size reduction was achieved. For steam reforming the preferred method described is wet grinding to sizes of less than 1cm [49].

For HTR reactors there is an additional pre-processing step to be considered, namely the separation of fuel kernels from the graphite compacts. Some interesting work is taking place, which may prove valuable more generally for size reduction of graphite [82]. It has been found that application of electrical pulses to graphite compacts can efficiently lead to disintegration of the compacts and separation of the fuel kernels.

9.4 Incineration

It will be evident from the foregoing discussion on graphite-oxidation kinetics that deliberate use of incineration methods to dispose of irradiated graphite by oxidation presents a considerable technical challenge. However, it has been achieved on a pilot-plant scale by Framatome at Le Creusot, utilising a fluidised-bed approach.

Refs [81] and [83] provide the details of the latest development of this technology. The design covers not only the actual incineration, but the measures necessary to achieve it which include the crushing of sleeve and block material to particles not greater than a few millimetres across. Framatome made a careful assessment of the classical "Modes" of graphite oxidation in designing their plant, recognising the need for a high surface area to mass ratio (small particles), and even made allowance for the additional effective heating available from the small amounts of Wigner energy present in commercial reactor graphite. There is a problem if dusts of size <100μm are present because of problems with fluidised-bed efficiency (coagulation) and the carry over of dusts into later stages of the plant.

The process also requires high turbulence in the reaction zone and a high rate of air flow. The greatest efficiency of combustion was achieved only with a bed temperature in excess of 1100K. No obvious research effort appears to have been applied to the possibility of improving the process efficiency through the deliberate addition of a suitable catalyst of graphite oxidation, although Ukrainian work in support of Chernobyl has proposed exfoliation of the graphite prior to incineration in order to accelerate the oxidation rate [84, 85]. This requires the use of small amounts of fuming nitric or sulphuric acids, or alternatively perchloric acid with magnesium perchlorate at ambient temperature, followed by a few minutes heat treatment at 600ºC. Acceleration in rates of factors between 4 and 27 are reported.

A related technology was developed, apparently independently, by Westinghouse Idaho in the early 1980s to dispose of low-irradiated graphite matrix nuclear rocket fuels (‘Rover’ fuel) [86]. This fuel consists of uranium dicarbide spheres, coated with pyrolytic carbon and dispersed in a graphite matrix. The process designed combined three principles: utilisation of a granular alumina fluidised bed, the charging of whole fuel elements un-ground in order to minimise issues of dust generation and radioactive contamination, and separation of the active ash components from the fluidised bed utilising wet chemistry elutions. The technology proved to be reasonably successful, and useful lessons about the handling of active graphitic materials within an incineration technology were also learned.

A Japanese design variation on the fluidised-bed technology, proposed by NGK Insulators Ltd, includes a provision to recover the ^{14}C and ^{3}H as CO_2 and H_2O [87]. It is clear that there is still a strong interest in graphite incineration in Japan for dealing with the wastes from the Tokai I Magnox reactor: at the 2003 International Nuclear Graphite Specialists’ Meeting “INGSM-4” held in Japan, JAPC presented results of an initial study for incineration of pulverised sleeve and block graphite using an enriched oxygen supply in the air (30%) [88]. CEA in France has investigated a different approach, namely laser incineration of graphite, in which a high-intensity laser beam is “scanned” over the surface of graphite components in order to gasify them. The principles have been discussed in a series of papers [89 – 91] but work on this process has now been abandoned (*J. Costes, personal communication, 2004*). However, the earliest work in this area appears to have been associated with the re-entry of space vehicles as part of the US space programme, and examined the effect of graphite reflectivity upon the absorption of radiant energy [92].

The potential advantages of this alternative approach as a method of graphite disposal was that no prior separation on non-carbonaceous materials was necessary, and there was no requirement for prior crushing or other pre-treatment. The process was also developed to pilot scale at Bagnols-sur-Cèze, using a reciprocating laser beam at powers between 5 and 22 kW and a beam diameter of approximately 35mm. This raises the graphite temperature to around 1400K, after which oxygen was admitted to the furnace at which combustion with a blue flame (indicating the oxidation of CO to CO_2) was evident. The exothermic oxidation reaction then raises the temperature further, and rates of consumption of order 14 $kg.h^{-1}$ are claimed. It was considered that, once combustion had commenced, the addition of further oxygen should be unnecessary. Whilst the fluidised-bed process appears to be the most promising technical solution to the severe problem of incinerating nuclear graphite, other attempts with different approaches have been made. Westinghouse Idaho have demonstrated at the pilot scale a process for burning HTR fuel compacts which commences with radio-frequency inductive heating to the required temperature in an inert atmosphere, followed by the introduction of a ceramic thermic lance to provide oxygen to the combustion zone [63]. The reference also includes discussion of a fluidised-bed technology and claims that "crushed graphite burning" in shaft furnaces has been demonstrated both at General Atomics in San Diego CA USA and at KFA Jülich in Germany. A US patent also exists for disposal of graphite-based fuel compacts utilising oxidation by air or oxygen in a molten sodium-carbonate / sodium-sulphate bath between 950ºC and 110ºC [93]. It is claimed that the graphite is wholly oxidised to CO_2.

Another USA initiative comes from the Pacific Northwest National Laboratory in association with the Institute of Gas Technology in Chicago, and utilised a combustion chamber coupled with a molten-carbonate fuel cell [94], it being intended to oxidise whole graphite blocks from Fort St. Vrain HTR individually at 1273K in a refractory-lined steel combustion chamber heated with molybdenum silicide heaters. The exit gases, consisting primarily of oxygen and carbon dioxide, presented the optimum mix for transport through the fuel cell whilst the electrical polarity of the cell suppressed the transport of potentially radioactive cations. No pilot plant appears to have been constructed, and the aspirations relating to the combustion of the graphite appear to be rather unrealistic.

Concerns about activity release in the gas-phase effluent from incineration processes are separately addressed in Sections 8.3.2 and 9.10. It is assumed that much of the initial radioactivity is retained in the ash, and that steps are taken to trap any particulate emissions. Limited research has been conducted on the mobility of isotopes destined for ash: for example, [95] confirms the retention of calcium, chromium, manganese, iron, cobalt and caesium isotopes from partial ashing of graphite at 700ºC.

9.5 Chemical Decontamination

Chemical decontamination is a technique frequently applied to materials which are contaminated with radioactivity on their surfaces. A review of chemical decontamination and its historic development is available [96]. The objective of chemical decontamination is usually to remove a surface layer, which contains the bulk of radioactivity, by dissolution. Traditionally the solution would then be discarded as liquid waste, but in more recent times processes have been devised to collect the dissolved layer (including the radioactivity) in solid form for waste management.

Chemical decontamination is most normally applied to hard, massive, impervious materials which have not been activated in a neutron flux. In such cases the removal of a surface layer just a few microns thick can be expected to reduce the radioactive inventory of the object very effectively (by at least one, or even several, orders of magnitude). In many cases the radioactivity can be removed to such an extent that the object itself can be released from radioactive material control and recycled or disposed of in conventional industry [97].

It is possible that decontamination could be applied to massive graphite (*e.g.* entire blocks) to remove contamination that arises through operating or handling procedures. Graphite would be a target material very different from metals because it has a porous structure and the radioactivity is distributed throughout the bulk of the material by virtue of the distribution of impurities which become activated by neutrons. Additionally, activation of adventitious impurities may occur: in UK reactor-operating experience there are examples of the transport of metal oxides from corrosion in boiler units to the graphite where they have become activated. Such material is usually associated with the geometrical surfaces of the graphite components although there is some penetration of the porosity close to the surface especially where permeable flows through the transport porosity occur. The techniques selected for removal of graphite during dismantling should seek to avoid any further contamination of the surface of the blocks.

It appears unlikely that there will be any parallel for graphite with the high degree of effectiveness achievable with chemical decontamination of metallic components. Hence, chemical decontamination of graphite is likely to be limited to specific instances where a modest reduction in radioactive inventory may nevertheless achieve some useful purpose. The removal of radioactivity by deliberate leaching (enhanced by chemical and physical means) could have useful benefits in reducing the subsequent loss of radioactivity by leaching in a disposal site. In this case, grinding to increase the surface-to-mass ratio could be very beneficial, as suggested by the ^{36}Cl-release data in [67, Section 8.4]

9.6 Mobilisation of Isotopes by Heating and Grinding

It has been noticed that the heating of graphite can, at least in some cases, lead to selective loss of isotopes (particularly tritium and ^{14}C) from the graphite structure [37]. This phenomenon is worthy of study since it might be exploited as a form of decontamination of graphite in advance of disposal or recycle.

Graphite has a porous structure, as referred to elsewhere in this report. A proportion of the pore volume is open, meaning that it is connected with the gas atmosphere in which the graphite resides. During operation with graphite in a reactor core, isotopes such as ^{14}C and tritium may accumulate on the surface of the pores through a variety of possible mechanisms:

- Isotopes formed in the bulk gas phase may diffuse into the pore volume and deposit on the pore surfaces
- Neutron irradiation of gases in the pore volume may yield isotopes absorbed on the pore surfaces.
- Species absorbed on the surface of the pores during manufacture, or during exposure of the graphite in air, may be activated in the neutron flux. This mechanism is particularly relevant to nitrogen species yielding ^{14}C, but may be relevant to other nuclides as well.

Any of the above mechanisms may yield a pore surface layer enriched in radioactive isotopes, which might then be released by gasification, by heating either in an inert atmosphere or one which encourages gasification of carbon (such as steam). This procedure might then yield a small fraction of the graphite carbon containing a significant proportion of radioactive isotope inventory, which would be a most desirable outcome - effectively “decontamination”.

Unfortunately there are likely to be limitations on what can be achieved by such a procedure. Some of the contamination mechanisms described above will be relevant to the closed pores, which may not release their inventory during the heating procedure. Furthermore there will be isotopes formed by activation of bulk materials and impurities in the graphite. Enhanced release in an early fraction will not be possible for these.

The loss of tritium and ^{14}C from graphite during heating has been the subject of a detailed preliminary study at FZJ Jülich [98]. The conclusions of this study are as might be expected, namely that a carbon fraction enriched in ^{14}C and tritium can be released by heating the graphite to about 1100C in various atmospheres. The degree of enrichment achievable is dependent on the temperature profile and the gas composition, and more remains to be learnt about the mechanism to optimise this. It seems unlikely (however carefully it is optimised) that more than about 60% of the ^{14}C and 80% of the tritium can be released in the first few per cent of carbon lost. This observation is confirmed by preliminary work on blocks removed from the UK GLEEP reactor [41]. This might nevertheless be a very useful result, particularly if this degree of decontamination were sufficient to permit the bulk carbon to be discharged to atmosphere as carbon dioxide. It is also likely to be important in recycling scenarios, since any ^{14}C contamination of new products will need to be kept to the minimum possible.

There is one final aspect of decontamination by heating. If the carbon in graphite is completely gasified (*e.g.* by steam reformation or air oxidation) the remaining non-volatile isotopes will be left behind as a residue, while semi-volatile isotopes (such as ^{137}Cs) may be collected with the non-volatile ones, or in adjacent low temperature zones. This behaviour has been confirmed in the Jülich study [98]. Total gasification provides the means to collect these isotopes in a concentrated form for waste management. This is a most important outcome, since the non- and semi-volatile isotopes include all the principal gamma-emitting ones, hence allowing all further downstream operations with the carbon (after the initial gasification) to be performed "hands-on". The separation of volatile non-carbon isotopes such as tritium and ^{14}C can be readily accomplished during gas phase processing: for example tritium can be converted to water and separated from the off gas carbon dioxide.

The evidence of significant and rapid losses of ^{36}Cl following pulverisation of bulk graphite reported earlier (Section 8.4 and [67]) suggest that this phenomenon should be studied much more extensively in order that its potential for isotopic release may be better understood. Such behaviour has diverse consequences: (i) a potential for inadvertent releases of activity if graphite is damaged during dismantling, and (ii) a possible route for deliberate decontamination of graphite in order to lower its waste category or to prepare it for recycling. One consequence of this is that CEA, on behalf of EdF, plan to study the potential release of tritium during compressive-strength tests on small sample of graphite from the UNGG reactors. This will be done by surrounding the anvil of the test machine with an impermeable membrane and then sampling the gases using liquid scintillation counting after the samples have been crumbled. The kinetics of the processes will also be evaluated.

9.7 Pyrolysis and Steam Reformation

Pyrolysis and steam reformation is a technique commonly applied to organic radioactive wastes to reduce their volume. The process normally involves two stages, which may in fact happen simultaneously in the same equipment. In the first stage ("pyrolysis") organic material is heated, typically in a closed system, in the presence of limited oxidant, to produce a "char". This char material is rich in carbon and becomes susceptible to gasification by the application of steam according to the following reaction ("steam reformation"):

$$C + H_2O \text{ - - - - -> } CO + H_2$$

This can then be taken one step further in which the carbon monoxide and hydrogen are oxidised by air or oxygen to yield carbon dioxide and water (the water can then be recycled to react with more carbon).

The inherent advantages of the overall process are underlined by the fact that there is considerable nuclear industrial scale experience with it. Probably the principal advantage is the excellent off-gas control achievable by pyrolysis and steam reformation in comparison with direct incineration. When incinerating organic materials in air it is necessary to have sufficient air present to allow complete oxidation, and this almost inevitably requires a continuous flow of air during the process. This flow then becomes an off-gas, which creates difficult circumstances for the prevention of loss of radioactivity. By contrast, pyrolysis and steam reforming take place in an enclosed system, with final off-gas release taking place in highly controllable circumstances.

Probably the main facility for pyrolysis and steam reforming to date has been the Studsvik plant in Erwin, Tennessee USA [99], which processes ion exchange resin waste and other materials for nuclear customers. The process employs a fluidized bed technology in which the waste is pyrolysed and steam reformed in different parts of the same vessel. Non volatile radionuclides and residue are collected in the form of dust by filtration. The process is also being applied to other types of nuclear waste for the US Department of Energy, the so-called “THOR$^{\text{SM}}$” Process [100].

With respect to graphite the pyrolysis stage of the above process would be unnecessary, because the graphite is already at the “char” stage. The steam reforming and oxidation steps would, however, be applicable to graphite. It might be expected that (rather un-reactive) graphite would be much harder to steam reform than a char produced by pyrolysis of organic materials, and this seems to be the case. Steam reformation in the Studsvik plant takes place at about 700ºC, whereas graphite is likely to require at least 900-1100ºC for the reaction to take place, even if the graphite is first size-reduced, as would be required for entry into a fluidized bed reactor. In principle the steam reformation reaction could be catalyzed.

In all industrial applications to date of the process the carbon in the waste has been released as carbon dioxide. An intriguing possibility for the process is that it could be modified in the case of application to graphite to reverse the steam-reformation step and return powdered carbon. Alternatively the carbon monoxide could be used to form organic chemical products. The development of these possibilities provides the potential to define methods to recycle graphite, since (for example) the powdered carbon could be formed into new graphite. This is discussed further below.

Another possibility for final waste management of gases arising from pyrolysis and steam reforming would be to introduce the resultant carbon dioxide into other fossil fuel combustion gases destined for “carbon sequestration”. The technique of carbon sequestration is being developed to avoid the release of carbon dioxide into the atmosphere and to retain these gases securely for the foreseeable future. Clearly the development of this technique provides an intriguing possibility to manage the graphite wastes by inexpensive gasification but without allowing their radioactive content to escape into the biosphere.

9.8 Vitrification

Russian researchers, faced with a number of situations in which extensive fuel contamination is associated with the graphite stacks (*e.g.* Beloyarskaya graphite reactors and the Mayak production reactors) are developing a chemical process of vitrification of the graphite into a ceramic matrix in which the contaminating fuel debris and fission products are effectively immobilised. This is described as the ‘self-propagating high-temperature synthesis’ (‘SHS Process’) [101] and a pilot plant is understood to be under construction at the Beloyarskaya site after successful tests on the laboratory scale.

Related work on the topic is being undertaken at The Department of Engineering Materials at The University of Sheffield, UK, following transfer of one of the principal researchers from the Russian State Unitary Enterprise ‘RADON’ in Moscow. Publications originating from Sheffield [102 – 104] offer more detail on the process, sometimes described as the ‘burning-wave’ process and related to the classical ‘Thermit’ process.

Essentially, the process requires prior grinding of the graphite to permit an intimate mixture to be formed of graphite (9.5% by weight), aluminium (28%) and titanium dioxide (62,5%), this ‘optimum’ mix having been arrived at from careful scrutiny of thermodynamic data. Experiments conducted under an argon atmosphere have confirmed that, after ignition, the reaction wave front becomes self-propagating through the mixture with a velocity of approximately 1 $mm.s^{-1}$ whilst a reaction temperature of 2320K is achieved, very close to the theoretical value of 2328K calculated from the thermodynamic and property data. The product is a matrix of titanium carbide and corundum (alumina) with some formation of Al_4O_4C.

Studies have been made of the potential release of isotopes both into the cover gas during reaction and subsequently leached from the vitrified mass. It is claimed that over 99.9% of ^{14}C is retained within the solid as titanium carbide, with only a very small loss as carbon monoxide. Whilst the leaching of ^{137}Cs and ^{90}Sr from the products are described as “within acceptable limits”, it is noted that the leach rate can be reduced by 50% if a small quantity of zircon ($ZrSiO_4$) is included in the original mixture.

The strength of the resultant matrices are also under investigation, and preliminary data suggest that the graphite particle size has a crucial effect on the compressive strength, which rises from 7.2 to 13.4 MPa is the original graphite particle size is increased from 50 µm to 100 µm, whilst the final density increases slightly from 1.6 $g.cm^{-3}$ to 1.8 $g.cm^{-3}$. Modified formulations utilising barium metatitanate ($BaTiO_3$), quartz sand, and wollastonite (calcium metasilicate ($CaSiO_3$) are also under investigation.

Whilst the merit of containing fuel and fission products in this vitrified product are clear, the process overall is complex and results in a large increase in volume compared with the original graphite. Consequently, its usefulness is probably limited to these special situations. However, a very recent publication from the group [65] specifically comments about the containment of ^{14}C by the ‘SHS’ technology and suggests this as a superior solution to the perceived risks of ^{14}C-methane release from repositories where graphite is present.

9.9 Recycling and Reuse

The possibility of recycling and reuse of graphite has not really been considered seriously until very recently, although a 1993 paper from Russia examined some of the options [105]. Carbon is a plentiful and inexpensive element and the production processes for graphite are complex, using hard-to-simulate materials such as pitch and coke. The production processes would not be easy to replicate with recycled material, particularly if this has to be done under radioactive material control. Using recycled carbon will almost inevitably make new graphite or other components more (not less) expensive unless the waste graphite comes with a financial credit attached to it. It is perhaps unsurprising that graphite manufacturers have hitherto not been enthusiastic about recycling graphite.

However, it is in the context of *waste minimization* that there is a new driving force to consider recycling graphite. The cost of disposal of graphite as intermediate level waste in the UK (*e.g.* about $170,000 per cubic metre) would dwarf the cost of manufacture of new graphite components. Graphite manufacturers could expect to receive graphite to recycle with a financial credit attached to it, provided that their subsequent activities (including secondary waste conditioning and disposal) constitute an acceptable final disposition of the waste graphite.

New HTR designs imply the production of over 2,500 m^3 of fuel waste over the reactor lifetime for a 300 MW module [106]. This is a large amount of high level waste per unit electricity production, a rather unattractive proposition and a significant drawback for the design. However, some 94% of this waste is graphite and, if the graphite could be separated from the waste and recycled, the waste would be reduced and the prospect of building the reactor in the first place could thereby be improved. For the graphite manufacturers the choice may be rather stark – either continue to insist on using fresh carbon for graphite products and have no nuclear market, or develop recycling methodologies. Recent discussions with graphite manufacturers have indicated that there is a new willingness to address the possibilities of recycle *(P. Homerin, Graftec Intl. Ltd, Personal Communication).*

A group of interested parties has come together under the chairmanship of Dr von Lensa of Forschungzentrum Jülich (FZJ). This has led to a proposal to EURATOM for joint work to consider (*inter alia*) recycling of graphite. The overall proposal is called GCR-MINWASTE. Although these discussions are at an early stage, they have brought together a number of interested parties, including those with interest in the science and technology of waste management (*e.g.* NRG Petten, CEA France) graphite manufacturers (Graftech, SGL) and waste processors (Studsvik). If the proposal is approved it will provide an exploratory path forward for considering all aspects of graphite recycle, and will provide much base data necessary to evaluate the alternatives. Even if the proposal is not approved the contacts gained and discussion held will form a useful input to future work on the topic.

9.9.1 Restrictions on Use of Recycled Graphite

Despite the selective decontamination possibilities mentioned above, the treatment of graphite prior to recycling will be unlikely to achieve a complete and clean separation of ^{14}C from the bulk of the carbon. For this reason it seems most likely that *all* products made from recycled graphite will be restricted to controlled uses in the nuclear industry. In particular cases where the inventory of ^{14}C is sufficiently low to allow unrestricted release, the direct release of the carbon to atmosphere (as carbon dioxide) is likely to be a far more economic option than recycle.

9.9.2 Methods for Recycling Graphite

The simplest method of recycling graphite is to re-form new graphite from old without any intervening chemical transformation. Graphite manufacturers sometimes incorporate some scrap graphite into their production processes already as a finely-ground flour in the initial coke-pitch mix. The advantage of this option is simplicity, but it is likely to be of rather limited use, because there is no opportunity for significant decontamination of the graphite before recycle, and the products that can be formed this way may not have suitable properties for many applications.

Another route to recycle of graphite is to gasify waste graphite and to re-form new graphite or other products from the gaseous products. The gasification process allows effective decontamination for radionuclides other than ^{14}C. At the moment we are not aware of an established scheme for producing intermediates required for new product formation. However, the proposed GCR-MINWASTE international collaborative programme has, as one of its tasks, to identify the optimum types of intermediate (*e.g*. lampblack, granular carbon, hydrocarbons, organics) to be used by the product manufacturers for their products, and the means of producing these intermediates from the initial graphite treatment process.

Forming graphite for new reactors, moderators, fuel components etc is the most important potential recycle opportunity but also the most technically challenging, because of the high specifications of graphite required. Nuclear graphite is currently manufactured from pitch and coke (see Section 2 above) and thus the recycled carbon would need to be fed into one of these components, or the graphite manufactured from some other intermediate (*e.g*. lampblack). The use of recycled graphite may not be entirely negative for meeting product specifications, since the purification of the graphite which occurred for first use can be an advantage when the material comes to be recycled.

There are many potential uses for recycled carbon other than new reactor graphite. Examples would be use in graphite electrodes for the immobilisation by high temperature processing of certain nuclear wastes, or activated charcoal filters. Opportunities may be more limited, but the technical quality of the required materials may be less demanding than the reactor application and hence easier to achieve. One key target for any recycle effort will be to use the recycled carbon for production of silicon carbide. Silicon carbide has many potential uses in high temperature reactor technology and also in nuclear waste management (*e.g.* use as an encapsulant). Calcium carbonate has also been mentioned as a possible use for recycled carbon, but there may be only limited uses for this [49].

