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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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Chapter contents

1. Graphite disposal

1.1 Graphite-waste management

So far, no country has actually started to dispose of its graphite waste resulting from the operation of nuclear-power reactors. However, some governments have already determined deadlines. On the Hanford Site, in the United States, for instance, the monitored storage period of graphite reactor components is limited to 75 years after shutdown (i.e., between 2040 and 2060.

Studies focus on two major management options, as follows:
the conditioning of graphite waste as is, before disposal, and
the incineration of graphite waste with subsequent disposal of combustion ashes and other waste.

Pending the dismantling of reactors, most countries have left the existing graphite in place. Some of them have considered that the nuclear island may be used for storage purposes until its final dismantling. At Hanford, the island is protected by an external envelope (or cocoon) over each reactor which still contains its graphite components.

In some cases, such as the Windscale-1 pile, in the United Kingdom, and Russian storage facilities in Siberia, early unloading and dismantling are necessary due to the presence of damaged fuel elements or to the degradation of the facilities themselves.
After many years of preparation, the International Atomic Energy Agency (IAEA)[1] is now ready to prepare a summary report on the characterisation, treatment and conditioning of radioactive graphite waste generated by nuclear reactors. Since the Bath Symposium[2] held in 1995, the IAEA has been constituting an international database working on the properties of irradiated graphite. With the contribution of several countries, it has gathered various data on the physical, chemical, mechanical, as well as miscellaneous characteristics on those materials. Since a graphite-moderated reactor core may contain up to 2,000 t of graphite, the resulting quantity of waste may rapidly represent a huge volume.

In addition, the properties of irradiated-graphite inventories are likely to generate a significant Wigner energy[3], in the form of an exothermal reaction. Such violent release of energy represents an effective danger for reactors, although it is reduced in some of them: in British Magnox-type and advanced gas-cool-type (AGR) reactors; in French, Spanish, Japanese and Italian uranium-fuelled graphite-moderated and gas-cooled reactors, as well as in all others high-temperature gas-cooled reactors (HTGR). Indeed, the operating temperatures of those reactors are equivalent to or higher than 200°C, the temperature level at which that energy is released.
In all cases, the specific properties of irradiated graphite, the Wigner energy, the explosibility of dust, the release of radioactive gases, etc., must be characterised for future treatment, conditioning and containment purposes.

Their physico-chemical properties, together with the presence of tritium, carbon-14 or chlorine-36, distinguish graphite waste from other radioactive waste. During the irradiation of graphite, several phenomena may appear, such as dimensional changes, the decay of thermal conductivity by a factor of 100, embrittlement, chemical reactivity (oxidation) and explosion risk of graphite dust. Although the actual irradiation does not really alter their mechanical strength and insolubility, the waste requires special conditioning before disposal.

Carbon-14 constitutes the major contributor to the radioactivity of graphite; its concentration varies in relation to the neutronic flow and proves to remain relatively stable within the material.

Chlorine-36, resulting from the activation of the residual chlorine used during the graphite-purification process, constitutes another contaminant. That isotope has a long radioactive half-life and is not well contained by the geological barrier. Several studies have been conducted with a view to taking into account the properties of chlorine-36 in the concept of a deep geological repository and in conditioning specifications.

Depending on the practical uses of tritium and carbon-14 as moderator and neutron reflector or as fuel sleeve and core, the presence of corrosion, impurity-activation and fission products, as well as small quantities of transuranic element may also be detected.

The main precautions involved with the characterisation, treatment, conditioning, storage and disposal of radioactive waste pertain to the large quantities at stake and the potential contamination by long-lived radioelements, such as carbon-14, chlorine-36, nickel-63, etc.

For the moderator, it is often necessary to plan for a long waiting period of several decades in order to favour the radioactive decay of short-lived elements prior to unloading and disposal.

1.1.1 Specific situations of graphite waste

There are several geometries for using graphite in reactors. In some older generations of Russian graphite-moderated pressure-tube reactors with boiling light-water coolant (LWGR), for instance, it is impossible to separate graphite from the fuel. In other reactors, such as the gas-cooled reactors (GCR), the fuel is inserted in protective sleeves that are removed when unloading the fuel from the reactor. Moreover, in other reactors, such as British advanced-cooled reactors (AGR), the core is separated from the fuel during reprocessing.
Certain Russian power reactors contain specific fuel elements. Together with their cooling tubes, they are placed in a graphite-sleeve system that forms an integral part of the fuel and is removed with it.

In RBMK reactors, the fuel may be unloaded during operation, thus generating an additional and non-negligible quantity of graphite waste (see below), which is likely to constitute some sort of accumulated residual energy.

In the case of helium-cooled graphite reactors, the direct disposal of both fuel and graphite may be envisaged. In the United States, however, significant efforts are being made in order to take advantage of separation and volume reduction with a view to developing the best possible environmental compromise when disposing of the waste generated by the Peach Bottom 1 and Fort St. Vrain reactors.

The same question applies to graphite and carbon-based materials used in fuel elements in the form of balls.

Lastly, there is also an important quantity of non-irradiated graphite in countries equipped with a nuclear arsenal, where it is contaminated with plutonium in the production of weapons.

1.1.2 IAEA's selected options

IAEA has selected two options: either the immediate dismantling of the moderator or its on-site containment in order for the radioactivity of the short-lived elements present in the waste to decay considerably. With respect to safety, there is no international consensus on a specific storage period for decay purposes. Removing and storing the core as soon as possible is normally the solution preferred by national safety authorities (e.g., ASN in France) and advocated by the IAEA.