9.9.3 Recycling – the Path Forward

It will be appreciated from the above that the concept of recycling graphite is hardly more established than a set of ideas at present. However, the subject is one of great importance to the nuclear industry's future, since without such recycle the disposition of graphite waste (both past and future) represents a difficult and expensive problem.

If recycle of graphite is to take place it will require a set of well-organised and appropriately funded demonstrations to take place. These projects should start by using material of low radioactive inventory (such as zero energy reactors) to establish the principles of recycling, with provisions for gaining detailed data relevant to later recycling efforts with material of higher radioactivity.

9.10 Carbon-14 Isotope Separation Techniques

Reference was made above to the separation of a radioactive isotope fraction by heating. Reference was also made to the separation of non-carbon radioactive isotopes during gasification. Once the ^{14}C and non-radioactive carbon are together in the gas phase the only remaining option to achieve further separation is to use an appropriate isotope-separation process.

Isotope separation is often thought of in terms of the relatively high cost, high technology operations necessary to enrich uranium. Isotope enrichment of low mass elements at the top of the periodic table tends to be easier to accomplish by conventional techniques such as fractional distillation.

Two publications from Japan [88, 39] refer to the separation of ^{14}C using so-called "pressure swing absorption" technology with carbon monoxide. In this method carbon monoxide is absorbed and desorbed from an appropriate absorbent at reduced temperature. With seven stages of enrichment a virtually pure ^{14}C fraction can be achieved.

A Canadian patent [107] refers to the cryogenic distillation of carbon monoxide as a means of enriching ^{14}C in a single stage. Although simpler than the Japanese technology, the very low temperatures required for this process are a drawback. It is important to note that the initial ratio of ^{14}C:^{12}C considered in this patent is much higher than one would obtain from a graphite-incineration process (for example) and thus that the number of distillation stages required, and hence the cost, would be very high. This procedure was further developed by Ontario Hydro for the separation of ^{14}C from CANDU resin beds used as clean up for the annulus-gas system [108]. In this application the separation is effected as the dioxide, using a recirculating system on successive batches of resin until the ^{14}C in the dioxide builds up to a sufficient concentration using an adaptation of the pressure-swing absorption technology. At this point, separation can be effected, again as the monoxide, using zinc as a reductant.

Gas centrifuge techniques could also be used in principle to enrich ^{14}C.

Little information is yet available on the economics of isotope separation, but it is likely that any isotope enrichment process will be relatively expensive and unlikely to be applicable to the majority of the graphite waste. However, isotope separation could be important for certain specific graphite wastes, or fractions thereof. For example, if a small ^{14}C-rich fraction were released from graphite by the heating options described above, this fraction could undergo isotope separation to yield a pure ^{14}C product. The ^{14}C could potentially be given to users of the isotope (such as producers of isotopically labelled chemicals), thereby displacing alternative production of ^{14}C for these purposes. Another potential use of isotope enrichment would be where a particular waste stream just fails to achieve acceptable limits for release to atmosphere. The removal of some of the ^{14}C by isotope separation would then allow release of the remaining bulk.

10

DECOMMISSIONING PLANNING IN NEW REACTOR DESIGN

Reference has already been made to the proposal GCR-MINWASTE recently submitted to the European Union under the Euratom programme. A partial motivation for this is the realization that mistakes made in the specification of early graphites for nuclear applications which are now leading to difficulties in the decommissioning process must not be repeated in any new generation of graphite-moderated plant. These will most likely be pebble-bed or fuel-matrix designs of high-temperature reactor (or VHTR).

A particular example is that UK AGR graphites in some cases contain levels of cobalt which already lead to handling problems for small ‘monitoring’ samples and which will undoubtedly lead to delays in their eventual decommissioning. Although some of this cobalt is transported as oxide corrosion products from other areas of the plant (*e.g.* boilers) and then becomes trapped in the graphite and activated, a significant proportion arises from the original ‘permitted’ impurity concentration in the virgin graphite.

In the licensing of new plant, a comprehensive decommissioning plan is now required by regulatory and/or waste bodies before a construction permit can be granted. This provides a further impetus for the lessons now being learned about decommissioning to be fed back into the formulation and manufacture of new nuclear graphites.

The OECD’s Nuclear Energy Agency has been fairly prominent on this topic in its series of meetings on High-Temperature Engineering held between 1999 and 2003 and designed to assist the new HTR development programmes. [109] offers a succinct summary of the importance of purity with respect to isotopes which can become activated, but it is noticeable that some comprehensive analyses of the necessary properties of new graphite materials for HTR use concentrate heavily on the irradiation behaviour of the material with respect to changes in physical and chemical behaviour whilst paying scant attention to issues of decommissioning {*e.g.* [110]}.

In brief, the most critical issue is that of impurity control, but facilitating dismantling is also very important, and much can be done at the design stage to minimize future difficulties in (for example) retrieving graphite blocks from within a pressure vessel after they have been subjected to potential dimensional changes resulting from irradiation.

It is considered that continuous feedback between the decommissioning developments and the designers of new reactor plant is highly desirable in order to optimize the operation of the entire build-operate-decommission lifecycle of future plant.

11

DISCUSSION

This discussion attempts to summarize the findings of this report

11.1 Safety of Graphite Dismantling, Handling and Treatment

A great deal of effort has been put into assuring that graphite moderators can be stored “in-situ” safely for a prolonged period - the SAFESTORE policy. This is discussed in Section 5 above. The information so gained is helpful background if there is to be conversion to a new policy of early dismantling, processing and disposal.

There has been concern about the problem of Wigner energy, not least because the phenomenon achieved notoriety due to its role in the Windscale Pile 1 fire of 1957. However, Wigner energy is a well understood and highly predictable phenomenon. Significant stored Wigner energy is only present in old reactor moderators which have operated at low temperature. The issue is thus irrelevant to the majority of graphite waste. Where Wigner energy is relevant the main precaution necessary is to ensure that the graphite is kept sufficiently dispersed that the potential rate of energy release as a function of temperature increase cannot exceed the specific heat capacity (Section 4.2). Other precautions include avoidance of heating that could initiate an energy release, and processing the graphite to release the stored energy safely under controlled conditions.

Concerns with fire and explosion have been fully covered in this report. Although there is a perception that graphite “fires” have occurred in accidents such as Windscale and Chernobyl, the truth is rather different. Graphite is actually an extremely difficult material to oxidise and is very different from coal, for example. Whereas coal dust represents a severe potential explosion hazard, graphite is far more benign. Advantage should be taken of the generally non-combustible and non-explosive natural properties of graphite when considering the safety of handling and processing the material.

There is some limited experience of dismantling and removal of graphite blocks from reactors, at Fort St Vrain, Windscale AGR and elsewhere. Relatively simple techniques have been used to dismantle and remove the moderators of these reactors with success. There is an ongoing debate about whether dismantling should take place underwater or not. The experience at Windscale AGR (dismantling in air) has been satisfactory, and may suggest that caution should be exercised before deciding to adopt underwater techniques. Another issue arises where extreme weight loss may have caused weakening of the graphite, hence making dismantling a little more difficult.

The isotope inventory of graphite waste is variable and rather unusual (compared to most other nuclear wastes). Short-term concerns are generally dominated by ^{60}Co and tritium, whereas long term safety concerns are dominated by isotopes such as ^{14}C and ^{36}Cl. Despite its extended residence in core, the specific activity of graphite is usually relatively low, *e.g.* in comparison with in-core metallic components. Activity levels have been adversely affected by past production and manufacturing practices. There is considerable scope to reduce the radioactivity of future graphite by controlling impurities.

11.2 Graphite Disposal

It can be seen that graphite waste management is full of paradoxes. In terms of its radioactive content graphite might be considered as inconsequential low level waste, and yet the presence of isotopes such as ^{14}C and ^{36}Cl in graphite could significantly complicate the safety case for a waste site if graphite was disposed there. This is because the isotopes concerned are chemically labile and difficult to confine over long periods of time. Despite this, it is virtually impossible to envisage circumstances where these particular isotopes would actually do any discernible damage to human health or the environment, since the perceived dangers consist of "collective doses" integrated over long periods of time where many individuals each receive a very small (and effectively negligible) dose.

Societal pressure has strongly discouraged "dilute and disperse" practices in waste management, in most cases with good reason. However, graphite is a rather special case. The incineration (or steam reforming) of graphite and discharge as carbon dioxide (with rigorous retention of all non-carbon radionuclides) represents a simple and effective low cost management option, to which it is extremely difficult to raise a substantive and logical objection. Provided that the processing is done carefully the only safety issue is the emission of ^{14}C and this is a radionuclide naturally present in the atmosphere. The increase in atmospheric concentration of this isotope above natural values (from graphite incineration) would be negligibly small as referred to in Section 8.3 above, and only the population doses immediately in the vicinity of the plant discharges would need to be considered and appropriately engineered. If the practice of graphite incineration is forbidden through societal pressure there will be other costs to society - financial, environmental and even health and safety – of following an option more complex than this base case.

We will now consider the interactions between technical and societal factors in graphite disposal. One of the present authors (AJW) has presented an objective analysis [4] of the range of societal and political issues associated with the three main options for disposal of graphite wastes – land disposal, incineration, and sea disposal (the analysis is not prejudiced by the current existence of treaties banning the last of these routes). It is useful to re-state these issues from [4] in full here, in order to further illustrate that the choice of any one of these routes is not necessarily a simple option, and to justify further investigation of alternatives:

Land Disposal Issues

- Public opposition to any local repository site;
- Public opinion turning in favour of supervised shallow or surface storage, with consequent ongoing personnel costs;

- Public perception of handing on the problem to future generations to deal with, especially with a ‘history’ of accidents on land-based sites *e.g.* Windscale, Chernobyl;
- Need to ‘guarantee’ seismic stability;
- Groundwater analysis from the point of view of corrosion and leaching, and coastal proximity, means that the possibility of long-term leaching into sea water needs to be considered;
- Time to achieve acceptability and construct suitable sites is not compatible with present disposal requirements;
- High cost of construction;
- High volumes of waste to be disposed if not pre-treated; *and*
- Long-term environmental risk remains (thousands of years) because material is not truly ‘removed’ from the environment.

Sea-Disposal Issues

- High probability of breach in outer containment in short time due to corrosion by salt water;
- Re-negotiation of international agreements required;
- Consequences of leaching are less significant than in a land-based repository;
- Long-term environmental risk remains but remote from human population and food chains;
- Widespread public opposition (essentially subjective);
- No requirement for permanent land-based facilities, leading to large cost savings in comparison with other options;
- Waste volume is unimportant; and
- Disposal could commence immediately after facilities for filling containers are established.

Incineration Issues

- Major political and environmental concerns about the release of 14C despite the favourable comparisons with the natural production rate;
- Similar concerns about CO2 release and ‘greenhouse effect’ despite the total quantity being little more than a large coal-fired power station burns in a few days;
- Technology to trap 14C would be expensive;
- Effective half-life of 14C in the environment is very low compared with the actual decay half-life; and
- Only small residues (ash) remain for long-term disposal, minimizing cost.

Ref [4] concludes that a proper sequence of activity for the industry and its interaction with the public should be the following:

- Evaluate fully all scientific options;
- Evaluate the associated (true) risks and perform an unbiased analysis of those risks;
- Factor in the costs and cost benefits;
- Determine the optimum technical strategy on the basis of this analysis;
- Then address public opinion, treaties, political views etc., arguing the scientific case very strongly to all interested parties and providing the fullest possible information to all stakeholders including the public; and, finally

Reach a consensus.

The present authors believe that all stages of this process need to be re-visited, or in some cases addressed for the first time, in the case of disposal options for irradiated nuclear graphite. Some valuable initiatives have recently been taken in this regard for nuclear wastes in general (*e.g.* the CoRWM review in the UK), but there is no evidence to date that the wastes have been considered on the basis of their chemical nature – rather simply as LLW, ILW and HLW.

The radiation protection principle of ALARP needs to be considered. For example, one route to achieving acceptability of graphite incineration might be to arrange to do everything "reasonably practicable" to remove the ^{14}C inventory before release. In this context the mobilization of isotopes by heating or grinding (Section 9.6) may be important, along with the technical options for separation of ^{14}C from the off gases. Another option would be to consider the carbon sequestration route described in Section 9.7 above.

Disparities currently exist between technically sound and politically expedient approaches. For example, when compared with the incineration alternative, the maintenance of waste graphite in solid form (hence keeping the ^{14}C "concentrated") makes it marginally more likely that some individual will get a non-trivial dose of radiation from it at some point in the future. The best technical way to defend against this possibility would be to sea-dump the solid graphite, thereby ensuring that the ^{14}C is slowly diluted into the massive carbon pool in the oceans. Sea dumping is, however, currently "unacceptable" on account of societal pressure and international regulation.

Of course, the industry has to accept that the public's opinion, expressed through the processes of democracy and regulation, is paramount and that alternatives must be found to graphite incineration if the public remains unconvinced. It is not the remit of scientists to decide such questions, but merely to provide the necessary information.

If simple options such as incineration and sea dumping are ruled out as above, then there are other options for graphite management consistent with a philosophy of "concentrate and contain" of radionuclides. Despite the comments above, direct burial of graphite could be very effective on technical and cost grounds, provided that care is taken to avoid certain special risks (such as the set up of electrochemical cells referred to in Section 7).

Finally there is the possibility of recycling. In other fields of nuclear industry activity the option of recycling materials back into nuclear industry components is one of the few waste management strategies which commands widespread support across all categories of stakeholders in the industry [111]. The option satisfies fundamental tenets of sustainable development. Provided that the costs are not prohibitive, the possibility is well worth considering. Frequently in waste management there are two options for solving a problem, one slightly cheaper than the other, but the other more acceptable to the public. The industry tends to choose the cheaper alternative and then struggles to get it accepted, thereby incurring huge costs. If the more expensive, but more acceptable, option had been chosen in the first place the overall result would be cost saving.

Although graphite recycling technology is in its infancy, encouragement of commercial ingenuity and competition is likely to enhance the technology and reduce the costs of recycle. There has been very little progress as yet, but there is increasing interest in it. If new graphite moderated reactors are to become a feature in future, it is almost essential that ways are found for graphite to be continuously recycled, consistent with a philosophy of avoiding waste and being “sustainable”.

The worst option is to do nothing at all (SAFESTORE), which convinces the public that there is *no* acceptable solution to the problem.

This report highlights two opportunities to avoid adventitious and unnecessary production of anthropogenic radionuclides. The first is the control of impurities in new graphite as discussed in Section 8. The second is the potential for pure ^{14}C to be harvested from graphite processing for use in products where the isotope is required for other purposes, thereby displacing additional production for these purposes (Section 9-11).

There is no “perfect” solution to the problem graphite waste management, but there may be several good options. Individual countries will choose the most suitable options for their purposes. This report is intended to assist individual countries and their associated institutions to define appropriate strategies for graphite management.

12

CONCLUSIONS

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1. Adequate information exists to enable graphite moderators to be safely dismantled and processed.
2. Concerns about Wigner energy are limited to the minority of reactors in which the moderator operated at low temperature. The phenomenon is well understood, and appropriate precautions can be defined to avoid unacceptable energy release.
3. Fire and explosion hazards of graphite have been thoroughly considered in this report. Although graphite is a form of carbon and therefore potentially combustible, it is nevertheless relatively rather resistant to oxidation, which is of value when considering the safety of handling, processing and disposal.
4. The radionuclide inventory of irradiated graphite is unusual in comparison with other nuclear wastes. The principal isotopes of short term importance are cobalt-60 and tritium; in the longer term carbon-14 and chlorine-36 are dominant.
5. The three main options for disposal of graphite are oxidation to the gas phase and release as carbon dioxide, direct burial or recycling into new products for the nuclear industry. In each case opportunities exist for pre-processing to concentrate or remove radionuclides and thereby enhance the safety of the chosen option.
6. The possibility of recycling of graphite into new nuclear industry products is in its infancy. In due course this possibility may become very important, particularly if it is proposed to construct new graphite moderated reactors.
7. It is unlikely one solution to graphite management will be appropriate everywhere. There are issues which may lead to different solutions being adopted in different countries.

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REFERENCES

[1] NIREX: “The NIREX Mission”; Annual Report and Financial Statements 2004 – 2005 *page* 1.

[2] White I.F., Smith G.M., Saunders L.J., Kaye C.J., Martin T.J., Clarke G.H. and Wakerley M.W., “Assessment of Management Modes for Graphite from Reactor Decommissioning”, Commission of the European Communities Report EUR 9232, 1984, ISBN 92-825-4292-0

[3] Wickham A.J., Neighbour G.B. and Dubourg M., “The Uncertain Future for Nuclear Graphite Disposal: Crisis or Opportunity”; Proc. IAEA Technical Committee Meeting on ‘Nuclear Graphite Waste Management’, Manchester UK, October 1999, IAEA NGWM/CD 01-00120

[4] Neighbour G.B., Wickham A.J. and Hacker P.J., “Determining the Future for Irradiated Graphite Disposal”; Nuclear Energy, **39**, 2000, *179-186*

[5] Marsden, B.J., “Graphite for High Temperature Reactors”; EPRI, Palo Alto, CA: 2001, 1003013

[6] Arnold, L., “Windscale 1957: Anatomy of a Nuclear Accident”; Macmillan 1992

[7] Wickham A.J., “Caring for the Graphite Cores”; Proc. Seminar ‘The Review of Safety at Magnox Nuclear Installations’, London, March 1989, I.Mech E. *pp.* 79-87[15]

[8] Telling R.H., El-Barbary A., Ewels C.P. and Heggie M.I., “Wigner Defects Bridge the Graphite Gap”; Nature Materials, **2**, 2003, *pp.* 333 – 337

[9] Lexa D. and Kropf A.J., “Thermal, Structural and Radiological Properties of Irradiated Graphite from the ASTRA Research Reactor – Implications for Disposal”; J. Nuclear Materials*, in press*

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[15] This reference was issued by the publisher with Figures and their captions incorrectly assigned. The correct assignments are obvious.

[10] Marsden B.J., Preston S.D., Wickham A.J. and Tyson A., “Evaluation of Graphite Safety Issues for the British Production Piles at Windscale: Graphite Sampling in Preparation for the Dismantling of Pile 1 and the Further Safe Storage of Pile 2”; Proceedings of a Technical Committee Meeting ‘Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal’ Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.*213-223

[11] Guppy R., McCarthy J. and Wisbey S.J., “Technical Assessment of the Significance of Wigner Energy for the Disposal of Graphite Wastes from the Windscale Piles”; Proc. IAEA Technical Committee Meeting on ‘Nuclear Graphite Waste Management’, Manchester UK, October 1999, IAEA NGWM/CD 01-00120

[12] Ellis A., “The Management of Magnox Graphite Reactor Cores to Underwrite Continued Safe Operation”; proc. Conf. “Ageing Management in Graphite Reactor Cores”, Cardiff UK, November 2005, *to be published by The Royal Society of Chemistry in Spring 2006*

[13] Holt G., “The Decommissioning of Commercial Magnox Gas-Cooled Reactor Power Stations in the United Kingdom”; Proceedings of a Technical Committee Meeting ‘Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal’ Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.* 71-83

[14] Wickham A.J., Marsden B.J., Sellers R.M. and Pilkington N.J., “Graphite Core Stability during ‘Care and Maintenance’ and ‘Safe Storage’”; Proceedings of a Technical Committee Meeting ‘Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal’ Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.* 225-232

[15] Nuclear Decommissioning Authority: “Strategy – Draft for Consultation”; 2005

[16] Wörner J., Botzem W. and Preston S.D., “Heat Treatment of Graphite and Resulting Tritium Emissions”; Proc. IAEA Technical Committee Meeting on ‘Nuclear Graphite Waste Management’, Manchester UK, October 1999, IAEA NGWM/CD 01-00120

[17] Anderson Axdal, S.H. and Chung D.D.L., “A Theory for the Kinetics of Intercalation of Graphite”; Carbon, **25**, 1987, *pp*. 377-389

[18] Inagaki M., Rouillon J.C., Füg G. and Delhaes P., “Physical Properties of Graphite Nitrate Residue Compound”; Proc. 2nd German International Carbon Conference, Baden-Baden, June 1976, Deutsche Keramische Gesellschaft, *pp.* 273-276

[19] Diefendorf R.J., “The Effect of Atmosphere on the Stregnth of Graphite”; Proc. 4th Conference on Carbon, Buffalo, USA, June 1959, Pergamon, *pp.* 489-496

[20] Logsdail D.H., “The Effect of Gaseous Environment on the Flexural Strength of Graphite”; UKAEA internal document (UK)

[21] Romanoski G.R. Jr. and Burchell T.D., “Specimen Size Effects on Fracture Toughness of Nuclear Graphite”; Proc. 20th Biennial Conference on Carbon, Santa Barbara USA, July 1991, American Carbon Society, *pp.* 584-585

[22] Stumm W. and Morgan J.J., “Aquatic Chemistry”; John Wiley and Sons, 1981, *p.* 740

[23] Best J.V., Wickham A.J. and Wood C.J., “Inhibition of Moderator Graphite Corrosion in CEGB Magnox Reactors: Part 2 – Hydrogen Injections into Wylfa Reactor 1 Coolant Gas”; J. Brit. Nucl. Energy Soc., **15**, 1976, *pp.* 325-331

[24] Godfrey W. and Phennah P.J., “Bradwell Reactor Coolant Chemistry”; J. Brit. Nucl. Energy Soc., **7**, 1968, *pp.* 151-157 *and* 217-232

[25] Fischer P.G., Stöver D., Röhrig H.D. and Hecker R., “Der Tritiumkreislauf in Hochtemperaturreaktoren”; Proc. Reaktortagung Berlin, April 1974, Deutsches Atomforum e.V., *pp.* 420-423

[26] Marsden B.J., Hopkinson K. and Wickham A.J., “The Chemical Form of Carbon-14 Within Graphite”; Serco Assurance Unclassified Report SA/RJCB/RD03612001/R01 Issue 4, March 2002 *(available through UK NIREX website)*

[27] Wickham A.J., “Radiation Chemistry in Gas-Cooled Nuclear Reactors”; Chem. in Britain, **15**, 1979, *pp.* 286-292

[28] Schweitzer D.G., Gurinsky D.H., Kaplan E. and Sastre C, “A Safety Assessment of the Use of Graphite in Nuclear Reactors Licensed by the US Nuclear Regulatory Commission”; Brookhaven National Laboratory Report BNL-NUREG-52092, NUREG/CR-4981, 1987

[29] McKee D.W., “The Catalysed Gasification Reactions of Carbon”; Chemistry and Physics of Carbon Series, **16**, Marcel Dekker 1981, *pp.* 1-118

[30] Smith R.N., Pierce C. and Joel C.D., “The Low Temperature Reaction of Water with Carbon”; J. Phys. Chem., **58**, 1954, *pp.* 298 – 302

[31] Gray W.J. and Morgan W.C., “Leaching of ^{14}C and ^{36}Cl from Hanford Reactor Graphite”; Pacific Northwest Laboratory Unclassified Report PNL-6789, 1989

[32] ISO 6184-1 “Explosion Protection Systems – Determination of Explosion Indices of Combustible Dusts in Air”; 1985 (also issued as European Standard EN 26184-1 [1991] and British Standard BS 6713-1 [1986] under the title: “Explosion Protection Systems: Part 1; Method for Determination of Explosion Indices of Combustible Dusts in Air”)

[33] Robinson S., “Decommissioning WAGR: Is Nuclear Graphite a Fire Hazard?”; Proc. Nuclear Decon ’02

[34] Field P., "Dust Explosions"; Volume 4 of Series "Handbook of Powder Technology" *eds.* Williams J.C. and Allan T., Elsevier, 1982

[35] "Dust – The Coal Mines (Precautions against Inflammable Dust) Regulations 1956". S.I. 1956 No. 1769. (As varied by the Coal Mines (Precautions against Inflammable Dust) (Variation) Regulations 1960, S.I. 1960 No. 1738).

[36] Andrews G.E., Cross M.T., Ingamells W., Phylaktou H. and Wickham A.J., "Evaluation of the Potential for Carbonaceous Dust Explosibility in the Decommissioning of the Windscale Piles"; Proc. CESEP'05, 1st International Conference on 'Carbon for Energy Storage and Environment Protection', Orléans, France, October 3rd – 6th, 2005

[37] Petit A. and Brié M., "Graphite Stack Corrosion of Bugey I Reactor (Synthesis)"; Proc. IAEA Specialists Meeting 'Graphite Moderator Lifecycle Behaviour', Bath UK, September 1995, IAEA-TECDOC-901

[38] Fujii S., Shirakawa M. and Murakami T, "Study on Efficient Methods for Removal and Treatment of Graphite Blocks in a Gas-Cooled Reactor"; Proc. IAEA Technical Meeting, Manchester UK, on 'Nuclear Graphite Waste Management', published on CD-ROM IAEA-NGWM/CD 01-00120, October 1999

[39] Ishikura T., and Fujii S., "Graphite Waste Treatment for Decommissioning" 2005 ANS Topical Meeting on Decommissioning, Decontamination and Re-Uutilization, Denver, Colorado 2005, *pp*. 640 – 643

[40] Holland D., Quade U., Bach F.W. and Wilk P., "A German Research Project about Applicable Graphite Cutting Techniques"; Proc. IAEA Technical Meeting, Manchester UK, on 'Nuclear Graphite Waste Management', published on CD-ROM IAEA-NGWM/CD 01-00120, October 1999

[41] Bradbury D., Mason J.B., Wickham A.J., Buffery J. and Fachinger J., "Pyrolysis / Steam Reforming and its Potential Use in Graphite Disposal"; Proc. 3rd EPRI International Decommissioning and Radioactive Waste Workshop, October 25th – 29th 2004, Lyon, France

[42] Fisher M., "Fort St. Vrain Decomissioning Project"; Proceedings of a Technical Committee Meeting 'Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal' Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.*123-131

[43] See www.ukaea.org.uk/wagr/progress.htm

[44] Perera J., "The Nuclear Industry in the Former Soviet Union: Transition from Crisis to Opportunity" (in two volumes); Financial Times (London) Energy Publishing (Pearson Professional Ltd), 1996

[45] Marsden B.J. and Wickham A.J., "Graphite Disposal Options: A Comparison of the Approaches Proposed by UK and Russian Reactor Operators"; Proc. Nuclear Decommissioning '98, I.Mech.E. Conference Transactions, 1998-12, *pp.* 145-153

[46] Wickham A.J. and Ingamells W., "The Oxidation Characteristics of Nuclear Graphite Components and Dusts: Separating Fact from Fiction for Decommissioning"; Proc. 3rd EPRI International Decommissioning and Radioactive-Waste Workshop, 25th-29th October 2004, Lyon, France

[47] Wickham A.J. and Ingamells W., "Evaluation of the Condition of Graphite in the Fire-Damaged Zone of Windscale Pile No. 1"; Proc. CESEP'05, 1st International Conference on 'Carbon for Energy Storage and Environment Protection', Orléans, France, October 3rd – 6th, 2005

[48] BGRR, "Brookhaven Graphite Research Reactor Decommissioning Project: Final Characterisation Report for the 701 Below-Ground Structures, 702 Pile and Remaining Soils"; BGRR-055, Volume 1, May 2003

[49] Mason J.B. and Bradbury D., "Pyrolysis and its Potential Use in Nuclear Graphite Disposal" Nuclear Energy (BNES), 2000, **39,** *pp.* 305 - 310

[50] Ashida A. K. and Kuniaki W., "Diffusion Constants of Tritium in Graphites and Compensation Effect. Journal of Nuclear Materials, **183**, (1991), *pp.* 89 – 95

[51] Gaiko V.B., Korablev N.A., Solov'ev E.N., Trosheva T.I., Shamov V.P., Umanets M.P. and Shcherbina V.G., "Discharge of ^{14}C by Nuclear Power Stations with RBMK-1000 Reactors"; Atomic Energy **59**, 1986 *pp.* 703 – 705 *(translated from Atomnaya Énergiya* ***59****, 1985, pp. 144 – 145)*

[52] Konstantinov E.A., Korablev N.A., Solov'ev E.N., Shamov V.P., Fedorov V.L. and Litvinov A.M., "^{14}C Emission from RBMK-1500 Reactors and Features Determining It"; Atomic Energy, **66**, 1989. *pp.* 77 – 79 *(translated from Atomnaya Énergiya* ***66****, 1989, pp. 57 – 58)*

[53] Bushuev A.V., Verzilov Yu.M., Zubarev V.N., Kachanovsy A.E., Proshin I.M., Petrova E.V., Aleeva T.B., Samarkin A.A., Silin B.G., Dmitriev A.M., Gosatomnadzor R.F., Zakharova E.V., Ushakov S.I., Baranov I.I., Kabanov Yu.I., Kolobova E.N. and Nikolaev A.G., "Radionuclide Characterisation of the Graphite Stacks from Plutonium Production Reactors of the Siberian Group of Chemical Enterprises," Proc. IAEA Technical Meeting, Manchester UK, on 'Nuclear Graphite Waste Management', published on CD-ROM IAEA-NGWM/CD 01-00120, October 1999

[54] Greening F.R., "The Characterisation of Carbon-14 Deposits formed from the Nitrogen Gas-Annulus Systems of 500 MWe CANDU Reactors"; Radiochimica Acta, **47**, 1989, *pp.* 209-217

[55] Paasch R.A., “A Compilation of Carbon-14 Data” *(for the USA Hanford Reactors)*; UNC Nuclear Industries Unclassified Report UNI-3499, July 1985

[56] Miller R.L. and Steffes J.M., “Radionuclide Inventory and Source Terms for the Surplus Production Reactors at Hanford”; UNC Nuclear Industries Unclassified Report UNI-3714 Revision 1, April 1987

[57] Wichner R.P. and Dyer F.F., “Carbon-14 Production in the Peach Bottom HTGR Core”; Oak Ridge National Laboratory Unclassified Report ORNL-5597, July 1980

[58] Takahashi R., Toyohara M., Maruki S. and Ueda H., “Investigations of Morphology and Impurity of Nuclear Grade Graphite, and Leaching Mechanism of Carbon-14”; Proc. IAEA Technical Meeting, Manchester UK, on ‘Nuclear Graphite Waste Management’, published on CD-ROM IAEA-NGWM/CD 01-00120, October 1999

[59] Nair S., “A Model for the Global Dispersion of ^{14}C Released to the Atmosphere as CO_2”; Journal Soc. Radiol. Protection, **3**, 1983, *pp.* 16-22

[60] Suess H.E., “Radiocarbon Concentration in Modern Wood”; Science, **55**, 1955, *pp*. 414 *et seq.*

[61] Morgan, W.C. *Discussion comment at* IAEA Specialists Meeting ‘Graphite Moderaotr Lifecycle Behaviour’, Bath UK, September 1995: summarised in Editorial Section ‘Future Activities, *page* 15

[62] Dubourg M., “The Carbon-14 Cycle”; Proc. IAEA Technical Committee Meeting ‘Technologies for Gas-Cooled-Reactor Decommissioning, Fuel Storage and Waste Disposal”, Jülich, Germany, 1998, IAEA-TECDOC-1043, *pp.* 233 – 237

[63] Carlos-Lopez J., Lords R.E. and Patrick-Pinto A., “Integrated Conditioning process for Spent Graphite Fuels”: Westinghouse Idaho Nuclear Company Report WINCO-1194, March 1994, *and* Proceedings of Conference ‘Waste Management 94: Working Towards a Cleaner Environment’, Tucson Arizona USA, 278th Feb – 3rd March 1994, **1**, *pp.* 571 – 574

[64] Jefferies N.L., “The Evolution of Carbon-14 and Tritium-Containing Gases in a Radioactive Waste Repository”; NIREX Report NSS/R198, 1990 *(available from the NIREX website)*

[65] Karlina O.K., Klimov V.L., Ojovan M.I., Pavlova G.Yu., Dmitriev S.A. and Yurchenko A.U., “Immobilisation of Carbon-14 from Reactor Graphite Waste b Use of Self-Sustaining Reaction in the C-Al-TiO_2 System; J. Nucl. Materials, **345**, 2005, *pp.* 84 - 85

[66] Brown F.J., Palmer J.D. and Wood P., "Derivation of a Radionuclide Inventory for Irradiated Graphite: Chlorine-36 Inventory Determination"; Proc. IAEA Technical Meeting, Manchester UK, on 'Nuclear Graphite Waste Management', published on CD-ROM IAEA-NGWM/CD 01-00120, October 1999

[67] Rahmani L, "Chlorine Degassing from Nuclear Grade Graphite";presented at 6th International Nuclear Graphite Specialists' Meeting, Chamonix, France, September 2005, *published on CD-ROM by SGL Carbon Ltd, available from the present authors*

[68] Gray W.J. and Morgan W.C., "Leaching of ^{14}C and ^{36}Cl from Hanford Reactor Graphite"; Pacific Northwest Laboratory Unclassified Report PNL-6769, 1988

[69] Gray W.J. and Morgan W.C., "Leaching of ^{14}C and ^{36}Cl from Irradiated French Graphite"; Pacific Northwest Laboratory Unclassified Report PNL-6989, 1989

[70] Gray W.J., "A Study of the Oxidation of Graphite in Liquid Water in Radioactive Waste Storage Applications"; Rad. Waste Management and The Nuclear Fuel Cycle, **3**, 1982, *pp.* 137-149

[71] Costes J.R., Koch C., de Tassigny C., Vidal H. and Raymond A., "Conditioning of Radioactive Graphite Bricks from Reactor Decommissioning for Final Disposal"; Commission of the European Communities Report EUR 12815, 1990

[72] Costes J.R., de Tassigny C. and Vidal H., "Conditioning of Graphite Bricks from Dismantled Gas-Cooled Reactors for Disposal"; Waste Management, 10, 1990, *pp.* 297-302

[73] Hespe E.D., "Leach Testing of Immobilised Radioactive Waste Solids: A Proposal for a Standard Method"; Atomic Energy Reviews, **9**, 1971, *pp.* 195 - 207

[74] Howarth A., Heath T.G. and Tweed C.J., "HARPHRQ: A Computer Program for Geochemical Modelling"; UK NIREX Report NSS/R380, 1995 *(available via the UK NIREX Ltd web site)*

[75] "Review of Radioactive Waste Management Policy: Final Conclusions"; Cmd. 2919, London, HMSO, July 1995

[76] Kelly, J., "EPRI International Site Assistance Programme Results", *presented at* 4th EPRI International Decommissioning and Radioactive Waste Workshop, October 24th – 27th 2005, Madrid, Spain

[77] Rao, K.R., "Radioactive Waste: The Problem and It's Management"; Current Science, **81**, No.12, 25 December 2001, *referenced in* Buckley M., "Disposal in Subduction Zones", CoRWM Document No. 627, August 2004 *(available at www.corwm.org.uk)*

[78] Hemingway K., “Jointly Commissioned Research on Radioactive Waste Management: Product Evaluation Task Force, Phase 2 Report for CAGR Graphite”; UK Department of Energy Report DoE/HMIP/RR/91/012, 1991

[79] Holderness S.G. and Lewin R.G., “Electrochemical Separation of Contaminant Metal from Scrap Graphite”; UK Patent GB 2269601, June 1993

[80] Esteban-Duque A., Uriarte A., Suarez A., Fabrellas B. and Gonzalez A., “Characterisation and Conditioning of Radioactive Graphite”; Proceedings of the 1993 International Conference on Nuclear Waste Management and Environmental Remediation, September 5th – 11th 1993, Prague *pp.* 641 – 648

[81] Guiroy J.J., “Graphite Waste Incineration in a Fluidised Bed”; paper presented by M. Dubourg at IAEA Specialist Meeting on “Graphite Reactor Lifecycle Behaviour”, Bath UK, September 1995, IAEA-TECDOC-901, 1996, 193-203

[82] Bradbury D. “Review of Chemical Decontamination Technology Development 1977-2000” BNES Water Chemistry of Nuclear Reactor Systems 8, BNES UK, **1**, *pp.* 173-178

[83] Dubourg M., “Feasibility Testing of the Incineration of Contaminated Graphite in a Pilot Fluidised Bed”; paper presented at the Second Seminar on “Practical Decommissioning Experience with Nuclear Installations in the European Community”, September 1991

[84] Jaroshenko A.P., Savos’kin M.V. and Popov A.F., “The Gasification via Exfoliation as a New Route of Utilisation of the Graphite Wastes from Chernobyl Nuclear Power Plant”; Dopovyidyi Natsyional Noyi Akademyiyi Nauk Ukrayini, No. 5, 1995, *pp.* 148 – 152

[85] Jaroshenko A.P., Savos’kin M.V. and Kapkan L.M., “Graphite Gasification via Exfoliation: Novel Approaches to Advanced Technologies”; Proc. European Carbon Conference ‘Carbon 96’, Newcastle UK 1996, *pub.* The British Carbon Group, *pp.* 218 – 219

[86] Roeh A.P., “Rover Fuel processing – A Success with Lessons Learned”; Westinghouse Idaho presentation to The American Society of Mechanical Engineers, ref. 84-WA/PVP-7, 1984

[87] Tejima K., “Processing Method for Radioactive Graphite Waste”; Japanese Patent Document 6-94896/A/, 1994 (Patent Application No. 4-244816, 1992)

[88] Karigome S., “Tokai-I Decommissioning Project: Investigation of Graphite Treatment and Disposal”; Proc. Fourth International Nuclear Graphite Specialists’ Meeting INGSM-4, Marugame, Japan, September 2003, *published on CD-ROM only and available from the present authors*

[89] Costes J.R., Caminat P. and Bournot P., “Continuous CO_2-Laser-Controlled Combustion of Graphite Blocks at Pilot Scale”; Paper presented to “Incineration ‘91”, Knoxville TN USA, May 1991, Proceedings pp. 303 – 309

[90] Costes J.R., Barbannaud N. and Caminat P., “Advanced Powerful CO_2-Laser-Controlled Incineration of Waste Graphite Blocks”; Paper presented to “Incineration ‘92”, Albuquerque USA, May 1992

[91] Costes J.R., Guiberteau P., Caminat P. and Bournot P., “CO_2-Laser-Aided Waste Incineration”; Tenth International Symposium on Gas Flow and Chemical Lasers, Friedrichshafen 1994, pub. SPIE – The International Society for Optical Engineering, **2502**, ed Bohn W.L. and Hügel H., 590 – 596

[92] Wakefield R.M. and Peterson D.L., “Graphite Ablation in Combined Convective and Radiative Heating”; NASA J. Spacecraft, **10**, 1973, 149 – 154

[93] Gay R.L., “Method for Disposing of Radioactive Graphite and Silicon Carbide in Graphite Fuel Elements”; US Patent 5,449,505, September 12th 1995

[94] Señor D.J., Hollenberg G.W., Morgan W.C. and Marianowski L.G., “Destruction of Nuclear Graphite using a Closed-Chamber Incineration from Extraction and Processing for the Treatment and Minimisation of Wastes”; Proceedings, 123rd Annual Meeting of the Minerals, Metals and Materials Society, San Francisco USA, ed Hager J., Hansen B., Imrie W., Pusatori J. and Ramachandran V., pub. The Minerals, Metals and Materials Society, 1993, 875 – 893

[95] Gorbunova L.B., Kuteinikov A.F., Marunina N.I. and Sukhov G.V., “Possible Losses of Impurity Elements in High-Purity Graphite during Ashing”; Russian Journal of Analytical Chemistry, 1976, **31**, *pp.* 1506 – 1508 *(translated from Zhurnal Analiticheskoi Khimii. 1976, **31**, 2061 – 2064)*

[96] Bradbury D., “Review of Chemical Decontamination Technology Development 1977-2000”; BNES Water Chemistry of Nuclear Reactor Systems 8, BNES UK, **1**, *pp.* 173-178

[97] Bradbury D. et al, “The EPRI DFD Process, Decontamination for Decommissioning” Proceedings of ANS Topical Meeting on Decommissioning, Decontamination and Reutilization of Commercial and Government Facilities, September 1997, *pp*. 463-468

[98] Podruzhina T., “Graphite as radioactive waste: Corrosion behaviour under final repository conditions and thermal treatment” Berichte des Forschungzentrums Jülich 4166, ISSN 0944-2952, 2004

[99] See,for example, www.studsvik-inc.com

[100] Anon, “Process Flow Diagrams”, THOR Treatment Technologies, www.thortt.com

[101] Yarmolenko O.A., Romenkov A.A., Sudareva N.A., Sukhovski E.V., Konovalov E.E., Bogdanovich N.G., Karlina O.K., Pavlova G.A. and Yurchenko A.Yu., “Development of Technique for High-Level Radwaste Treatment to Ceramic Matrix by Method of Self-propagating High-Temperature Syntheses”; Presented at 7th International Conference ‘Nuclear Technology Safety 2004: Radioactive Waste management’, 27th September – 1st October 2004, St. Petersburg, Russia

[102] Dmitriev S.A., Karlina O.K., Klimov V.L., Ojovan M.I., Pavlova, G.Yu. and Yurchenko A. Yu, “Retention properties of Carbide-Corundum Ceramics Containing Carbon-14, Caesium-137 and Strontium-90”; Proc. ICEM’03, The 9th International Conference on Environmental Remediation and Radioactive Waste Management, September 21st – 25th 2003, Oxford UK, *(paper ICEM03-4567)*

[103] Ojovan M.I., Karlina O.K., Klimov V.L., Bergman G.A., Pavlova G.U., Yurchenko A.Yu. and Dmitriev S.A., “Investigations of Reactor Graphite Processing with the Carbon-14 Retention”; Materials Research Society Symposium Proc., **757**, *paper II3-13-1*

[104] Ojovan M.I., Lee W.E., Sobolev I.A., Dmitriev S.A., Karlina O.K., Klimov V.I., Petrov G.A. and Semenov C.N., “Thermochemical Processing Using Powder-Metal Fuels of Radioactive and Hazardous Waste”; Proc. Inst. Mechanical Engineers, 2004, **218** Part E, J. Process Mechanical Engineering, *pp.* 1 – 9

[105] Virgil’ev Yu.S., “Radioactive Waste Reactor Graphite and its Utilisation”; Fizika I Khimiya Obrabotki Materialov, No. 6, 1993, *pp.* 131 – 134

[106] Greneche, William J. S. “The Areva HTR Fuel Cycle - An Overview Of Technical Issues And Potential Industrial Solutions” 2nd International Topical Meeting on High Temperature Reactor Technology Beijing, CHINA,, September 22-24, 2004

[107] Chang F.H., Vogt H.K., Krochmalnek L.S., Sood S.K., Bartoszek F.E., Woodall K.B. and Robins J.R.; “Producing Carbon-14 Isotope from Spent Resin Waste”, US Patent 5,286,468, February1994

[108] Dias S. and Krasznai, “Selective Removal of Carbon-14 From Ion-Exchange Resins using Supercritical Carbon Dioxide; Proc. International Topical Meeting on Nuclear and Hazardous Waste Management ‘Spectrum ‘96’, August 18th – 23rd, 1996, Seattle USA (*pub.* American Nuclear Society) *based upon* Ontario Hydro Technologies Report A-NBP-95-123, August 1995

[109] McEnaney B., Wickham A.J. and Dubourg M., “Planning for Disposal of Irradiated Graphite”; Basic Studies in the Field of High-Temperature Engineering, Second Information Exchange Meeting, 10th – 12th October 2001, Paris France, OECD Nuclear Energy Agency, 2002, *pp.* 281 – 291

[110] Marsden B.J. and Preston S.D., “Graphite Selection for the PBMR Reflector”; Basic Studies on High-Temperature Engineering, First Information Exchange Meeting, 27th – 29th September 1999, Paris France, OECD Nuclear Energy Agency 2000, *pp.* 235 - 245

[111] www.peoplescienceandpolicy.com/llw/papers/Recycle.doc

A

APPENDIX A—DEFINITIONS

AGR	Advanced Gas-Cooled Reactor (UK design)
AVR	Arbeitsgemeinschaft Versuchsreaktor *(Experimental HTR formerly operated at Forschungszentrum Jülich, Germany)*
BNES	British Nuclear Energy Society
BNGG	Brookhaven Graphite Research Reactor, New York State, USA
CEA	Commisariat a L'Énergie Atomique, France
CEGB	Central Electricity Generating Board *(former nationalised electricity-supply body in the UK)*
CIDEN	Centre d'Ingénierie Déconstruction et Environnement *(of EdF, based in Lyon, France)*
CNPP	Centre National de Prévention et de Protection *(French fire research centre at Vernon, Normandie)*
CoRWM	Committee on Radioactive Waste Management, set up in the United Kingdom in 2003 with a three-year remit to evaluate general radwaste disposal options
EdF	Electricité de France
FAZ	Fire-Affected Zone *(of Windscale Pile No. 1 following the 1957 accident)*
GRSAC	Graphite Reactor Severe Accident Code *(developed by ORNL, USA, in association with the Los Alamos laboratory)*
HLW	High Level Waste *i.e.* High β/γ, significant α, high radiotoxicity, high heat output
HTTR	High Temperature Test Reactor *(Japanese test reactor at Oarai)*
HTR	High Temperature Reactor *(helium cooled)*
HTR-10	Chinese 10-Megawatt prototype High Temperature Reactor located north of Beijing
IAEA	The International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
ILW	Intermediate Level Waste, *i.e.* Intermediate β/γ, low or significant α, intermediate radiotoxicity (more than 4 GBq/te for α activity and 12 GBq/te for β/γ in the UK), low heat output
INERIS	Institut National de l'Environnement Industriel et des Risques
ISO	International Organisation for Standardisation
LLW	Low Level Waste

MTR	Materials Testing Reactor
NDA	The United Kingdom Nuclear Decommissioning Authority
NEA	Nuclear Energy Agency of the OECD
OECD	Organisation for Economic Cooperation and Development *(of which the Nuclear Energy Agency is the most relevant division here)*
PBMR	Pebble-Bed Modular Reactor *(South African design)*
PGA	Pile Grade 'A' graphite: a petroleum-coke extruded material used for Magnox-reactor moderators in the UK
RBMK	*Russian acronym for* "Channelised Large Power Reactor"
SHS	Self-Propagating High Temperature Syntheses *(Russian Process for Immobilisation of Graphite Waste containing Fission Products and Fuel Debris)*
SoGIN	Società Gestione Impianti Nucleari *(Italian authority with responsibility for decommissioning)*
UKAEA	United Kingdom Atomic Energy Authority
UNGG	Unité Nucleaire Gaz-Graphite *(French Magnox-type reactor design)*
VHTR	Very High Temperature Reactor *(helium cooled)*
WAGR	Windscale (Prototype) Advanced Gas-Cooled Reactor

B

APPENDIX B—THE OXIDATION CHARACTERISTICS OF SOLID GRAPHITES IN AIR

B.1. Kinetics

Graphite is a material of low chemical reactivity and generally benign properties. Chemical reaction takes place only with extremely powerful reagents. Gas-phase oxidation of graphite, particularly very pure nuclear grades where catalysts are absent, is also surprisingly difficult. Graphite has a high thermal conductivity compared with most carbonaceous materials and, although the thermal conductivity reduces upon irradiation, it remains difficult for the bulk graphite to retain heat locally to promote the oxidation reaction. Graphite is also a near-perfect "black body radiator", offering a further means for efficient heat removal. There is also only an insignificant amount of ash formed, which could otherwise assist in heat retention.

There is an extensive literature relating to the oxidation of graphite in air. This derives not only from the nuclear industry but also from many other fields in which graphite and other forms of carbon are utilised in industry. A comprehensive review of this literature was carried out in 1989-1990 by AEA Technology [1] covering some 130 references, including the pioneering work of P.L. Walker Jr. and his colleagues (*e.g.* [2]).

Oxidation in air is thermodynamically favoured at any temperature below about 4000K. Three distinct "Modes of Oxidation" can apply, although the transition between them is generally gradual:

"Mode I" is characteristic of low-temperature oxidation in which there is an unlimited supply of air. This is known as the "Chemical Rate" regime. Here the oxidation obeys a simple Arrhenius rate law with an activation energy around 40 kcal.mol^{-1}; a typical oxidation rate, say at 723K which is a commonly-used experimental temperature, might be around 40 $\mu\text{g.g}^{-1}.\text{h}^{-1}$ for a sample of unirradiated or so-called "virgin" graphite[16]; somewhat higher values are found in practice for samples removed from an operating reactor and this is discussed later. Oxidation in Mode I is generally uniform within the accessible pore structure and there is thus a uniform reduction in bulk density as oxidation proceeds;

"Mode II" becomes important at higher temperatures where the potential oxidation rate (as predicted from the Arrhenius equation) is high, but diffusional control is imposed upon the reaction by the structure of the open porosity of the graphite such that the oxidation rate of the internal pore surfaces cannot achieve that predicted from the equation because of lack of sufficient oxygen arriving at the sites of reaction;

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[16] Which is to say, micrograms graphite oxidised per gram of original graphite in one hour.

"Mode III" applies at still higher temperature, in which the limitation imposed by the rate of diffusion becomes subordinate to mass-transport limitations affecting the supply of reactant air to the graphite component; under these conditions, oxidation behaviour is dominated by reaction at geometrical (external) surfaces of the component.

The typical activation energy and reaction rates already quoted for "Mode I" conditions effectively preclude significant oxidation of nuclear-grade graphites below about 623K. This remains essentially true also for irradiated graphite, where there is however a modest increase in rate arising from irradiation effects (fast-neutron damage to the reacting surfaces and an opening of the porosity as a result of gamma-radiation induced oxidation, which occurs throughout reactor operation for both air-cooled and carbon-dioxide-cooled designs). These effects have been approximately quantified: for example, for Pile Grade 'A' graphite in the UK Magnox reactors, an equation of this form applies:

$$\textit{Reaction rate} = a\,(1 + 0.0035\,DR(\theta) + 12.5(1 - \exp[-W/3]))$$

where a is the unirradiated reaction rate (units of $\mu g.g^{-1}.h^{-1}$ are customarily employed), W is the weight loss in percent arising from gamma-induced oxidation, and $DR(\theta)$ represents the effective damage dose from the fast neutrons [3] and is calculated from the adjacent fuel dose in $MWd.te^{-1}$ (D) and a polynomial expression ($R(\theta)$). Additional enhancement of reaction rate through catalysis arising from chemical impurities in the reactor environment is discussed separately.

The experimental data quoted thus far have largely been obtained with small samples, typically one centimetre diameter and generally not more than 10 centimetres long. In large blocks of graphite, the problems of diffusion control ("Mode II") and mass-transport limitations ("Mode III") can manifest themselves at surprisingly low temperatures, thereby further alleviating the potential for oxidation. As an example, [4] gives evidence of "Mode III" behaviour at a temperature as low as 733K.

It is a characteristic of graphite oxidation that when the supply of air is restricted, as in Modes II and III, there is no longer complete combustion to carbon dioxide (CO_2) according to the classical reaction $C + O_2 \rightarrow CO_2$ and a proportion of carbon monoxide (CO) is found in the product gases as a result of the reaction $2C + O_2 \rightarrow 2CO$. The proportion of CO formed tends to rise as the temperature increases and one progresses through the higher modes. This has the effect of allowing more carbon to be removed for a given amount of oxygen. Ong [5] summarises this in a general rule whereby $CO/CO_2 < 1$ at high pressure and low temperature, >1 at low pressure and high temperature. CO_2 production is effectively zero at ~ 1750K, as determined in [6].

There have been two apparent recent observations of this phenomenon from the nuclear industry. Chi [7], reporting on the thermal oxidation of ion-irradiated Toyo Tanso graphites IG-11, IG-110 and IG-430 at the Korea Atomic Energy Research Institute, observed the expected saturation of oxidation (limited by the oxygen supply in "Mode III") between about 1000 - 1200ºC but then observed a sudden increase in carbon loss rate as the temperature was further increased. This was particularly apparent with the IG-11 material. In discussion of this paper at a recent conference, L. Brissoneau of CEA Cadarache confirmed that similar observations had recently been made, but claimed that gas-chromatography measurements had suggested that an increase in the production of CO was *not* the explanation. However, no specific alternative was offered, except for a suggestion that differential oxidation rates of filler and binder particles in the graphite might be responsible. This could lead to the possibility that separation of the structure could occur at higher weight losses, with some of the grains simply falling out. Whilst Brissoneau claims that this might have occurred in his samples, Ong [5] however claims that there is only one type of oxidation site. This issue remains unresolved at this time.

This observation of increased CO formation is extremely relevant when classical situations in which so-called “graphite fires” have been reported. If the term “fire” is equated with visible flame, then it is clear that, in such situations, a flammable product is burning – the carbon monoxide ($2CO + O_2 \rightarrow 2CO_2$). With graphite, which is a pure form of elemental carbon and can only oxidise through one of the two chemical equations quoted, it is clear that a flammable product can only form in a restricted supply of air. Thus it is extremely difficult indeed to have graphite ‘ignite’ since, if there is sufficient air to make this possible in theory, a non-flammable product results. This may be readily demonstrated by holding a small sample of graphite in the flame of a gas torch. The graphite will glow red hot, but does not inflame. Where reports of burning graphite do arise (*e.g.* The Windscale Accident, Chernobyl), what is seen must in fact be carbon monoxide, formed through a deficit of air at the oxidation site, which subsequently ignites when it (the gaseous product) encounters a greater supply of air whilst still at a sufficient temperature to do so.

B.2. Recommended Nomenclature

The following terms and definitions can all be related to the well understood scientific basis of graphite oxidation which has been reviewed above, and represent the preferred usages in the opinion of the present authors:

B.2.1. Oxidation

“Oxidation” is simply the name for the chemical reaction of a material with oxygen. The term may separately be used in what are termed redox processes in chemistry to indicate the elevation of a cation (usually) to a greater valence state (such as ferrous iron to ferric iron), and in some cases to represent reaction with materials other than oxygen, but these situations are irrelevant here.

In the present context, it means the reaction of graphite with oxygen to form the usual gaseous products CO_2 and CO, depending upon the availability of oxygen at the reaction site. These reactions are inevitable above about 623K: the rates are generally low and become controlled by diffusion and then by mass-transfer limitations as the temperature is increased. They are also hindered by radiative heat loss and by heat conduction through the graphite away from the reacting site.

Under certain circumstances, oxidation reactions may become *self-sustaining*. The criteria for this situation with respect to graphite are discussed below.

B.2.2. Combustion

"Combustion" is the term used to describe the burning of material – *i.e.* a *self-sustaining* oxidation reaction in air or oxygen (through self heating or autocatalysis) and usually, but not necessarily, with a sustainable visible flame arising from the combustion of gaseous oxidation products. Generally this means a vigorous oxidation in the gas phase of vaporised material, although some specialists would contend that combustion can be supported by a surface reaction. Graphite is reported to have a sublimation temperature in excess of 3300K at atmospheric pressure, implying that a very high temperature indeed would be necessary to support genuine combustion in air if prior vaporisation were essential. Hot or glowing material is not in itself evidence of combustion.

B.2.3 Spontaneous Ignition

"Spontaneous ignition" can occur in a porous substance or in deposited material which is initially at a sufficient temperature to undergo some exothermic chemical process (which *may* be oxidation) or even a microbiological process (*e.g.* in poorly constructed stacks of hay or straw). It does not require any external energy source and may require long times to become evident. If the heat generated is unable to escape and therefore the temperature of the underlying material rises, the rate of the exothermic process may further increase, perhaps limited by the access of oxygen, until it is sufficiently hot for combustion to commence at exposed surfaces without any external ignition source. Thus, whilst it is conceivable for carbonaceous or graphitic dust to undergo spontaneous ignition given an appropriate combination of circumstances, it is largely irrelevant for bulk graphite.

B.2.4. Ignition Temperature

Ignition temperature is not a material property, but depends upon geometry, heat-generation and heat-loss rates, and sometimes upon the history of the specimen. It is the lowest temperature at which the rate of heat generation due to exothermic reaction (with air or oxygen in the case of graphite) exceeds the rate of heat loss from the system such that it will continue to undergo oxidation until either the graphite or the oxygen is consumed.

More loosely, it has been taken to be the lowest temperature at which a substance held in a free supply of air or oxygen (whichever is defined) will engage in combustion with a visible flame. Although the term has been mis-applied to graphite oxidation, it is not relevant for bulk graphite, as may readily be demonstrated by the numerous various tests which have been undertaken.

B.2.5. Smouldering

"Smouldering" is essentially a slow exothermic oxidation, generating sufficient heat to be self-sustaining, within a porous material but where sufficient heat loss can occur to prevent full ignition (*i.e.*with a visible flame). For organic or carbon-based matter, it is usually limited to materials which form (or already are) a carbonaceous char, and represents the further oxidation of the material in underlying regions. Again, for bulk nuclear-grade graphite, it is largely irrelevant.

B.2.6. Incineration

“Incineration” is a process whereby a material is placed in a special facility designed to wholly oxidise it. Generally such a facility has a forced supply of air and it may be the case that an enriched oxygen supply is needed either to initiate or to sustain the reaction at a sufficient rate. Industrial incineration of graphite is difficult, but it is possible in a specialised facility. Two such processes proposed for the disposal of nuclear graphite, one of which has reached the pilot-plant stage, are described in a later section.

B.2.7. Calcination

Occasionally, a material may be heated for a secondary purpose rather than to provide oxidation. There are many examples in industry: for example, the manufacture of quicklime from limestone. Often, air is actually excluded.

This process has been applied by UKAEA for graphite from the GLEEP experimental pile at Harwell (UK), but it has been mis-described in their documentation as “incineration”. The objective here has been to mobilise certain radioactive isotopes. The confusion arises through the use of an industrial incinerator to effect the change. This operation has in fact yielded very useful data about the slow rate of graphite oxidation in this industrial configuration, despite high temperatures and an assisted supply of air, and the work is therefore described in more detail in the body of the report.

B.3. Catalysis of Graphite Oxidation

B.3.1. Experience in UK Reactors

Impurity materials potentially able to catalyse graphite oxidation in air may become associated with reactor graphite. They are usually not present initially – the purity specification of nuclear graphites is very high, even with early material – but they may be drawn in with the reactor coolant, as in the air-cooled Windscale Piles or, in recirculating systems such as Magnox reactors or AGRs, be mobilised and transported from other areas of the reactor circuit such as heat exchangers.

An example of the former, arising from the analysis of swab samples from the fuel channels of both Windscale piles, is the observation of enhanced concentrations of calcium and sodium arising through entrainment of concrete dusts from the air ducts, together with sea salt from the air [8]. For the latter, the products of metal corrosion in boiler tubes is offered as an example [3]. In special cases, such as the Windscale Pile 1, the fire has apparently resulted in locally high concentrations of aluminium (from damaged fuel cartridges), whilst in both Piles there is evidence of contamination by lead (from the melting and dispersion of lead spacers used in isotope cartridges and elsewhere). There are recent measurements of reaction rate at 673K[17] for graphite samples trepanned from Windscale Pile 2, which show a wide variability with the

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[17] Note that this is 50K *lower* than the typical temperature used for measurement: the Arrhenius equation predicts values approximately 7.8 times lower at this temperature than at 723K

majority of results falling in the range 30-700 $\mu g.g^{-1}.h^{-1}$ and isolated results which are very much higher [8]. Results for pure unirradiated PGA graphite would be expected in the range 30 – 50 $\mu g.g^{-1}.h^{-1}$. Similar data to those from Pile 2 were subsequently found for Pile 1 although interestingly, the highest value found overall was associated with a so-called "high-reactivity zone" in Pile 2 first identified many years previously [9].

These results make an interesting contrast with the extent of catalytic effect found in UK Magnox reactors. In this case, the effect of up to 30 years power operation may be considered to have increased the oxidation rate (at 723K) by a factor 2 – 3 at most [3].

B.3.2. Inorganic Catalysts

The subject of catalysis of graphite oxidation in air is covered in a major review by McKee published in 1981 [10]. For the absolute clarity of nomenclature and the avoidance of subsequent confusion, we should note that McKee unfortunately expresses his results in terms he describes as "the lowering of ignition temperature…..". Careful examination of his technique reveals that this is ***not*** ignition as such, but simply a temperature at which a high rate of increase in oxidation in air occurred. It is unfortunate that McKee used this as his means of comparison, being unable in his controlled-atmosphere microscope to obtain direct measurements of oxidation rate or to define parameters in the Arrhenius equation.

This example of loose wording is typical of writing which has lead to unnecessary fears about graphite 'ignition' and 'fires', and led to the definitions of nomenclature proposed above. In fact, McKee's data *in no way* compromise the thesis that it is extremely difficult to "burn" or "ignite" graphite in air.

McKee identifies four major factors which influence the oxidation rate of carbonaceous materials:

- The concentration of active (*i.e.* oxidisable) sites on the surface;
- The crystallinity and structure of the carbon *(his review covers "carbons" in general)*;
- The presence of inorganic impurities; *and*
- The diffusion of reactive gases to the reaction sites.

It will be seen that this mirrors (and confirms) the basic features of the standard modes of oxidation already discussed, and it is the third item which merits additional treatment here.

It is convenient to treat the inorganic impurities in three groups:

B.3.2.1. Alkali Metal Compounds

The potential relevance under this heading is contamination by sea salt entrained in the air coolant of reactors sited on coasts, such as the Windscale piles. For Magnox and AGRs, which experience air in the vessel only during maintenance periods (and obviously during their construction phase), station chemists have been rather careful to ensure that impurities do not enter the reactors under these conditions.

In general, alkali-metal carbonates have been found to be more active as catalysts than the corresponding oxides or halides. It has been observed [11] that concentrations up to around 2% by weight will cause a proportionate drop in the temperature corresponding to a particular gasification rate (*i.e.* oxidation rate, both terms being in common usage), with 2% corresponding to a fall of around 200K. In the case of sodium, molten sodium peroxide Na_2O_2 which is mobile on the graphite basal planes is implicated in the mechanism.

B.3.2.2. Alkaline Earth Compounds

This group is important for all reactors with concrete pressure vessels or with concrete access ducts for the coolant. In the case of calcium, the oxide was shown to be the important compound in promoting the reaction of both nuclear graphite and single-crystal (natural) graphite with oxygen [12]. Independent evidence of the catalytic effect of calcium has been confirmed on samples of graphite from UK Magnox reactors using controlled-atmosphere electron microscopy [13].

Calcium and the alkaline earths are, however, considered to be less powerful catalysts of graphite oxidation than the alkali metal compounds. According to Amariglio and Duval, who have published one of the definitive works on the relative catalytic activity [14] working with Pechiney graphite grades “20-30” and “30-60” which are rather similar to the UK Magnox type PGA, the order of catalytic activity for an equivalent quantity of impurity, generally applied to the graphite as an aqueous solution of the acetate salt, is Na>Li>Ba>Sr>Ca>Mg. Under equivalent conditions to the lowering of the temperature of relative oxidation rates by 200K, mentioned above, substitution of the equivalent mole fraction of calcium for the sodium would reduce the difference in temperature to 60K.

B.3.2.3. Transition Metals and Other Elements

Amariglio and Duval’s comparison [14] shows these to be the most active catalysts, the mechanism of catalysis often depending upon the “redox” processes, which means switching between oxidation states to facilitate the oxidation of the carbon. Under normal circumstances the function of a catalyst is to reduce the activation-energy barrier for the reaction: in the case of some transition metals this barrier is apparently *not* lowered, the effect instead arising from an increase in the surface density of reaction sites in the presence of the catalyst (see [15], which also provides a comprehensive “merit order” for 21 catalysts, largely similar to that of Amariglio and Duval).

The most powerful graphite-oxidation catalyst so far known is lead. Experimental data are available from CEGB studies supporting the possible loss of a fragment of a lead block into a Magnox reactor vessel[18] (*A.J. Wickham, personal communication*) which confirm the observation of Amariglio and Duval that a small quantity of lead or a lead compound, suitably applied to the graphite, can increase the reactivity by several orders of magnitude.

Uranium oxides and other transuranic compounds, which are likely to be present in regions of the fire-affected zone, are also potential catalysts, but there is only limited experimental information of their effectiveness in promoting graphite oxidation. Sampath *et al.* [16,17] have examined the oxidation of intimate mixtures of graphite powder with the oxides of uranium, cerium, thorium, lanthanum, neodymium and plutonium using a thermogravimetric method with a constant rate of temperature rise (4k/min) up to around 1000ºC, comparing the results both with pure graphite and with graphite mixed with alumina. The method identified reductions in both the activation energy and the pre-exponential factors of the Arrhenius relationship, as expected, but the usual mechanism of a reduction/oxidation cycle did not appear to be supported by the results, which were comparable for all the oxides tested despite the absence of multiple stable oxidation states in all cases (*e.g.* thorium). The order of catalytic activity was $U_3O_8 > ThO_2 \sim CeO_2 > PuO_2 \sim La_2O_3 \sim Nd_2O_3$. It should be borne in mind that the results were obtained with fine powders and that particle-size effects on the chemical rates were clearly observed.

B.3.3. General Issues on Inorganic Catalysis

With all catalysts, the degree of intimacy of the impurity with the graphite is extremely important in determining the outcome. It is entirely possible for a potentially catalytic material to have much less than the suspected effect if its particles are not in suitable contact with reaction sites. Thus, it is not possible to make accurate predictions about the effects of possible catalysts in the context (for example) of reactor decommissioning, where additional foreign materials might be introduced at the dismantling stage in addition to those introduced during the operating period. The only sure way to obtain a definitive result on the reactivity of the graphite at the time of dismantling is to remove samples and make reaction-rate measurements using a microbalance or similar apparatus. The probability is that it is unlikely for a commercial reactor to have experienced any degree of catalysis which would result in a potential problem for planned dismantling operations. However, as the data already quoted for swab and graphite samples from the UK Windscale Piles has shown, there is a *possibility* that extremely large catalytic effects may apply in some cases.

To illustrate that the general magnitude of effects of transition-metal and other metal oxides arising from normal operation is quite low, a useful example concerns a study in which powdered nuclear graphite was oxidised in the presence of AGR circuit dusts characteristic of those collected in the central inertial collectors originally employed in some fuel stringers to collect particulates from the coolant. The maximum enhancement factor found at 623K was 10, but this was also associated with a lowering of the activation energy (the well-understood "compensation effect"). This means that at *higher* temperature, the relative enhancement would be less since the rate of rise of oxidation rate with temperature is a strong positive function of the value of the activation energy.

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[18] In fact, no lead had entered the reactor vessel.

B.4. The Effect of Water on Graphite Oxidation in Air

Water or steam ingress into graphite-moderated reactors has occurred occasionally, through failures in boiler tubes introducing superheated steam into the coolant circuit and, on one occasion, an AGR in Scotland became partially filled with sea water following a complex series of valve failures. The issue is also relevant for Windscale Pile 1 in the UK where water was deliberately introduced as a last resort to quell the reactor fire [18] in 1957 and, peripherally, for any reactor where underwater dismantling is contemplated.

There are three ways in which the effects of water might be relevant:

- the direct effect of contamination, washing material into the graphite;
- the direct effect of water on graphite oxidation rate in air; *and*
- the influence of water on the catalytic potential of other contaminants.

The first of these issues is essentially covered, in the case of the Windscale Pile 1, by the sampling of core graphite which has subsequently taken place. In that example, the effects of water could not be distinguished since catalysed graphite reactivities in the two Piles were rather similar. No measurable effects were found on graphite reactivity to air in the Magnox reactors where steam/water ingress took place, and the effect on the gilsocarbon graphite in the Scottish AGR was modest. Any other situation where this problem might arise must be dealt with by sampling and analysis.

There is some ambiguity about the *direct* effect of water or water vapour, and the subject is worthy of brief review here. This issue is extensively discussed by Lewis [19]. Although his review is over 30 years old, in the present authors' opinion it reflects the current understanding of the subject. However, within this field there are some conflicting observations.

Lewis states: "Most authors report that moisture inhibits the oxidation of pure graphite, the biggest decrease occurring when the moisture level is raised from about 10vpm to 200 vpm…" *(i.e. well below atmospheric concentration)* … "Heuchamps *et al.* [20] found the inhibiting action of water to be less marked at lower temperatures and there to be no effect below 500ºC."

The difficulties appear to arise when catalyst(s) are present along with the water, when the effect of the water itself may be reversed to become a separate catalytic contribution. UK industry experiments in which graphite was deliberately contaminated with various acetate salts found a non-zero intercept on a plot of 'graphite oxidation-rate enhancement' *versus* 'salt concentration' (*A.J. Wickham, personal communication).* [19] notes a similar effect with solutions of alkali-metal compounds upon spectroscopically-pure graphite: when small concentrations of sodium, potassium and borate were present *without* moisture, the oxidation rate of graphite at 900K increased by a factor of 4, but upon adding water to a mole fraction of 3×10^{-4}, *a further rate increase of* × *1.6 occurred.* Without the simultaneous presence of the alkali-metal ions and borate, a net *decrease* in rate of × 1.8 would have been expected.

The issue was still controversial in 1992 [21] when it was concluded that water exerts a detrimental and irreversible influence on the physical and chemical properties of various non-graphitic carbon materials.

Where large effects have been observed on carbonaceous materials, these are generally on so-called "active carbons" of very large internal surface area such that, for a given vapour-phase water concentration, large quantities of water would be available per unit mass of carbon. Such materials have accessible surface areas of order 100 $m^2.g^{-1}$ compared with values in the range 0.17-0.24 $m^2.g^{-1}$ for nuclear graphites. For conventional carbons, an early stage in the adsorption process is the formation of surface oxides [22]. However, graphite previously irradiated in either air or carbon dioxide is likely to be well furnished with surface oxides from the outset, so any large effect of a water incursion seems improbable.

For completeness we should note that Lang [23] provides a concise summary of the three stages of the interaction of water with graphite: first, reversible *physisorption*, where the mass of water absorbed per unit mass of graphite increases as the volume of the sample decreases and can exceed the amount capable of entering the open pores as a vapour *(i.e. multilayer absorption)*; secondly irreversible *chemisorption*, where the graphite surface is modified and the reactivity of the material is affected; finally, *oxidation*, which is extremely slow at temperatures below 973K. Generally, physisorption dominates below 378K and the quantity of water absorbed increases with increasing temperature. In the range 383-573K the quantity absorbed increases only slightly; above 573K there is decreasing absorption with the slow formation of reaction products (CO, H_2, CO_2 and CH_4) which increase when temperatures capable of giving significant rates of oxidation are reached (> about 973K). These observations build upon the classic work of Dubinin on absorption on active carbons [24].

Although the mechanistic consequences of the presence of water are not precisely explained, the possible magnitude of the effects on the rate of graphite oxidation in air (other than the direct washing in of catalytic contaminants) appears to be sufficiently small that it may be discounted as a significant contribution to the reactivity of graphite in comparison to the effects of the original reactor irradiation.

B.5. Criteria for Self-Sustaining Oxidation of Graphite

The essential concern for decommissioning activities is the possibility of initiating a self-sustaining graphite oxidation at some point in the decommissioning process, whether it be within the reactor vessel during dismantling, or at a subsequent storage stage.

Schweitzer, for many years a specialist in graphite oxidation and combustion chemistry at Brookhaven National Laboratory, New York State, USA, provides in [25] a "check-list" of conditions which must be satisfied *simultaneously* before "burning"[19] of graphite (which in *their* definition is a self-sustaining oxidation but *not necessarily with visible flame*) can exist:

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[19] Schweitzer unfortunately also uses this word out of context, although he is careful to define (in the bracketed section of the same sentence) what is really meant, and vindicates himself later in his paper with the following comment: *"There is a common perception taken from our experiences with coal and charcoal that when a mass of these fuels achieves a glowing red condition, a self-sustaining combustion is under way. Transferring the perception to graphite has led to repeated references to 'burning' graphite when, in fact, a self-sustaining reaction was not in progress. The test sequences described...........demonstrate how difficult it can be to achieve conditions for self-sustained combustion of graphite."*

1. a minimum temperature of 650ºC[20]
2. maintenance of this temperature either by heat of combustion or by some outside energy source
3. an adequate supply of air or oxygen
4. the gaseous oxidant source must flow at a rate capable of removing gaseous products but without excessive cooling of the graphite surface
5. a suitable configuration of graphite and oxidant *(a reactor channel was considered to be "suitable")*

Note that here, self-sustaining combustion would almost always require an artificially-sustained supply of air, without which the available oxygen would quickly become exhausted. Condition no. 2 is extremely difficult to achieve in what is a near-perfect black-body radiator whose combustion produces a negligible quantity of ash which could otherwise retain heat. Even irradiated graphite, when reheated to temperatures approaching 923K, exhibits reasonable thermal conductivity so that bulk components are further prevented from attaining combustion by this additional heat-removal mechanism.

Schweitzer describes experiments designed to support an operational life-extension for the 'N' reactor at Hanford (USA). Two oxy/acetylene torches delivering a combined 2.7×10^5 BTU.h^{-1} (78.3 kW) were allowed to impinge side-by-side upon one of the larger faces of a rectangular block of graphite approximately 15 × 15 × 40 cm supported across two hollow blocks (equivalent to the configuration of a Hanford fuel channel). After five minutes the surface temperature was estimated at 1000ºC and the region below the torches was glowing yellowish-white. After 57 minutes the surface temperature at the point of impact of the torches was estimated as 1650ºC and the entire graphite block was glowing red. The whole block was at >1025ºC. Small craters were produced below the flames.

At this point the acetylene to one torch was shut off, allowing pure oxygen to impinge on the graphite alongside the other flame which was maintained. *The jet of pure oxygen could not sustain an oxidation reaction in the red-hot graphite and the region below the nozzle cooled quickly.*

This is a most graphic illustration of the difficulty of so-called "burning" graphite, and has since been replicated in similar tests in the UK, Italy and France in support of their various decommissioning programmes.

<u>References to Appendix 2</u>

[1] Stairmand, J.W., "Graphite Oxidation – A Literature Survey"; AEA Technology plc Report AEA-FUS-83, 1990

[2] Walker P.L., Rusinko F. and Austin L.G., "Gas Reactions of Carbon"; Advances in Catalysis, 11, 1959, *pp.*123-221

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[20] In the absence of a catalyst.

[3] Wickham A.J., "Caring for the Graphite Cores"; Proc. I.Mech.E. Seminar on "The Review of Safety at Magnox Nuclear Installations", Thursday March 9th 1989, Institution of Mechanical Engineers (London), *pp.* 79-88[21]

[4] Hawtin P., Gibson, J.A., Murdoch R. and Lewis J.B., "The Effect of Diffusion and Bulk Gas Flow on the Thermal Oxidation of Nuclear Graphite: 1. Temperatures below 500ºC"; Carbon, 2, 1964, *pp.* 299-309

[5] Ong J.N. Jr, "On the Kinetics of Graphite Oxidation of Graphite", Carbon , 1964, **2**, *pp.* 281 – 297

[6] Okada J. and Ikegawa T, J. Appl. Phys, 1963, **24**, *pp.* 1249 *et seq.*

[7] Chi S.H., "Comparison of 3 MeV C^+ Ion Irradiation Effects in IG-110 and IG-430 of Different Filler Materials"; presentation at the 6th International Nuclear Graphite Specialists' Meeting, Chamonix, France, September 2005 *(presentations published on CD-ROM by SGL Carbon Ltd and available from the present authors)*

[8] Marsden B.J., Preston S.D., Wickham A.J. and Tyson A., "Evaluation of Graphite Safety Issues for the British Production Piles at Windscale: Graphite Sampling in Preparation for the Dismantling of Pile 1 and the Further Safe Storage of Pile 2"; Proceedings of a Technical Committee Meeting 'Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal' Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.*213-223

[9] Wilkinson V.J., Robinson P.J. and Lind R., "The Oxidation Characteristics of Windscale Pile 2 Graphite: An Estimate of Maximum Permissible Temperatures"; UKAEA Report IG 58 (RD/W), 1959 *(available through the UK Public Records Office)*

[10] McKee D.W., "The Catalysed Gasification Reactions of Carbon"; Chemistry and Physics of Carbon Series, 16, Marcel Dekker, 1981, *pp.* 1-118

[11] McKee D.W. and Chaterji D., "The Catalytic Behaviour of Alkali-Metal Carbonates and Oxides in Graphite Combustion Reactions"; Carbon, 13, 1975, *pp.* 381-390

[12] Cairns J.A., Keep C.W., Bishop H.E. and Terry S., "Controlled Atmosphere Electron Microscopy Observations and Identification of the Particles Responsible for the Catalytic Oxidation of Graphite"; J. Catalysis, 46, 1977, *pp.* 120-123

[13] Keep C.W. and Terry S., "The Observation and Identification of Catalytic Species Responsible for the Accelerated Oxidation of Reactor Graphite"; *UKAEA internal document*

[14] Amariglio H. and Duval X., "Étude de la Combustion Catalytique du Graphite"; Carbon, 4, 1966, *pp.* 623-635

---

[21] Note that the Figures are printed in the incorrect sequence relative to their captions in this publication.

[15] McKee D.W., “Metal Oxides as Catalysts for the Oxidation of Graphite”; Carbon, 8, 1970, *pp.* 623-635

[16] Sampath, S., Kulkarni N.K. and Chackraburtty D.M., “Influence of Selected Metal Oxides on the Oxidation Kinetics of Graphite”; Thermochimica Acta, 86, 1985, *pp.* 7-15

[17] Sampath S., Kulkarni N.K., Subramanian M.S. and Jayadevan N.C., “Effect of Lanthanaum, Neodymium, Thorium, Uranium and Plutonium Compounds on Graphite Oxidation”; Carbon, 26, 1988, *pp.* 129-137

[18] Arnold L., “Windscale 1957: Anatomy of a Nuclear Accident”; Macmillan 1992

[19] Lewis J.B., “Thermal Gas Reactions of Graphite”; *in* ‘Modern Aspects of Graphite Technology’ *ed.* Blakeman L.C.F., Academic Press, 1970 *pp.* 129-199

[20] Heuchamps C., Duval X. and Letort M., Comptes Rendus Hebd. Seanc. Acad. Sci. Paris, **260**, 1965, *pp.* 1657 *et seq.*

[21] Petit J.C. and Bahaddi Y., “Role of Water in the Ageing of Carbonaceous Materials”; Proceedings ‘Carbon ‘92’, Arbeitskreis Kohlenstoff der Deutschen Keramischen Gesellschaft e.V. 1992, *pp.* 253-255

[22] Smith R.N., Pierce C. and Joel C.D., “The Low-Temperature Reaction of Water with Carbon”; J.Phys.Chem., **58**, 1954, *pp.* 298-302

[23] Lang F.M. and Lafargue Y., “Study of the Action of Water on Graphite”; Proceedings of the Biennial Conference on Carbon, Chestnut Hill MA USA, 1969, American Carbon Society, *pp.* 125-126

[24] Dubinin M., “Structure and Properties of Active Carbons”; Chemistry and Physics of Carbon Series, **2**, *pp.* 51-120

[25] Schweitzer D.G., Gurinsky D.H., Kaplan E. and Sastre C, “A Safety Assessment of the Use of Graphite in Nuclear Reactors Licensed by the US Nuclear Regulatory Commission”; Brookhaven National Laboratory Report BNL-NUREG-52092, NUREG/CR-4981, 1987

C

APPENDIX C—FURTHER NUCLEAR INDUSTRY EVIDENCE ON GRAPHITE OXIDATION RESISTANCE

C.1. Recent Laboratory Research Conducted in the USA

Tests conducted in support of the extension of the operating life of the Hanford 'N' reactor have already been described at Appendix A2.5.

More recent tests on the combustibility of nuclear-grade H-451 graphite (a candidate graphite for the US modular HTR programme) were conducted at Los Alamos National Laboratory [1]. No combustion was achieved, and the author (Richards) opines that there is little evidence for combustion of graphite even in the Windscale Accident *("… … … oxidation occurred primarily with the metallic uranium fuel……..")* and at Chernobyl *("………heat removed by convection was predicted to be greater than heat generated by exothermic reaction of graphite with oxygen, and the dominant heat source causing the 'red glow' was the result of nuclear decay processes………")*. We address these specific accidents in detail in Appendix 4.

Richards' view on these crucial incidents was voiced two years earlier by Schweitzer in a contribution to an IAEA Specialists' Meeting on the response of gas-cooled reactor systems to accidental ingresses or air or water [2]. Both authors now concur that satisfying Schweitzer's criteria for self-sustaining combustion is both necessary and essentially unachievable in realistic situations.

C.2. SoGIN Work in Support of Decommissioning Latina NPP, Italy

Italian colleagues from SoGIN, in support of Latina Magnox-reactor decommissioning, have conducted a number of basic tests on both solid graphite and graphite dusts, including oil-soaked examples. Intense gas/oxygen flames have been allowed to impinge directly onto graphite blocks in a number of different geometries, in some cases with embedded thermocouples, for lengthy periods, and the results recorded on video. In no case was there any evidence of "burning", "combustion" or visible flames, and very slow and localised thermal transients were recorded[22]. Although these results have not been formally published, a comprehensive video record has been made available to the present authors[23].

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[22] In the case of irradiated graphite, the thermal transients would have been somewhat higher because of the reduced coefficient of thermal conductivity in irradiated material.

[23] The cooperation of Ing. Massimo Sturvi, formerly site manager, Latina, is gratefully acknowledged.

C.3. Work Conducted on Behalf of EdF, France[24]

The earliest work in this area by CEA is reported in [3]: *"……… the first experiment performed at CEA consisted of placing pieces of graphite into a coal stove. It did not burn………"*. This basic experiment was followed by more realistic tests performed at Cadarache, Marcoule and Saclay, along with German tests at a pilot-plant scale, they demonstrated the conventional incineration was possible, but was technically very difficult.

Some much more recent theoretical and literature-based studies have been conducted by the French INERIS organisation on behalf of EdF [4] INERIS confirm the absence of self-ignition risk at ambient temperature, even in the form of fine deposited dust. As for the possibility of an explosion in the context of the dismantling activities for a French UNGG (Magnox type) reactor, uncertainty remained with regard to the granulometry and composition of the dust, its required ignition energy, and available energy in case of an accident

CNPP therefore followed up the INERIS studies with new work [5]. Whilst much of this related to dust-explosion concerns, there is a description of heating what is described only as "a piece of graphite" in a muffle furnace, with the temperature raised from ambient to 1173K at a rate of between 3 and 4K.min^{-1}. Following this, a mass loss of 32% resulted. The phraseology used to discuss this experiment is unfortunate – "………*le graphite brûle mal lorsqu'il n'est pas très divisé*………" – "………the graphite burns poorly unless finely divided………" This was a poorly designed test on what has now been confirmed to be a very small piece of graphite with a correspondingly high surface-area-to-volume ratio. This fragment achieved a high degree of oxidation, which is not surprising given the length and temperature of exposure to air. CNPP, which had been asked by EdF to find out whether graphite *combustion* could produce soot (which it cannot), commented that none was found and, if it had formed, it would have burned completely at 1173K anyway.

More appropriate tests were then conducted with graphite cylinders. These were heated in four ways: (i) electrical heating with a current of 600 amps; (ii) an oxy-propane furnace at ~1123K; (iii) an oxy-acetylene torch; *and* (iv) a thermal lance, also at ~1123K. The following results were obtained:

(i) The electrical heating was applied to small cylinders 2.5 cm in length and 1 cm in diameter, clamped between two electrodes. Heating was continued until the electrodes fused (about 1773K). *"No trace of combustion appeared on the sample."*

(ii) A special concrete cell equipped with six oxy-propane burners was employed, with heating applied for approximately 90 minutes until the ambient furnace temperature was in excess of 1273K and the temperature at the centre of the graphite was ~1123K. The samples used in this study were solid cylinders approximately 60 cm long and 13.7 cm diameter, or hollow cylinders of similar overall dimensions and with a central bore 11 cm diameter. The samples, which bore other minor machined features, were unirradiated examples of various sleeve and core components from the UNGG reactors. Broadly, the results may be summarised as *"No visible combustion"*. It is almost certain that there was little oxidation either since the torch gases and their combustion products would have resulted in a considerable diminution of oxygen concentration within the cell

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[24] Permission to cite results from EdF studies has kindly been given by EdF-CIDEN, Lyon, France.

(iii) The oxy-acetylene flame test was similar to that of SoGIN. The flame temperature was estimated as between 1873-2073K. The flame was applied manually to the large graphite cylinders in the same cell as test (ii) and the result is *"The graphite did not suffer any combustion………Graphite does not burn"*.

(iv) A thermal lance consists of a steel tube packed with iron threads. The end is heated with an external torch and the oxidation of iron is then sustained by high-pressure oxygen passed through the tube. This enables temperatures of order 2273-2673K to be reached, and this device was used to bore holes directly through the large graphite cylinders. Again the temperature of the graphite cylinders reached about 1123K at the point of measurement, and the lance was then left within the graphite for some time. Although the graphite became covered with metal splinters, CNPP again concluded that *"………even after a meticulous examination, no propagation of the combustion is evident………"*

Thus, the overall conclusion of this CNPP work is that it is impossible to achieve "combustion" of the graphite: no flame was seen in any of the four kinds of test, even when the graphite glowed red or white hot. Unfortunately, this work offers no quantitative measure of the degree of *oxidation* achieved in the various components. However, the subjective observations of the state of the samples after their various treatments suggests that the mass loss was quite low.

The most important derivative of their conclusions is that it is highly improbable that graphite can present a combustion or oxidation hazard during decommissioning activities: this does not preclude the possibility of incineration in a suitably designed plant which enables the Schweitzer criteria to be satisfied.

C.4. UK Observations

C.4.1. Support for Flame Cutting Operations in Magnox Reactors

A number of basic studies of the potential for combustion of graphite were made at the time of the decision to use flame cutting in the Bradwell reactors (UK Magnox) to remove components known as latch rings and clamp tubes from fuel standpipes because of metal corrosion, and these have been reviewed in the context of decommissioning the Latina Magnox reactor [6].

Both unirradiated and irradiated bulk graphite samples of Pile Grade 'A' graphite were subjected to directly impinging oxy-acetylene flames, with some samples especially shaped to reduce the effect of thermal conductivity. Samples were also subjected to the full efflux from plasma-cutting operations in both air and CO_2 atmospheres for a sustained period. Some samples were also deliberately contaminated with flammable Magnox metal shavings.

In no case was any combustion or ignition possible, and oxidation was limited to that predictable from the data provided in the body of this report.

C.4.2. GLEEP Graphite

In the UK, UKAEA has dismantled the graphite stack from the very-low-irradiation GLEEP reactor at Harwell [7]. The irradiation was sufficiently low that it was possible to conduct this work under "contact-handleable" conditions. In order to reduce the quantities of ^{3}H and ^{14}C in the waste graphite presented for storage, it was decided to calcine the blocks (initially as whole blocks but subsequently milled into small lumps to increase the surface area) in an industrial incinerator which is licensed for the discharge of small amounts of radioactivity. It has been found that a treatment of whole blocks, at 1423K for around 3 hours in the presence of a forced air supply and other miscellaneous industrial waste items, is capable of mobilising typically 87% of the ^{3}H and around 63% of the ^{14}C, and thus represents an extremely useful reduction in the quantities of these isotopes in the graphite as presented for disposal as radwaste.

It was noted that the blocks returned from the incinerator showed little effect of oxidation other than some scarring on the geometrical surfaces. This damage is understandable given that the blocks were tumbled within the incinerator for three hours along with unidentified waste items. At the present authors' request, a returned block currently on exhibition at Harwell was weighed and compared with the average weight of an untreated block, which is around 41kg. The returned block weighed around 40.5kg.

Whilst this is a very crude measurement, it is very instructive. An individual intact block of GLEEP graphite, exposed at 1423K for three hours in a forced air supply (albeit with unknown depletion of oxygen within the incinerator), probably suffered no more than about 1.2% weight loss. Even if this weight loss was evenly distributed through the block, it would result only in about 6% reduction in net strength which, from the decommissioning stability point of view, could only be of significance in reactors which have already suffered a high degree of radiolytic weight loss in service. If, as is more likely, most of the weight loss was confined to the geometrical surface with "Modes 2 or 3" conditions limiting significant oxidation within the depths of the open pore structure, then a higher proportion still of the original strength in the block would have been retained.

The observation of low weight loss is also interesting in the context of the ^{14}C mobilised, since this is not lost primarily through oxidation and only a small amount of that formed from ^{13}C in the solid matrix could be removed through isotope exchange with atmospheric carbon dioxide with a diffusion gradient through the solid graphite. This indicates that the majority of ^{14}C in these GLEEP blocks resides on the surface in the form of sooty deposits derived from atmospheric $^{14}N_2$.

<u>References to Appendix 3</u>

[1] Richards M.B., "Combustibility of High-Purity Nuclear-Grade Graphite"; Proc. 22nd Biennial Conference on Carbon, San Diego, 16th – 21st July 1995, American Carbon Society, *pp.* 598-599

[2] Schweitzer D.G., "Experimental Results of Air Ingress in Heated Graphite Channels: A Summary of American Analyses of the Windscale and Chernobyl Accidents"; Proceedings of an IAEA Technical Committee Meeting on "Response of Fuel, Fuel Elements and Gas-Cooled Reactor Cores under Accidental Air or Water Ingress Conditions", Beijing, China, 25th – 27th October 1993, IAEA-TECDOC-784, *pp.* 50-54

[3] (Authors not identified) “Destruction by Incineration of the Moderator Graphite of UNGG Reactors: Dismantling”; CEA Institute of Protection and Nuclear Safety, Department of Protection (Technical Section for Research on Pollution in the Atmosphere and in Mines), CEA_Technicatome Contract TEC-302, Dec. 1978 (available as Pacific Northwest Laboratories Unclassified Translation PNL-TR-455, 1985)

[4] CNPP *(Centre National de Prévention et de Protection)*: “Première Campagne: Approche Expérimentale – Résultats de Programme d’Essais Graphite EDF-CIDEN”; CNPP Rapport No. PE 03 6570, 2004

[5] Gardiner D. and Bellard G., BNFL Internal Document prepared for SoGIN, Italy *(used with permission)*

[6] Bradbury D., Mason J.B., Wickham A.J., Buffery J. and Fachinger J., “Pyrolysis/Steam Reforming and its Potential Use in Graphite Disposal”; Proc. 3rd EPRI International Decommissioning and Radioactive Waste Workshop, October 25th-29th 2004, Lyon, France

[7] INERIS, “Étude de Risque Incindie-Explosion Lié at Graphite: Caractérisation du Graphite”; Final Report 14th November 2000

D

APPENDIX D—INTERPRETATION OF SPECIFIC ACCIDENTS IN GRAPHIC-MODERATED REACTORS

D.1. The Windscale Pile 1 Fire, 1957

This major reactor accident has often been described as a graphite ‘fire’, and this has often been publicly reported as the cause of the accident. That there was a fire is not in question but, in the light of the foregoing analysis of graphite-oxidation behaviour, it is important to re-visit the incident and to determine how the events described equate with this knowledge.

The Windscale Piles were air-cooled graphite stacks containing horizontal fuel channels with aluminium-clad uranium metal fuel elements. Charging of fuel channels was carried out from the front face of the reactor, with the most irradiated fuel being pushed out of the back of the channel as result and falling into special skips within a water-filled trough. Additional narrow horizontal channels were used for the irradiation of cartridges for the production of various isotopes.

A comprehensive and candid account of the events, including the reactor operating histories before it occurred, and the subsequent investigations, is given in [1], a book commissioned by UKAEA and published some 35 years after the accident.

The early history of the Windscale Piles was by no means trouble free. For example, a re-design of the graphite “boat” supporting the fuel cartridge was necessary after it was discovered that over 140 elements of the original design had worked their way out of the horizontal fuel channels under the pressure of the cooling air, and were hanging out of the back of the core in various attitudes.

However, a more serious problem, first encountered in Pile 2 in May 1952 and quickly followed by a similar event in Pile 1, was an unexplained temperature rise in part of the core which was then controlled by increasing the cooling air flow.

These heating events proved to be uncontrolled releases of Wigner energy, whereby regions of the core had heated to around 50K above their previous irradiation temperature due to changed operating parameters or fuel configurations, and were then able to release some part of their accumulated energy introduced to the graphite crystal structure by fast-neutron damage. This led to self-heating and, it was quickly realised, to a potential runaway liberation of heat if the rate of release per unit temperature rise exceeded the specific heat capacity of the graphite. As a result of this, deliberate anneals of Wigner energy were commenced in January 1953, whereby Pile 2 was re-started at limited power but with even more limited cooling. After a significant temperature increase, which was contained, the Pile was shut down and allowed to cool before being started again under “normal” conditions.

It was noticed that the anneals became less effective with time, and more difficult to control. It is now known that this arose because the repeated thermal cycles, whilst liberating some of the energy by allowing displaced atoms and vacancies in the graphite structure to return to their "correct" positions, were also transferring some displaced atoms to more stable higher-energy locations from which it then became more difficult to remove them. The operators were greatly concerned by this, since they realised that this could imply a continual build-up of Wigner energy which could eventually lead to an uncontrollable runaway in temperature.

A separate problem was also occurring. Burst fuel cartridges were a regular occurrence during early operation, and the consequent exposure of uranium metal to air implied the possibility of a fire. It was also found that fuel cartridges were jamming the in the burst-cartridge scanning gear at the discharge face after falling on to it, and in many cases the resulting damage also led to the potential exposure of uranium.

The significant events leading up to the Pile-1 accident started on Monday 7th October 1957 with a planned Wigner release which was less successful than expected. After an initial shutdown, it was decided to re-start the anneal, which continued uneventfully over the following two days until the target graphite temperature had been reached. The operators then took the normal measures to arrest the temperature rise, which was to permit a gentle flow of air through the core using the shutdown fan dampers. Initially this was successful, but temperatures then began to rise again. A further period of air cooling was ordered.

By this time the radioactivity release *via* the stack was increasing. By Thursday 10th October, the continuing increases in temperature could not be retarded by applying the maximum permitted air cooling. There were further increases in radioactive emissions. A visual examination was made of the channels giving high temperature and activity signals, and found them to be glowing red hot.

From this point on, the status of the core has frequently been described as a "fire", and *interpreted* as a graphite fire. Flames were seen emerging from the discharge face of the group of channels subsequently identified as the "fire-affected zone" ("FAZ"), whilst temperatures in excess of 1473K were recorded on fuel-cartridge thermocouples.

It was realised that the "cooling" air was increasing the supply of oxygen to the hot zone, encouraging additional oxidation within the graphite and fuel elements. Efforts were made to remove fuel manually with push-rods from the charge face.

A decision was finally taken to introduce water into the affected channels, although the attendant risk from an explosion in the hydrogen-rich 'water gas' likely to be formed was recognised. After one hour of water injection there had been little effect, and it was only after the shutdown cooling fans were turned off[25] that there was a dramatic reduction in the intensity of the heated zone. In some three hours, the immediate incident was over.

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[25] They had been left on in order to maintain tolerable working conditions at the charge face and to keep the bio-shield cool.

It is extremely important to consider what was actually reported at the time of the incident. There is, apparently, little doubt that the graphite in the FAZ was at least at red heat. A memorandum by J. Hill [2] written four months after the accident makes this very clear[26]:

"………when the charge plugs were first removed and the red hot uranium was discovered, there was no apparent centre to the fire but rather we had a large area of the pile, perhaps ten feet by eight feet, over which all channels were very nearly at the same red-hot temperature. At the edge of this zone, the temperature fell very rapidly over perhaps a distance of two pitches from being red hot to quite undamaged………"

This description clearly reflects the graphite temperature but does not imply any graphite "fire". No record has been found, either in the detailed compilation in [1] or elsewhere, of flames being reported in channels viewed from the charge-face end. The only flames reported were at the exit of the channels at the discharge face. We know that the cooling air supply was sustaining an oxidation reaction, and it is reasonable to assume that this includes the graphite as well as fuel or isotope cartridges which were involved. The graphite was almost certainly oxidising to carbon monoxide in admixture with carbon dioxide, and at the temperature of the exit of the affected channels, into the discharge void with a plentiful air supply, it is unsurprising that ignition of the carbon monoxide would have occurred. There is nothing reported which conflicts with the basic understanding of the graphite-oxidation behaviour reviewed earlier in detail.

There was then a significant dispute between the UK specialists and those from the USA who showed understandable concern about the potential threat to their own graphite-moderated plant. In particular, Schweitzer concerned himself with a justification for the continued operation of the air-cooled Brookhaven pile, and became extremely critical of the UK analysis of the Windscale accident. He produced an eloquent series of papers [4 - 8] examining the thermal stability of an empty graphite channel cooled by air and concluded that there was only a small region of thermal equilibrium. Ahead of this region heat is removed from the graphite, whilst beyond it, excess heat is generated, much of it *from the combustion of carbon monoxide*. Remember that this analysis is of the situation in the absence of any contribution from damaged fuel or isotope cartridges.

This contrasted strongly with the British view [9] which made an *assumption* that thermal equilibrium between heat removal and graphite oxidation occurred along large lengths of the channel. This led Schweitzer to comment on the UK work:

"………(their) model involves calculations that are very sensitive to ill-defined values and are subject to large errors………the use of these calculations indicates that their application to our [Brookhaven] work, the previous [UK] work, or a real reactor system, is of doubtful significance………"

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[26] However, caution is necessary. [3] includes a witness statement to the Court of Inquiry from an operator who claims to have seen glowing fuel cartridges at 1700h on the Thursday whilst ***"……the graphite surrounding the fuel appeared its normal black colour."*** Whilst this discrepancy is curious, if this witness is correct then the graphite was at a lower temperature anyway than has been thought and the residual graphite in the FAZ will presumably be greater, and stronger.

Even after 48 years have elapsed since the Windscale accident, no fully agreed position has emerged even about the initiating event, and significant uncertainties remain. Some specialists blamed a failed fuel element, others a failed lithium-magnesium isotope cartridge, and some preferred to blame the graphite, or at least the release of Wigner energy from it. The formal UK government enquiry report [10] stated that the over-rapid generation of heat from Wigner energy release in the graphite caused the failure of one of more fuel cartridges, whose contents then oxidised slowly leading to the "fire" in the reactor. It was suggested that the exposed uranium had smouldered throughout 9th October leading to additional failures in other cartridges, to their combustion, and then "*to the combustion of the graphite*". Here we must differ from this view, given the now much improved understanding of graphite oxidation and the extreme difficulty of initiating true combustion in it.

Later work suggested a more significant role for isotope cartridges in the incident, bearing in mind that magnesium (present in numerous cartridges) will, like uranium, burn in nitrogen as well as oxygen. Ref [2] comments forcefully that the sharp eutectic at 703K in the "AM" cartridges, implying a risk of sudden failure above this temperature, was a critical factor in determining the extent of the FAZ.

These later considerations also included the possibility that heat from graphite oxidation as well as from Wigner-energy release, had contributed to the propagation of the "fire". Schweitzer repeated his contention about the extreme difficulty of burning graphite, despite the apparent "evidence" of the Windscale accident, as recently as 1993 [11].

It is also relevant to consider the visual evidence of the state of channels just above the FAZ, obtained very recently as part of the planning for decommissioning [12]. Numerous incidences were observed where extremely hot fuel had been in contact with the graphite channel walls, leading to "scorch marks" on the channel wall suggestive of the deposition of metal oxides, but with only limited graphite weight loss (as assessed visually) and no evidence of friable material.

In one instance, however, evidence has been found of complete oxidation of the graphite. Although the fuel channels are horizontal, there are a small number of vertical channels for safety shut-down rods and others known as 'foil holes'. During examination of one fuel channel above the FAZ it was observed that the thin section of graphite between the fuel channel and the adjacent safety shut-down channel was absent, allowing the shut-down rod to be viewed from the fuel channel. It is considered that the vertical channel behaved as a chimney, allowing very hot gases from the FAZ to rise higher in the core and thus to facilitate a high rate of oxidation of the graphite, sufficient to break through into the fuel channel. Once a route had been established, additional oxidation occurred, widening the orifice. Within a few centimetres of the hole itself, however, presumably where the direct heating was less, the visual evidence suggests that the graphite weight loss itself is quite small. It is thought that the efficient heat conduction within the graphite itself meant that the graphite was always cooler than the gas at this point and that oxidation away from the actual gas pathway was minimal. There is no visual evidence of any "fire".

The present authors conclude that the overwhelming body of evidence serves to confirm that graphite never "burned" as such in the Windscale incident, but merely oxidised as one would predict at the very high temperatures reached, with carbon monoxide being prominent in the oxidation products as a result of a restricted supply of oxygen in comparison to the potential demand predicted from the lower-temperature Arrhenius rate equation – in other words, in "Mode 3".

However, it is probable that, at least for a part of the time, the "Schweitzer Criteria" for a self-sustaining graphite oxidation state, which were discussed in Section 6.1, were simultaneously satisfied as follows:

1. graphite temperature was in excess of 923K;
2. this temperature was maintained by Wigner release and by the combustion of fuel- and isotope-cartridge materials;
3. forced air circulation from shut-down fans took place for a significant time;
4. air circulation was nonetheless overall at a limited rate so that combustion-product gases were removed without excessive cooling effect;
5. reactor channels were a "suitable" configuration.

It is useful to mention a totally independent study of the Windscale accident conducted by Wichner and Ball of the Oak Ridge National Laboratory in the USA in support of the development of a general severe-accident code applicable to gas-cooled graphite-moderated reactors. The code is known as GRSAC (Graphite Reactor Severe Accident Code), and it is comprehensively documented in [3]. One of the present authors (AJW) was peripherally involved in the acquisition of data to assist in the validation of GRSAC against UK reactor systems.

We concern ourselves here only with the issues specific to graphite behaviour, but it is worthy of note that the GRSAC authors identify a potential source of heating within the FAZ which does not seem to have been considered in the various UK studies and reports of the accident (nor in the earlier US commentary either). This is exothermic oxidation of the aluminium fuel cladding, commencing at around 913K, and considered to be *"a powerful route for propagating the fire to the uranium"* which does not contribute significant heat itself until a temperature of roughly 1073K is reached.

The Oak Ridge study also considers that a failed AM (lithium-magnesium) cartridge was the initiating event, based upon consideration of the metallurgy of the various components in the core. Ref [2] notes that *"The AM cartridges have a very sharp eutectic at 436ºC [709K], and the extreme temperature dependence of the integrity of these cartridges leads me to believe that they were the principal factors in determining the extent of the fire zone."* Wichner and Ball comment that lithium is the "most combustible" material in the core and would be exposed following failure of the aluminium cladding at around 709K.

It is not appropriate here to describe the GRSAC model in detail. It is however important to understand that the GRSAC team, whilst making a very thorough study of the documented evidence about the Windscale Pile-1 incident, made many assumptions about the situation before and during the incident. Some of these assumptions appear reasonable and others, with hindsight, less so. As an example, they derived a rate law for the graphite oxidation which attempted to combine Mode I kinetics with a Mode-II type variation in attack rate with depth into the graphite blocks. Overall, the assumed scenario appears to be highly pessimistic, although the Oak Ridge authors do comment that the balance between a containable temperature excursion during the Wigner anneal and the loss of control which actually occurred was very fine.

More recently, a detailed study has been undertaken for UKAEA [13, 14] to assess the most probable extent of graphite weight loss in the FAZ, where it has previously been suggested on the basis of exaggerated perceptions of graphite behaviour that there might be a cavity within the graphite stack. Using the best-available current understanding of air flows around the core during the accident, including an assessment of the chimney draught under various conditions of damper settings, together with a careful application of the graphite-oxidation behaviour based upon available air supply during the highest-temperature phase of the accident, it is concluded that a pessimistic estimate of average graphite loss within this defined zone would be around 21%, with peak losses of up to 35% in the most affected blocks. These assessments were also supported by analysis of recent visual examinations in accessible channels above the FAZ and of the state of the channel exits from the FAZ region, and are consistent with the current view that no specific 'graphite fire' occurred during the accident.

D.2. Chernobyl Unit 4, 1986

The major accident of 26th April 1986 resulted in the destruction of the reactor core and large parts of the building in which it was housed. Within a short time of the accident, many articles appeared commenting on aspects of the incident, in many cases before the scenario had been fully assessed. Comments about the presence of graphite and its consequences were frequently made, even by quite senior people in respected organisations, without full verification or explanation. For example, Gary Vine of the Nuclear Safety Analysis Center at EPRI, a senior physicist but one whose experience lies primarily in submarine reactors, was quoted *"........the fact that the reactor's massive graphite core can burn in the presence of oxygen increases the potential seriousness of an accident........."* [15].

The underlying causes of the Chernobyl disaster, insofar as they have significance for other graphite-moderated reactors, are important. The official IAEA Summary Report [16] is very clear about the immediate consequences of the reactor instability:

1. the extreme power build-up led to an explosion with some materials ejected;
2. a second explosion occurred with fuel and graphite ejected *(there remains some dispute about the cause of this second explosion)*;
3. graphite blocks and fuel fragments were found outside the buildings, which were themselves severely damaged;
4. the crane and refuelling machine collapsed and the upper reactor plate was lifted into an upright position;
5. all channels were ruptured and the chain reaction stopped.

Specialists in the UK were quick to recognise the nature of the accident sequence and to evaluate its consequences, and these were discussed at a special meeting of the British Nuclear Energy Society in London. Young [17] discussed the accident primarily from the viewpoint of the reactor physics, but he noted that around 25% of the graphite blocks were ejected from the reactor and about 10% of the total graphite was consumed in the "fire". There is certainly no doubt that this quantity of material was lost through oxidation. The contribution of NNC Ltd to the BNES Meeting [18] notes *inter alia* that the graphite temperature in the reactor before the incident was *"………probably unacceptably high………"* (in comparison with basic safeguards against air ingress to the graphite stack).

We can also note that there was a large cavity beneath the reactor through which additional air was drawn into the damaged core (principally by convection) immediately following its disruption. This would of course exacerbate the situation.

Ref. [16] is potentially misleading through the use of imprecise words in relation to graphite behaviour. The report discusses the fire-fighting activities and repeatedly refers to *"………burning graphite blocks………"* and *"………the graphite fire………"* Most of the actual fires involving graphite which were approached by fire-fighters involved ejected material on bitumen-covered roofs, and the fires also involved the bitumen. It is stated: *"The fire teams experienced no unusual problems in using their fire-fighting techniques, except that it took a considerable time to extinguish the graphite fire."* These descriptions are not consistent with the later considered opinions of senior Russian specialists, which are discussed below. There is however no question that extremely hot graphite was ejected from the core and at a temperature sufficient to ignite adjacent combustible materials.

The observations of the late Academician Valeriy Alekseevich Legasov, who described in the newspaper 'Pravda' the appearance of the site from the air on the night of the accident [19], reveal other features of the explosion and fire. He describes the crimson glow visible from 8 – 10 kilometres with a column of white combustion products rising several hundred metres into the sky from the core. Legasov describes this "white smoke" as the products of graphite combustion, but this cannot be correct as the products of graphite oxidation are colourless gases and only a tiny amount of ash arising from impurities. Indeed, he continues, in the Pravda article, to express the view that it was not possible to determine whether the red glow simply indicated very hot graphite or an actual fire. He stresses twice that the colour in the sky was reflected from glowing graphite.

The presence in the plume of white dust strongly suggests the combustion or disintegration of fuel and fuel cladding rather than a graphite reaction - zirconium will burn in both oxygen and nitrogen at high temperature to give a white oxide - or perhaps, of reaction between fuel materials and graphite, changing the chemical form of the material. Legasov later refers to an unattributed "combustion speed" of graphite of 1 tonne per hour, but it is unclear what this means, nor how it could be justified.

Notes of a discussion in 1987 [20] between L.P. Leach of UNC Resources at Richland WA, USA, and Yevgeny Adamov, a robotics engineer closely concerned with the Chernobyl incident, quotes Adamov as saying *"I have never seen graphite burn."* Adamov comments that *"noisy experts"* were saying the graphite was on fire whilst *"quiet experts"* disagreed but were not reported. Adamov insisted that the decay heat was responsible for heating the core, and not a fire.

Published visual records and film of the damaged reactor show a red glow rather than flames, signifying extremely hot graphite but not necessarily burning graphite. One recent report places the glow some 15 metres away from the core vault itself, on the floor of the 'central hall' and claims that, as a consequence, its true identity has not been established [21]. This reference claims that, as a result of this mis-location, the 5000 tonnes of dolomite, clay, sand, boron carbide and lead dropped into the glowing mass from the air had little effect on the reactor vault itself and hence on the outcome of the accident.

The dolomite was intended to produce CO_2 and so to extinguish any fire; the boron carbide to insure against re-criticality; the clay and sand to blanket radioactivity releases and to provide a thermal blanket to quench the fire; and the lead was intended to melt and solidify later to seal and shield the core. There is some question about the chemical nature of this lead: Ref [16] states that *"2400 tonnes of lead"* were used whereas Ref [21] cites a Moscow Radio report that 700 tonnes of *red lead* (*i.e.* lead oxide) were trucked in. However, other comments in Ref [21] are poorly researched and it is considered here that this source should be regarded as unreliable. For example, a statement that *"graphite is known to burn for long periods"* is not only factually incorrect, but is attributed to a UK journal on *economics*.

In fact, the addition of lead or lead oxide may have had a dramatic effect on the outcome of the incident, including the initiation of the reported 'second peak' in radioactivity releases which has not been consistently explained. It has already been noted in Appendix A2.3.2.3 that lead in certain chemical forms is a powerful catalyst for graphite oxidation, and one of the present authors (AJW), along with senior CEGB personnel, analysed in some detail the possibility that the addition of lead or lead oxide could have encouraged renewed oxidation of the graphite which came into contact with it. Bearing in mind the limitations on oxidation rate through access of air when very high rates are predicted at high temperatures (Modes II and III), such catalysis by lead would have had the most significant effect when the graphite temperature had fallen, perhaps to around 800K, resulting in the oxidation of graphite being sustained when it would otherwise have fallen away rapidly with declining temperature, and possibly explaining the renewed activity release. However, this hypothesis was not accepted by Russian specialists.

An extremely detailed and comprehensive analysis of the graphite behaviour in the Chernobyl accident has been conducted by specialists from the Kurchatov Institute in Moscow. This was presented to a meeting of interested UK specialists in July 1995 by the late F. Zherdev, one of the scientists who entered the chambers beneath the damaged reactor in search of definitive evidence of the course of events[27]. Lecture notes and copies of overheads used in this presentation are available [22] together with a paper in English translated in the UK from an unidentified Russian publication.

Zherdev described how fragments of graphite found on the roof of adjacent buildings were fused into the bitumen waterproofing, and that larger fragments which had fallen on to steel surfaces became 'welded' to the steel. He considered that this represented the formation of 'pig iron' – a process that requires a temperature in excess of 1270K. Eyewitnesses had said that small pieces of graphite were still glowing 20 minutes after the explosion. Examination of recovered graphite fragments revealed a wide range of oxidation ranging from insignificant surface oxidation to almost 100%.

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[27] Zherdev subsequently died as a result of the radiation dose from this investigation.

The Kurchatov team attempted an assessment of graphite temperatures from a retrospective analysis of the fragments. It was assumed that the initial temperature had been 573K, and the irradiation history prior to the incident was taken into account to assess graphite properties prior to the incident. Using these pieces of information, some attempts were also made to relate fragments to their original position in the core.

Two basic techniques were employed for the assessment of temperature: (i) a study of the change in electrical conductivity resulting from the high-temperature annealing, and (ii) analysis of the behaviour of fission products within the graphite (mainly ^{134}Cs and ^{137}Cs).

The analyses of electrical conductivity implied that the samples had seen temperatures in excess of 1273K. The second method, which assumed that the isotopes arose through caesium from the fuel impregnating the graphite at the moment of the explosion by thermo-diffusion, transpiration or shock-wave intrusion, was rather less precise, and yielded temperature estimates of the order 1073-1773K.

Zherdev drew a personal conclusion from this work that the accepted scenario of the accident was in error. He stated that the cause of the secondary explosion could not have been the detonation of an oxygen/hydrogen mixture within the reactor vessel. Instead, after the initiating fuel explosion had caused loss of feed water cooling, the graphite temperature rose to around 1473K at which a nuclear reaction based upon the plutonium inventory accelerated into a nuclear explosion. Although he stated that this hypothesis had been confirmed in 1992, it does not appear in the paper apparently presented for publication [22], and other authors (*e.g.* [23]) deny the possibility.

Answering questions, Zherdev stated explicitly that the ejected graphite had been observed to be glowing rather than burning, and this observation is also credited to witnesses and fire-fighters in [22]. The hot graphite ignited adjacent materials, and in particular the bitumen roof sealant.

In [11], Schweitzer comments on the Chernobyl accident as follows: *"………graphite burned for many days supported by asphalt fires and decay heat from the buried fuel. Soviet teams tried to put out the fires by dropping massive amounts of material from helicopters. The attempts were not successful, presumably because the dropped materials insulated hot debris. Eventually liquid nitrogen was used to cool and inert the burning debris………"*

It is the present authors' opinion that the word *"oxidised"* should replace the word *"burned"*, and that the decay heat rather than a self-sustaining exothermicity of graphite was responsible for maintaining the oxidation.

Finally, the comments of Richards at Los Alamos [24] on Chernobyl are that:

"………heat removal by convection was predicted to be greater than heat generated by exothermic reactions of graphite with oxygen, and the dominant heat source causing the 'red glow' was the result of nuclear decay processes………"

In summary, there is no doubt that graphite reached exceedingly high temperatures: the evidence about ‘burning’ graphite is rather contradictory but it is considered that this arises from the imprecise use of words, especially in translation. The visual evidence *never* reports graphite in flames, but only glowing hot and subsequently cooling down although exposed to the atmosphere. Certainly there was no self-sustaining combustion once the graphite had been ejected from the core.

It is the view of this author that the graphite behaviour in the Chernobyl disaster remained consistent with the Schweitzer criteria of Section 6.1. There was self-sustaining oxidation at the moment of destruction of the core, when first exposed to air. The necessary conditions were:

1. a temperature greatly in excess of 923K;
2. a large energy source (over criticality);
3. adequate oxygen supply (as core disintegrated);
4. gaseous products easily lost to atmosphere; *and*
5. a suitable configuration for graphite and oxidant.

However, from the moment of disintegration, these criteria were *not* fully satisfied, since:

1. the temperature was not maintained in ejected materials;
2. the heat of combustion alone was insufficient to prevent cooling of isolated ejected graphite blocks;
3. the ‘configuration’ was no longer favourable and so ejected blocks cooled, although temperatures remained sufficiently high to start fires in adjacent combustible materials.

References to Appendix 4

[1] Arnold L., “Windscale 1957: Anatomy of a Nuclear Accident”; Macmillan, 1992

[2] Hill J.M., “A More Detailed Assessment of the Early Stages of the Windscale Fire”; memorandum to Sir Leonard Owen, Jan 17th 1958

[3] Wichner R.P. and Ball S.J., “Potential Damage to Gas-Cooled Graphite Reactors Due to Severe Accidents”; Oak Ridge National Laboratory Report ORNL/TM-13661, April 1999

[4] Schweitzer D.G., Hrabak G.C. and Singer R.M., “Oxidation and Heat-Transfer Studies in Graphite Channels. I. The Effect of Air Flow Rate on the C-O_2 and CO-O_2 Reactions”; Nuclear Science and Engineering, **12**, 1962, *pp.* 30-45

[5] Schweitzer D.G. and Gurinsky D.H., “Oxidation and Heat-Transfer Studies in Graphite Channels. II. Thermal Changes with Time and Distance in Air-Cooled Graphite Channels”; Nuclear Science and Engineering, **12**, 1962, *pp.* 46-50

[6] Schweitzer D.G. and Singer R.M., "Oxidation and Heat-Transfer Studies in Graphite Channels. III. The Chemical Reactivity of BNL Graphite and its Effect on the Length of Channel Cooled by Air"; Nuclear Science and Engineering, **12**, 1962, *pp.* 51-58

[7] Schweitzer D.G., "Oxidation and Heat-Transfer Studies in Graphite Channels. IV. Combined Effects of Temperature, Flow Rate, Diameter and Chemical Reactivity on the Length of Channel Cooled by Air"; Nuclear Science and Engineering, **12**, *pp.* 59-72

[8] Schweitzer D.G., "Oxidation and Heat-Transfer Studies in Graphite Channels. V. Thermal Properties of Air-Cooled Graphite Channels"; Proc. Fifth Conference on Carbon, Pergamon Press, 1962, *pp.* 241-246

[9] Robinson P.J. and Taylor J.C., "Thermal Instability due to Oxidation of a Graphite Channel Carrying an Air Flow"; Proc. of the US/UK Meeting on "The Compatibility Problems of Gas-Cooled Reactors", TID 7597, 1961

[10] Cmnd. 302, "Accident at Windscale No. 1 Pile on 10th October 1957"; HMSO London, 1957

[11] Schweitzer D.G., "Experimental Results of Air Ingress in Heated Graphite Channels: A Summary of American Analyses of the Windscale and Chernobyl Accidents"; Proceedings of an IAEA Technical Committee Meeting on "Response of Fuel, Fuel Elements and Gas-Cooled Reactor Cores under Accidental Air or Water Ingress Conditions", Beijing, China, 25th – 27th October 1993, IAEA-TECDOC-784, *pp.* 50-54

[12] Marsden B.J., Preston S.D., Wickham A.J. and Tyson A., "Evaluation of Graphite Safety Issues for the British Production Piles at Windscale: Graphite Sampling in Preparation for the Dismantling of Pile 1 and the Further Safe Storage of Pile 2"; Proceedings of a Technical Committee Meeting 'Technologies for Gas-Cooled Reactor Decommissioning, Fuel Storage and Waste Disposal' Jülich, Germany, September 1998, IAEA-TECDOC-1043, 1998, *pp.*213-223

[13] Wickham A.J. and Ingamells W., "The Oxidation Characteristics of Nuclear Graphite Components and Dusts: Separating Fact from Fiction for Decommissioning"; Proc. 3rd EPRI International Decommissioning and Radioactive-Waste Workshop, 25th-29th October 2004, Lyon, France

[14] Wickham A.J. and Ingamells W., "Evaluation of the Condition of Graphite in the Fire-Damaged Zone of Windscale Pile No. 1"; Proc. CESEP'05, 1st International Conference on 'Carbon for Energy Storage and Environment Protection', Orléans, France, October 3rd – 6th, 2005

[15] Moore T. and Dietrich D., "Chernobyl and its Legacy"; EPRI Journal, June 1987, *pp.* 4-21

[16] International Nuclear Safety Advisory Group, "Summary Report on the Post-Accident Review Meeting on the Chernobyl Accident"; Safety Series No. 75-INSAG-1, IAEA, 1986

[17] Young, J, "Chernobyl: The Accident Sequence"; *in* "Chernobyl: A Technical Appraisal": the Proceedings of a Seminar organised by The British Nuclear Energy Society, London, October 3rd 1986, pub. BNES 1987, *pp.* 27-41

[18] Smith D.R., Luckhurst D.P. and Maccabee A.R., "Design and Control Characteristics of the RBMK Reactor"; *in* "Chernobyl: A Technical Appraisal": the Proceedings of a Seminar organised by The British Nuclear Energy Society, London, October 3rd 1986, pub. BNES 1987, *pp.* 3-25

[19] Legasov V.A., *reported in* Pravda, Moscow, 20th May 1988, pages 3 and 8

[20] Leary L.P., Notes on "Chernobyl – Discussion with Soviet Engineers"; UNC Resources Internal Note 3rd April 1987

[21] Sich A.R., "The Chernobyl Active Phase – Why The Official View is Wrong"; Nuclear Engineering International, April 1996, *pp.* 22-25

[22] Platanov P.A., Karphukin V.I., Zherdev F.F., Markushev V.M. and Bespalov V.N., "Evaluation of the Temperature of Constructional Elements in the Core of a Malfunctioning Reactor at the Moment of Explosion"; BNFL translation (1995) of an (unidentified) Russian-language publication (available, with additional presentational material from a meeting in July 1995, *via* the authors)

[23] Denton H.R., "The Causes and Consequences of the Chernobyl Nuclear Accident, and Implications for the Regulation of US Nuclear Power Plants"; Annals of Nuclear Energy, 14, 1987, *pp.* 295-315

[24] Richards M.B., "Combustibility of High-Purity Nuclear-Grade Graphite"; Proc. 22nd Biennial Conference on Carbon, San Diego, 16th – 21st July 1995, American Carbon Society, 598-599

E

APPENDIX E—ASSESSING THE POTENTIAL RISKS IN DECOMMISSIONING FROM CARBONACEOUS DUSTS

E.1. Definition and Measurement of Dust Explosibility

A dust explosion occurs when finely divided combustible material is dispersed in an atmosphere containing enough oxygen to support combustion and when an ignition source of sufficient energy is present. In exceptional circumstances - for example, with magnesium dust - explosion in other gases such as nitrogen would be possible, but this is not relevant for carbonaceous materials. In the extreme case of evidence of contamination of graphite stacks with magnesium from damaged fuel cladding, then special considerations are clearly necessary which are beyond the scope of this review.

If a dust suspension is explosible it means that a flame can propagate rapidly through it; usually however this will be at significantly less than the speed of sound, in contrast to a gas explosion. The event is therefore usually a *deflagration* rather than a *detonation*, with a sub-sonic pressure wave. Nonetheless, high pressures can be generated as a result of the sudden combustion of solid particles to gaseous products. A dust explosion can be more violent than a gas explosion because of the larger mass of material capable of conversion to gaseous products within a given volume.

A definitive work on this subject is that of Field [1], now over 20 years old, which contains a lengthy consideration of the classification of substances as explosible or non-explosible on the basis of a variety of test procedures. Carbonaceous materials, according to their precise chemical and physical nature, appear in both categories. Unlike coal dust, which is a familiar cause of explosions in mines, graphite and coke dusts were formally classified as non-explosible at ambient temperature and atmospheric pressure on the basis of standard UK Fire Research Station tests. Carbon black, activated carbons and similar materials are borderline cases depending upon precise conditions. At elevated temperatures, and in material containing volatile matter, a greater risk exists.

A dust suspension was defined as explosible if, in the standard tests of the time, there was any evidence of a visible flame moving away from the ignition source. At the time that [1] was written, three separate tests were used in the UK to ascertain explosibility. The first used a vertical tube containing either an electrical spark source or a wire coil heated to around 1000ºC into which approximately 0.5 g of dust was suspended with an air blast; the second used a horizontal tube with a platinum wire at 1300ºC with approximately 2 g dust propelled across it in air; and the third was a more complex version of the vertical arrangement known as an ‘inflammator’ using around 2 g of dust.

Currently there is in place an international standard ISO 6184/1 [2] which is based upon the older 'Hartmann Bomb' apparatus. The present standard equipment consists of a spherical vessel, usually of 1 m^3 volume, to which is attached a container of about 5 litre containing the test dust and this is pressurised to 20 bar. The dust is injected into the main vessel via a semicircular spray pipe when a quick-acting valve is operated. The initial pressure in the main vessel is slightly reduced such that when the injection of the material takes place, the final vessel pressure is 1 bar.

At the centre of the main vessel are two pyrotechnic igniters consisting of consisting of zirconium, barium nitrate and barium peroxide, and of total energy 10 kJ. These present a significant direct energy input and, in addition, generate their own pressure pulses which must be allowed for in the analysis of explosibility data. For this reason, in the opinion of these authors, the ISO standard test is well suited for comparative purposes but less so for absolute categorisation of explosibility characteristics. Results are commonly expressed in terms of the rate of rise of the pressure pulse and the maximum pressure attained under standard conditions.

E.2. Conditions for Achieving a Dust Explosion

It is helpful to understand the criteria, discussed in detail in [1], which must all be satisfied before a dust explosion can be initiated:

1. the dust must be combustible (the presence of volatile constituents is an important factor here);
2. the dust must be airborne, implying a need *either* for a turbulent gas flow *or* for some physical disturbance which allows the dust to fall freely through an oxidising gas;
3. the particle size must be optimised for flame propagation;
4. the dust concentration must fall within the explosible range (*i.e.* neither too high nor too low);
5. an ignition source of sufficient energy to initiate flame propagation must be in contact with the dust suspension (a high temperature surface may be sufficient for this, whilst a naked flame or electrical spark are obvious sources); *and*
6. the atmosphere must contain sufficient oxygen to support combustion (this allows the possibility to provide an inert atmosphere local to the scene of any cutting operation if there is cause for concern about the reactivity of any adjacent materials).

All of these conditions must be satisfied simultaneously. An additional requirement, if a disruptive explosion is to result, is that the dust suspension must be in a confined space which inhibits the relief of the pressure rise resulting from the ignition.

It is useful to expand upon two of these conditions:

E.2.1. Particle Size

In carbonaceous materials it is to be expected that the explosion hazard increases as the particle size is reduced. Ref [1] shows, for a typical dust (polyethylene), that a decrease in particle size brings about

1. a decrease in the minimum ignition energy;
2. a decrease in the minimum explosible concentration;
3. an increase in maximum explosion pressure (this is very sensitive to size and falls very sharply at larger particle sizes); *and*
4. an increase in the maximum rate of pressure rise.

It is difficult to define a particle size where the material is free from hazard, but it appears to be the general experience that particle sizes in excess of 500 μm are unlikely to initiate a dust explosion, although they may participate in secondary explosions.

E.2.2. Particle Concentration in the Suspension

The explosibility hazard of a dust suspension passes through a maximum with concentration in the same manner as the explosibility limits in a gas mixture. At very low concentration the separation of the particles is too great for a flame to propagate, especially when radiative heat losses are taken into account. This lower explosion limit is also dependent upon particle size and the combustibility of the material. Ref [1] cites minimum explosible concentrations for a selection of carbonaceous dusts although none are directly applicable here: Pittsburgh coal is quoted at 55 $g.m^{-3}$ and polyethylene at around 10 $g.m^{-3}$. Ref [3] quotes 60 $g.m^{-3}$ for charcoal and lampblack of small particle size.

The upper explosion limit is considered to be determined by the situation where the particles are so closely packed that the access of air is inhibited and flame propagation is again quenched. The heat capacity of the material is also relevant. This limit is considered [1] to be of order 5-10 $kg.m^{-3}$ for many materials.

Between these limits, the maximum explosion pressure is biased towards the lower concentration ranges, and the maximum rate of rise even more so. The most severe effects are not usually found to equate to the stoichiometric mixture because particulate material is usually left unburned in a dust explosion. Consequently the most severe effects are usually felt in suspensions where the dust is at 2 – 3 times the stoichiometric concentration.

E.3. Nuclear Industry Investigations on Graphite Dusts

E.3.1. United Kingdom

Within the UK nuclear industry, most effort in explosibility investigations has been placed on the study of graphite dusts because significant deposition of other carbonaceous dusts was not foreseen at the design stages of the reactor programmes. The earliest UK interest appears to have been in 1967 when design work was in progress on the feasibility of a reactor using a coolant consisting of carbon dioxide with suspended graphite dust, with the objective of increasing the heat-transfer capability of the coolant compared with a conventional gas-cooled system [4]. The potential explosibility in the event of air ingress was specifically investigated and results are quoted from tests using so-called “Foliac graphite powder” of mean size 4 μm heated in a steel cylinder to 600ºC. A 4000V arc discharge was initiated within the powder causing the suspension of the material. No explosions were observed unless the oxygen concentration exceeded 90% whilst the powder density was in the range 700-1600 $g.m^{-3}$. With powder of 1.7-2.2 μm the critical oxygen concentration fell to 50% and the critical powder density widened to 200-2000 $g.m^{-3}$. Only with much smaller particle sizes did an obvious hazard appear: particles of 0.3 μm initially at 90ºC after circulation tests in carbon dioxide self-heated to red heat upon exposure to air.

When the decommissioning of WAGR was being planned, a range of tests was carried out [5] using unirradiated graphite dusts of 200 and 20 μm average particle size. These tests included:

1. dropping the dust into a “cherry-red-hot” graphite block;
2. the burning of steel immediately above the dust;
3. dropping the dust on to a red-hot steel plate;
4. plunging a red-hot metal rod into the dust; *and*
5. flame-cutting a mild-steel block containing channels into which graphite dust had been introduced.

Although the burning gas jets caused some particles to reach white heat momentarily, no evidence of explosion was found.

The situation was again reviewed in 1982. The difference in explosibility between coal dust and graphite dust from (unirradiated PGA graphite) was confirmed in a horizontal tube with a red-hot centre section across which the dust was blown. However, it was decided to commission new tests at the UK Fire Research Station using equipment which was a forerunner of the ISO 6184/1 apparatus [2].

Initially a 100J capacitative discharge spark was used as the ignition source. The dust was placed in a 20-litre sphere and the pressure reduced to 0.4 bar. Re-pressurisation to atmospheric pressure activated the dust suspension and ignition took place 60 μs later. No flame propagation was observed. The concentrations were in the range 500-8000 $g.m^{-3}$; the particle size distribution quoted shows the majority to be in the range 45-180 μm. A second series of tests with a smaller size distribution (34% <45 μm rather than 22% previously but still with material up to 180 μm present). Similar negative results were obtained.

At the request of UKAEA a much higher igniter energy was then used – 20 kJ. On this occasion both samples of dust did explode, reaching a pressure of 4 bar. The report on this tests concedes an important point about the igniters: "*because they generate their own explosion pressure, … this …. would make it difficult to recognise ignition of the graphite dust*". This is extremely important: an explosion in the presence of energetic chemical igniters should not necessarily be taken as an indicator of a hazard existing with graphite dusts in a normal decommissioning environment.

Much more recently, the situation was reviewed prior to metal-cutting operations above the graphite in WAGR during decommissioning, and for the subsequent activity of removing the graphite blocks from within the pressure vessel. A brief summary of the arguments is given in [6]. Assessment of the energy available for ignition of dusts in the specific geometries involved showed there to be no need for concern, and an especial benefit was found to be gained from impurities in the dusts within the vessel because of their inerting effect (see Section A5.5).

Much more comprehensive studies have been undertaken in support of both internal investigations and the eventual dismantling of the Windscale Piles, situations complicated by the presence within the graphite of significant internal energy (Wigner energy) and also by widespread contamination of regions of the core with damaged fuel elements and isotope cartridges in the case if Pile No. 1. These studies were commissioned by UKAEA and undertaken by The University of Leeds Energy and Resources Research Institute, and are summarised in [7].

This work utilised PGA graphite characteristic of the Calder Hall Magnox reactors, the nearest currently available material to that used in the Piles. The work has revealed an unexpected influence of particle size, with only the very finest particles (< ~ 5μm) participating actively in combustion whilst larger particles behave as heat sinks and thus serve to suppress flame propagation. This results in a rather low reactivity of typical dust samples to the extent that a methane 'driver' has been utilised to produce the explosions necessary to study the full range of behaviour and to evaluate more detailed kinetics.

A major feature of the Leeds work is the ability to study the possibility of the initiation of secondary explosions and the effects of propagation of the pressure pulses between connected enclosures whose volumes are in approximate proportion to the volumes of the various reactor void-space areas. This is especially important in a reactor such as the Windscale piles where there is no pressure vessel.

Although the Leeds work confirmed that the graphite dust was weakly explosive under the ISO-test conditions, there were a number of important subsidiary findings:

1. Use of several different igniter energies and other types (*e.g.* 1 – 15 kJ pyrotechnic, continuous 4 J arc) illustrated that no explosion occurred at any graphite concentration up to 450 $g.m^{-3}$ in air unless at least 4kJ energy input from the chemical igniter was available, and that even then a large fraction of the graphite powder, initially present in the size range 2 – 25[28] μm, did not participate in the explosion but rather behaved as a heat sink, which reduces the possibility of secondary explosions to a very low probability indeed: an initial 'hot fireball' was necessary for a flame to propagate at all;

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[28] There is a significant peak in the size distribution at around 6 μm.

2. In the older ‘Hartmann Bomb’ apparatus (as used for the majority of test results cited in [1]), *no* ignition occurred with two types of 15 kJ igniters;
3. Only the finest particle sizes participated in the explosion, and it was separately noted that the samples tended to agglomerate quickly with storage (over a period of weeks following preparation) such that these fine particle sizes were no longer present in later tests: agglomerated masses were typically 1 mm diameter;
4. In order to get meaningful data on graphite-dust behaviour, most of the tests had to be ‘driven’ to explosion by the addition of methane gas, and the known characteristics of methane combustion then ‘subtracted’ from the total behaviour in order to provide data on graphite: the most reactive graphite concentration *in the presence of methane* was at 55 $g.m^{-3}$ but this requires a correction to be valid for graphite alone, and the figure then approaches the stoichiometric concentration of 105 $g.m^{-3}$;
5. The maximum overpressure was generated at a dust concentration of 440.$g.m^{-3}$ and was found to be extremely sensitive to the powder injection conditions and to the ‘age’ of the powder (presumed agglomeration mentioned in ‘2’);
6. The estimated peak deflagration index[29] (standard measure of flame propagation) was around 61 $bar.m.s^{-1}$ with an upper-bound value of 106 $bar.m.s^{-1}$, the difference reflecting the difficulty of extracting meaningful data for a substance so unwilling to participate directly in an explosion: this is a very low result in comparison with most explosible dusts;
7. Over-pressure calculations following explosions were specific to the Windscale Piles geometry, but were low (0.2 bar): this defines the necessary capabilities of the structure (and any connected enclosures subject to pressure waves or to secondary explosions) to withstand the consequence of the worst-case (highly pessimistic) scenario of an explosion.

Overall, this is a highly satisfactory result, confirming the difficulty with which pure nuclear graphite dust can be made to participate in a dust explosion and thus the relative ease with which it is possible to engineer in safeguards in decommissioning activities such that the simultaneous requirements for a dust explosion cannot occur.

The Leeds work continued to examine the effects of impurities specific to Windscale Piles, and these results are discussed in Section A5.5.

E.3.2. France

At the request of EdF, tests upon graphite dusts have been conducted in three stages: first a very limited investigation at the INERIS laboratory; secondly at the Centre National de Prévention et de Protection (CNPP) in Vernon and finally, under CNPP supervision, at an EdF facility near Paris known as ‘Les Renardières’

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[29] The deflagration index, K_{st}, is the product of the maximum rate of pressure rise and the cube root of the volume of the vessel in which the explosion test is conducted: thus, for a standard spherical vessel of $1m^3$ as recommended for the ISO test, the index reduces to the maximum rate of pressure rise.

INERIS demonstrated that graphite dust, in the size range 1 - 100µm, was explosible at a concentration exceeding 60 $g.m^{-3}$ with a 10 kJ igniter, thus confirming the UK observations using the ISO apparatus. No upper limit for an explosible concentration was defined although peak pressure decreases beyond a concentration of 250 $g.m^{-3}$.

The first CNPP tests were somewhat crude in nature and consisted of exposing samples of dust, sometimes pre-heated to 850ºC in an oven, to an oxy-acetylene flame. Some samples were contaminated with oil whilst others were subjected to molten metal as in the early UK studies and from arc welding. Unsurprisingly, the dust subjected to an oxy-acetylene flame became elevated and combustion was observed, although it was self extinguishing after about 10 seconds. Oil-soaked powder was also self extinguishing, although it was noticed that particles of approximate size 45 µm burned or smouldered for around 1 minute before extinguishing, where as smaller (15 µm) and larger (100-400 µm) dusts were much quicker to extinguish (again about 10 seconds).

A final test in this second investigation involved a ‘trail’ of oil-soaked graphite dust with what is described as a ‘camping-gas burner’ applied at one end. Combustion remained very limited, although the 15 µm granulometry again sustained combustion for longer, propagating 3cm in 10 minutes before extinguishing.

Noting that these results were encouraging, and broadly in line with UK and other experience, EdF devised with CNPP a third phase intended to replicate a realistic decommissioning situation with the objective of demonstrating that no unsafe conditions could be generated. A special apparatus consisting of a plexiglass tube, 4 m in length and 480 mm internal diameter was constructed. Graphite dust derived from unirradiated fuel sleeves from the St. Laurent des Eaux reactors (similar material to the moderator) was laid in a groove in the base of the tube and was elevated by compressed air to give a dust cloud along the length of the tube. Ignition at the closed end was effected by a powerful electric arc, between 59 and 70 kJ with a duration of 10 ms (approximately one ‘half-period’ of the alternating voltage). Arcs sustained for two and three half-periods were also applied to demonstrate the absence of any “cliff-edge” effect.

Progress of events was monitored by time-lapse photography, with opacimeters to measure dust concentration, pressure transducers and temperature probes. Unfortunately, the opacimeters saturated at 150 $g.m^{-3}$ and therefore could not provide concentration data for the full range of the tests. As the total graphite amount in the groove corresponded to a concentration of 650 g.m-3, it was certain that the actual concentration remained within the 150-650 $g.m^{-3}$ range, which had been associated by the INERIS tests with the highest peak pressure.

The igniter electrodes themselves were made of graphite with a copper, and a small amount of silver was also dispersed during the arc. Consequently, a visible short-lived ‘fireball’ of convecting matter occurred even in the absence of graphite. Tests with graphite present were therefore evaluated in comparison with an equivalent blank test. In every case studied, the ‘fireball’ in the elevated graphite dust moved a short distance down the tube, and was effectively extinguished within 80 – 500 ms (the longer period corresponding to the longer arc duration and higher input energy). The incandescence appears limited to the matter that is directly involved in the “fireball” and does not propagate further. The extent of the incandescent cloud along the tube was approximately 20% greater in the presence of graphite compared with that for incandescent material displaced from the arc when no graphite was present: about 1m for the lower-energy arc and 2.25 m (maximum result) for the highest energy arc.

The interpretation of these observations was that the incandescence in the presence of graphite was effectively self-extinguishing in all the situations studied.

E.3.3. Other Work

The potential explosibility of nuclear graphite has also been examined in Italy (in support of Latina decommissioning), in Germany, and in the USA. Except for the first of these, the work is rather old and is described briefly in [1].

SoGIN have conducted tests with Latina graphite dust (unirradiated) which broadly followed the same programme as the UK (blow torch, molten metal fragments, oil soaked powder etc.). These tests were part of a wider investigation on the potential for bulk graphite ignition, and the entire test programme was videoed, producing an extremely valuable piece of evidence that the risk of an incident involving graphite dust is extremely low. SoGIN plan further verification of the dust explosibility in due course, but have produced valuable evidence about the effect of reactor-circuit contamination already (see Section A5.5).

E.4. Non-Graphitic Carbonaceous Dusts

An issue which is important in the context of reactors which have been irradiated in CO_2-based coolants is the production of deposits of more reactive non-graphitic carbon from the radiolytic polymerisation of CO. There may also be a contribution from the irradiation of minor organic molecules such as methane.

These deposits are found both on graphite components and other reactor internals. Such deposits in association with graphite are generally well adherent to the graphite, being located both inside the accessible pore structure and on external surfaces, with a complex distribution around the core reflecting differences in temperature, radiation flux, and gas flows [8]. Local concentrations of up to 3% by weight of reactive deposit have been observed, although generally the amounts are much smaller. The reactivity to air, however, is around 100 times greater than that of graphite.

It is unlikely that this material would appear as loose deposits in quantities sufficient to form an explosible mixture in air, but care should nonetheless be taken to guard against the possibility when dismantling. The literature data on explosibility for amorphous carbon materials, especially those containing volatile components, leaves no doubt that such material is readily explosible in appropriate concentrations in air [1, 9, 10] provided that the basic criteria for initiating an explosion are met.

E.5. The Effects of Impurities

Important results in this context are available from the work programmes conducted at Leeds University (UK) and SoGIN (Italy).

The work described in [7] relates to the dismantling of the Windscale Piles, where contamination of the cores with lead is known to have occurred. Lead was used a filler and spacer material in isotope-cartridge holes and elsewhere within the cores, despite the core temperature being sufficient to melt this metal. Lead is known to be one of the most effective catalysts for graphite oxidation in air [11], a point confirmed for PGA graphite as used in UK Magnox reactors (*A.J. Wickham, personal communication*).

However, catalysis is important in bulk graphite only when the overall reaction rate is controlled by reaction kinetics, and not when it is controlled by diffusion considerations or by the available supply of oxygen. In the case of fine powder, the situation is potentially more complex.

Lead was mixed with the graphite in the form of the oxide Pb_3O_4 at 1000 wppm. The surprising result was that it had *no detectable effect* on the explosibility characteristics of the graphite. The implication of this is that the oxidation is equivalent to the 'Mode III' (gas-transport-controlled) oxidation of bulk graphite, where catalysis is ineffective. This seems inconsistent with expectation since, with the graphite in powder form at very small particle sizes, one might assume that the access of oxygen was at maximum efficiency and that the reaction would indeed be 'Mode I' (kinetic controlled) in which catalysis should play a significant role, speeding up the exothermic reaction and the release of heat, and thus facilitating flame propagation.

The implication is that the oxide particles and the graphite particles were effectively behaving independently, despite the employment of 'opposed jet milling' which is expected to give an intimate mixture, with the lead oxide thus behaving as an inert diluent. Whilst this issue is not properly resolved, the result of the test was deemed to give adequate comfort for the decommissioning programme and therefore the problem has not been further pursued.

A second impurity which it is considered could be present in Windscale Pile 1 from fire-damaged nuclear fuel, is aluminium oxide Al_2O_3. The Leeds study has showed that this, in 25% admixture, appears to lower the overpressures and reactivity somewhat, although the results remain within the scatter of the pure-graphite data. Here again, the impurity has no significant effect.

Admixture of flammable dusts with materials which are already fully or partially oxidised should be expected to lead to a general reduction in explosibility potential, otherwise described as 'inerting'. This phenomenon has been known for many years, wit the assessment of the inert content of dusts in coal mines being an important part of the assessment of explosion hazards [12] for routine safety assessments. The general reactor dust burden in a gas-cooled system is likely to arise from corrosion products of metal structures and will thus be in the form of oxides incapable of further oxidation – this effect is demonstrated by recent SoGIN work in which reactor dusts removed from the Latina Magnox reactor after nearly 30 years of operation were found to be unexplosible in the ISO test whereas pure unirradiated graphite was, as found by other workers, weakly explosible.

Generally, therefore, one may conclude that impurities in graphite dusts encountered in reactor decommissioning are unlikely to represent an additional explosibility hazard and are more likely to be beneficial, acting as 'inerter' materials and reducing the potential for any explosion.

References to Appendix 5

[1] Field P., "Dust Explosions"; Volume 4 of Series "Handbook of Powder Technology" *eds.* Williams J.C. and Allan T., Elsevier, 1982

[2] ISO 6184-1 "Explosion Protection Systems – Determination of Explosion Indices of Combustible Dusts in Air"; 1985 (also issued as European Standard EN 26184-1 [1991] and British Standard BS 6713-1 [1986] under the title: "Explosion Protection Systems: Part 1; Method for Determination of Explosion Indices of Combustible Dusts in Air")

[3] "Forschungsbericht Staubexplosionen, Brenn und Explosions Kenngrößen von Stauben"; Schriftenreihe des Hauptverbandes Gewerblich Berufsgenosschaften e.V., Bonn, 1980

[4] Ford G.W.K. and Hawes R.I., "A Study of the Application of Dust Suspensions for Use as Reactor Coolants"; UKAEA Report AEEW-R490, 1967 *(available through the UK Public Records Office or via the authors)*

[5] Cutler R.D., Smith G.P. and Crosby J.E., "An Investigation into the Reactivity of Unirradiated Reactor-Grade Graphite at Elevated Temperatures in Contact with a Source of Ignition"; *Windscale AGR Internal Document*

[6] Robinson S., "Decommissioning WAGR: Is Nuclear Graphite a Fire Hazard?"; Proc. Nuclear Decon '02

[7] Andrews G.E., Cross M.T., Ingamells W., Phylaktou H. and Wickham A.J., "Evaluation of the Potential for Carbonaceous Dust Explosibility in the Decommissioning of the Windscale Piles"; Proc. CESEP'05, 1st International Conference on 'Carbon for Energy Storage and Environment Protection', Orléans, France, October 3rd – 6th, 2005

[8] Wickham A.J., "Caring for the Graphite Cores"; Proc. Seminar 'The Review of Safety at Magnox Nuclear Installations', I. Mech Eng., London, March 1989 *pp.* 79 - 87[30]

[9] Raftery M.M., "Explosibility Tests for Industrial Dusts"; Fire Research technical paper No. 21 (revised by P. Field), HMSO London 1975

[10] Nagy J., Dorsett H.G. and Cooper A.R., "Explosibility of Carbonaceous Dusts"; US Bureau of Mines RI 6597, Washington 1965

[11] Amariglio H. and Duval X., "Étude de la Combustion Catalytique du Graphite"; Carbon, 4, 1966, *pp.* 623-635

[12] "Dust – The Coal Mines (Precautions against Inflammable Dust) Regulations 1956". Statutory Instrument 1956 No. 1769. (As varied by the Coal Mines (Precautions against Inflammable Dust) (Variation) Regulations 1960, S.I. 1960 No. 1738)

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[30] This reference was issued by the publisher with Figures and their captions incorrectly assigned. The correct assignments are obvious.

F

APPENDIX F—EXAMPLES OF RADIOACTIVE INVENTORIES IN IRRADIATED GRAPHITES (FROM PUBLISHED SOURCES)

As discussed within the main text of this report, reactor graphite core radionuclide inventories are very individualistic, depending not only the initial impurity content of the graphite but upon the way various reactors constructed using it have been affected by contamination incidents such as fuel failures, transport of other materials capable of activation in the neutron flux, the overall slow-neutron flux experienced, and the time of decay since the reactor ceased operation before the measurements were made. The radionuclide content of various components within the core may also differ widely, partly because of different radiation fluxes but also through local transport effects such as variations in permeable gas flow through the graphite pores.

Consequently, comparisons between the data collected here are not attempted, and any such comparisons attempted by the reader should be done with extreme caution.

The absence of significant published data from most UK reactors and French reactors must not be taken as an indication of specific problems, but rather as a consequence of original plans for lengthy ‘safe-storage’ periods and the resulting lack of attention to the matter. Only recently have renewed attempts to obtain such data re-started, and publications other than company technical reports are simply not yet available.

The data given here should therefore simply be taken as a ‘snapshot’ of the disposal issues which lie ahead.

F.1 Hanford Reactors

Ref [1] offers a comprehensive collection of estimates for all of the Hanford reactors except the N reactor (which was still in operation at the time the data were compiled). Citations here are limited to overall reactor estimates rather than data from small samples, with assumptions being made about initial impurities, activation and decay characteristics. The calculated results are whole-core inventories. They apply to March 1985, and are given in Table A6.1.

The estimates for ^{14}C take account of production from $^{14}N_2$ in the cover gas.

A more detailed compilation of ^{14}C data is available separately [2]. Much of this relates to the measured content of ^{14}C in stack emissions (which make an interesting contrast with today’s calculations of the quantities of natural ^{14}C emitted in fossil-fuelled power stations): some isolated measurements for graphite samples from the DR and KW reactors are as follows:

DR: four samples in range 0.67 – 2.36 μCi.g^{-1}, whence 2.47 – 8.73 × 10^{4} Bq.g^{-1}
KW: three samples in range 1.62 – 3.59 μCi.g^{-1}, whence 6.00 – 13.2 × 10^{4} Bq.g^{-1}

F.2 G2 Reactor, Marcoule

The data in Table A6.2 are taken from [3].

F.3 AVR, Forschungszentrum Jülich

The following data were provided by personal communication (*H.* Brücher) during a discussion at The University of Bath, UK, in October 1998:

Graphite:	^{60}Co:	approx 8 × 10^{4} Bq.g^{-1}
	^{14}C:	approx 1.3 × 10^{5} Bq.g^{-1}
	^{3}H:	approx 1.6 × 10^{7} Bq.g^{-1}
Carbon blocks:	^{60}Co:	approx 5 × 10^{6} Bq.g^{-1}
	^{14}C:	approx 2.1 × 10^{4} Bq.g^{-1}
	^{3}H:	approx 2.5 × 10^{6} Bq.g^{-1}

A more comprehensive assessment was then given at an IAEA meeting in 1999 [4] and the data provided are shown in Table A6.3.

F.4 Vandellos Sleeve Graphite

Ref [5] provides analyses of two Vandellos sleeves of different irradiation times after a similar period of cooling (295 days). These are given in Table A6.4.

F.5 Russian Production Reactors at 'Tomsk-7' (Seversk)

Ref [6] offers data for a number of isotopes assayed in samples trepanned from the cores of the I-1 EI-2 and DR reactors. These data are collected in Table A6.5.

In addition to the data cited in the Table, [6] also includes a detailed analysis of the ^{60}Co distribution which illustrated specific contamination at the channel surfaces in addition to the activity arising from impurity cobalt in the graphite.

F.6 Calculations for UK Reactors

In the absence of extensive measurements so far, calculations of typical inventories have been made for the so-called 'reference Magnox' and 'reference AGR' in [7]. Such calculations in general ***do not*** take any account of transport and activation of materials not originally present as impurities in typical graphites as assayed at the time of manufacture, although in some minor cases, particular assumptions have been built in.

It is the general experience now that comparisons are being made between calculated inventories and actual measurements, that significant differences indeed exist, for the reasons already given *(L. Rahmani, EdF CIDEN and CEA personnel, personal communication)*.

Examples of the reference calculations are given in Tables A6.6.

References to Appendix 6

[1] Miller R.L. and Steffes J.M. (eds); "Radionuclide Inventory and Source Terms for the Surplus Production Reactors at Hanford"; UNC Nuclear Industries Unclassified Report UNI-3714 Rev. 1, April 1987

[2] Paasch R.A., "A Compilation of Carbon-14 Data"; UNC Nuclear Industries Unclassified Report UNI-3499, July 1985, *quoting a memorandum from W.C. Morgan to J.A. Adams dated 28th June 1984*

[3] Costes J.R., de Tassigny C. and Vidal H., "Conditioning of Graphite Bricks from Dismantled Gas-Cooled Reactors for Disposal"; Waste Management, **10**, 1990, *pp.* 297 – 302

[4] Bisplinghoff B., Lochny M., Fachinger J. and Brücher H., "Radiochemical Characterisation of Graphite from Jülich Experimental Reactor (AVR)"; Proc. IAEA Technical Committee Meeting on 'Nuclear Graphite Waste Management', Manchester UK, October 1999, IAEA NGWM/CD 01-00120

[5] Esteban-Duque, A., Uriarte A., Suarez A., Fabrellas B. and Gonzalez A., "Characterisation and Conditioning of Radioactive Graphite"; Proc. International Conference on Nuclear Waste Management and Environmental Remediation, Prague, September 1993, *pp.* 641 – 649

[6] Bushuev A.V., Verzilov Yu.M., Zubarev V.N., Kachanovsky A.E., Proshin I.M., Petrova E.V., Aleeva T.B., Samarkin A.A., Silin B.G., Dmitriev A.M., Zakharova E.V., Ushakov S.I., Baranov I.I., Kabanov Yu.I., Kolobova E.N. and Nikolaev A.G., "Radionuclide Characterisation of Graphite Stacks from Plutonium Production Reactors of the Siberian Group of Chemical Enterprises"; Proc. IAEA Technical Committee Meeting on 'Nuclear Graphite Waste Management', Manchester UK, October 1999, IAEA NGWM/CD 01-00120

[7] White I.F., Smith G.M., Saunders L.J., Kaye C.J., Martin T.J., Clarke G.H. and Wakerley M.W., "Assessment of Management Modes for Graphite from Reactor Decommissioning", Commission of the European Communities Report EUR 9232, 1984, ISBN 92-825-4292-0

Table A6.1: Hanford Reactors: Activity in Core Graphite (Estimated)

Data are presented in Curies. For Bq.g^{-1} multiply by 3.7×10^4 and divide by mass of graphite in tones

Reactor	**B**	**C**	**D**	**DR**	**F**	**H**	**KE**	**KW**
Nuclide								
^{3}H	8300	8900	7700	4900	5800	5500	30000	27000
^{14}C	4500	4500	4300	3200	3700	3500	7000	6700
^{60}Co	100	60	90	30	70	40	5	5
^{63}Ni	180	28	280	95	190	120	11	15
^{59}Ni	1	1	2	1	2	1	-	-
^{36}Cl	42	12	34	26	33	17	54	52
^{239}Pu	1	1	1	1	1	1	1	1
^{241}Am	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
^{90}Sr	10	10	10	10	10	10	10	10
^{137}Cs	30	30	30	30	30	30	30	30
^{133}Ba	32	1	34	10	26	11	1	1
^{152}Eu	40	40	40	40	40	40	40	40
^{154}Eu	20	20	20	20	20	20	20	20
^{41}Ca	190	14	150	90	140	54	1	5
Mass of Graphite (tonnes) *	1070 (630)	1070 (630)	1070 (630)	1070 (630)	1070 (630)	1070 (630)	1610 (1000)	1610 (1000)

* Main figure is moderator mass, figure in parentheses is reflector mass.

Table A6.2: Marcoule G2 Reactor Measured 9 Years after Shutdown

Data are presented in kBq.g^{-1}

Nuclide	Reflector	Moderator
^{60}Co	2	6-13
^{133}Ba	0.06	0.1-0.2
^{137}Cs	0.01	0.1
^{154}Eu	0.45	0.4-0.8
^{3}H	400	400
^{14}C	6	15-25
^{63}Nb	2	5-7
^{36}Cl	0.4	0.5-1.5
^{93m}Nb	$\leq$0.1	$\leq$0.1

Table A6.3: AVR Reactor, Jülich, Germany (Shutdown December 1988, Measurements in 'Early' 1999

Data are presented in Bq.g^{-1}

	Carbon Block	**Graphite**
Nuclide		
Total α	51	18
Total β/γ	2.3 × 106	2.0 × 106
^{228}Th	<10	4
^{230}Th	<2	<1
^{231}Pa	<2	<1
^{233}U	5	<1
^{236}U	<2	<1
^{237}Np	<2	<1
^{238}Pu	<21	<1
$^{239/240}$Pu	<2	2
^{241}Am	<2	<1
^{242}Pu	<2	<1
$^{243/244}$Cm	<2	<1
^{245}Cm	<2	<1
^{226}Ra	<2	<1
^{232}Th	<2	<1
^{235}U	<2	<1
^{238}U	<2	<1
^{3}H	3.8 × 107	1.2 × 106
^{14}C	3.7 × 106	63000
^{36}Cl	800	24
^{41}Ca	n.d.	<5000
^{55}Fe	1.22 × 106	255000
$^{59/63}$Ni	64000	106000
^{90}Sr	9300	920000
^{93}Mo	n.d.	n.d.

^{93}Zr	<250	<100
^{126}Sn	<230	<100
^{22}Na	<70	no data
^{60}Co	2.4 × 106	410000
^{126}Sb	<230	100
^{133}Ba	4300	1700
^{134}Cs	13000	<210
^{137}Cs	4400	4400
^{152}Eu	n.d.	<150
^{154}Eu	90000	9700
^{155}Eu	37500	2100
^{166m}Ho	n.d.	<70

n.d.: none detected above threshold

Table A6.4: Vandellos Sleeves.

Data are presented in Bq.g^{-1} after 295 days ‘cooling’. Note that the sleeves were removed from the fuel elements *under water* and this needs to be considered when examining the results. Data come from a number of powder samples from each sleeve together with material from the inner surface of sleeve 1.

The higher activity (in some undefined standard configuration) of sleeve 1 relative to sleeve 2 is presumed to arise primarily from the γ-emitting ^{60}Co and $^{134/137}$Cs.

	Sleeve 1	**Sleeve 2**
Relative Dose Rates in an Equivalent Position	8.3	1
Nuclide		
^{14}C	15564	11157
^{3}H	1841	50301
Others	823	8015
of which		
^{65}Zn	74	
^{60}Co	609	4794
^{54}Mn	63.9	227
^{137}Cs	64	148
^{134}Cs	12	2846

Table A6.5: Russian Production Reactors

Data are given in Bq.g^{-1} (time since shutdown not clear)

Radionuclide	I-1 Reactor	Calculated Values
^{3}H	3.4 × 103	3.2 × 106
^{14}C	1.2 × 106	4.2 × 105
^{36}Cl	54 – 110	8.8 × 103
^{63}Ni	250 - 2200	8.9 × 103

Sample Number	I-1 Reactor				EI-2 Reactor	
	Cell 0320		Cell 2516		Cell 3326	
	^{241}Am	^{244}Cm	^{241}Am	^{244}Cm	^{241}Am	^{244}Cm
1	430	11000	2000	3400	13	1500
2	121	4200	17	4400	5.4	560
3	146	5400	14	3800	5.1	530
4	150	5000	12	2300	7	730
5	48500	1.8 × 105	3700	6.3 × 105	1000	86000

Reactor	Relative Fluence	^{137}Cs 105 Bq.g-1	^{106}Ru 103Bq.g-1	^{90}Sr 104Bq.g-1
EI-2 Cell 3425	0.46	1.38	1.3	7.4
	0.96	1.23	1.2	4.7
	0.61	32.3	29	160
I-1 Cell 3644	0.55	5.62	1.9	29
	0.82	3.00	1.2	17
	0.80	1.00	0.30	7.5

Table A6.6: Calculated Activation Inventories for UK ‘Reference’ Magnox and AGR

Data are given in Bq

Reference Magnox Reactor after 10 years decay (Assumed Graphite Mass 2233 tonnes)	
3H: 1.2 × 1014	93Mo: 8.5 × 108
10Be: 7.1 × 1010	93mNb: 5.5 × 108
14C: 8.5 × 1013	94Nb: 1.0 × 105
36Cl: 9.5 × 1011	99Tc: 1.7 × 108
41Ca: 7.3 × 1011	108mAg: 2.3 × 1010
54Mn: 2.7 × 108	113mCd: 1.0 × 1010
55Fe: 1.5 × 1013	121mSn: 4.5 × 1010
59Ni: 9.3 × 1010	133Ba: 5.6 × 1011
60Co: 2.7 × 1013	152Eu: 2.2 × 1011
63Ni: 1.3 × 1013	154Eu: 5.2 × 1012
65Zn: 2.1 × 108	155Eu: 1.6 × 1012

Reference AGR after 10 years decay (Assumed Graphite Mass 1633 tonnes)	
3H: 7.6 × 1013	93Mo: 5.6 × 1010
10Be: 2.3 × 1011	93mNb: 3.4 × 1010
14C: 1.9 × 1014	94Nb: 8.4 × 105
36Cl: 2.3 × 1012	99Tc: 5.6 × 109
41Ca: 1.2 × 1012	108mAg: 3.6 × 1010
54Mn: 5.2 × 109	113mCd: 4.4 × 1010
55Fe: 9.3 × 1013	121mSn: 2.8 × 1012
59Ni: 5.5 × 1011	133Ba: 3.1 × 1011
60Co: 9.8 × 1014	152Eu: 1.0 × 1011
63Ni: 1.1 × 1014	154Eu: 2.9 × 1012
65Zn: 3.7 × 109	155Eu: 9.4 × 1011

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