Graphite may be either sorted into three categories according to its activity, radioactive half-life, etc., or grouped into a single category. Various procedures are possible:

- decontamination, surface treatment by coating or embedding;
- containerisation;
- graphite incineration (with recovery of released carbon) and conditioning of concentrated radioactive ashes;
- pyrolysis and release of accumulated energy, and
- fluidisation of carbon.

Three further solutions are also examined:

- storage in appropriate containers;
- subsurface disposal, and
- deep geological disposal.

Other graphite waste is stored in silos, in dry storage facilities or under water, but only temporarily.

1.2 Russian Federation

Two LWGR reactors (AMB 100 and 200) from Beloyarsk, which were shut down in the 1990s, are currently being dismantled. Their fuel has been removed and stored partly on site and partly

at Mayak. The two units are monitored on the basis of the design studies prepared by Moscow's Research and Development Institute of Power Engineering (NIKIET).

The decision whether to reprocess the fuel used in the AMB-100, -200 reactors, which preceded the RBMKs, and of all other graphite-moderated fuel types in Russia and in the former Soviet Union, is still pending. That led to the construction of spent-fuel storage facilities, although some of the fuel elements are damaged.

For about 40 years, the Mayak Centre has produced plutonium metal for military purposes from five LWGR reactors. The first graphite reactor was commissioned in 1948 and was followed by four others. All of them were shut down permanently at the end of the 1980s. They all revealed core expansions (e.g., 140 mm in the case of Reactor A) having generated ruptures in the graphite blocks. The fuel was thoroughly removed from the reactors, the core of which has the particularity of being buried at a depth of 55 m underground. After several pre-monitoring studies, the core supports were reinforced, but the graphite blocks were left in place.

Due to its physico-chemical and radioelement-retention properties, radioactive graphite fulfils Russian requirements for the disposal of solid waste.

However, reviewing the radiological inventory of moderators and of the other graphite elements used in nuclear reactors reveals that it is impossible to accommodate the graphite in disposal facilities without specific conditioning. The following options were investigated, but none was actually selected:

- direct disposal after appropriate conditioning;
- disposal of high-level conditioned ashes after incineration and advanced filtration (without any possible retention of carbon-14 by filters), and
- disposal after chemical reprocessing (liquid and gaseous extraction), followed by protective impregnation and conditioning.

In addition, two disposal options were examined: one on the ground surface, and the other, deep underground. The AMB power reactors at Beloyarsk and the mixed thermal-power reactors at Bilibino all contain a fuel type with a specific design where the graphite sleeves forms an integral part with the fuel. Most AMBs and RBMKs allow for fuel replacement during operation. When replaced, graphite sleeves and integrated cooling tubes generate an increasing quantity of waste. Furthermore, graphite components are used for moving control rods. Although their volume is smaller, those parts are likely to maintain a significant residual energy (Wigner energy) resulting from the low temperature under which they were irradiated. The management and disposal of graphite waste constitute a delicate challenge for the Russian Federation, as for any other country that used or are still using such similar reactors. In addition, RMBK components are subject to long-term degradation in the absence of appropriate treatment or disposal.

1.3 Lithuania

At the Ignalina NPP[4], dismantling of Unit No. 1, which has been shut down since 2004, started earlier in 2008 and preparations are underway for the scheduled dismantling of Unit No. 2 in 2009.

Approximately 46 m^3 of graphite waste weighing 55 t (out of 2,000 t) and originating from Unit No. 1 will be stored by 2010 for an expected period of 50 years in the new planned facility for the solid waste resulting from the dismantling of the facility.

A specific facility (measuring 60 m by 20 m) will accommodate about 2,000 m^3 of long-lived waste, including graphite waste, activated metal waste and disused sealed sources, which will be laid out in separate cells and conditioned in 2.5 m^3 containers. Biological protection is ensured by the building structure and wall thickness. Packages will be remote-handled with bridges and conveyors. The building will be ventilated. Package removal and transfer are the subject of design studies and of a description in the safety report. The facility forms an integral part of the waste treatment and storage complex under construction near the power plant and should be operational by 2009.

Table 1 : Characteristics of existing and planned graphite waste at the Ignalina NPP until 2010

Waste type	**Graphite**
Volume (m^3)	46
Weight (t)	54.5
Density (kg/m^3)	1185
Radionuclides	**Specific activity (*Bq/kg*)**
H-3	1.83E+10
C-14	3.20E+07
Cl-36	5.10E+05
Fe-55	7.70E+06
Co-60	1.50E+07
Ni-59	1.20E+04
Ni-63	2.10E+06
Total	**1.84E+10**

EIA Program for New Solid Waste Management and Storage Facilities at Ignalina NPP, Oct. 2006, NUKEM

1.4 United States

Starting with the Manhattan Project, in the early 1940s, the Hanford Site has played a crucial role for more than 40 years by producing materials for nuclear weapons. The facility included nine plutonium-fuelled reactors, but only the most recent one has been connected to the grid. Those reactors have all been shut down permanently[5] and mothballed under a protective cocoon, after dismantling, for a period up to 75 years in order to let radioactivity decay down to an acceptable level[6]. In 2002, the cost for the protective cover of a single reactor amounted to approximately 27 million dollars (Reactor C, Hanford Reach 14 October 2002).

The mothballing operation consists in dismantling all reactor buildings, except the reinforced-concrete walls surrounding the reactor core. Doors and openings are sealed and a roof is installed over the structure.

During the 75-year mothballing period, the U.S. Department of Energy (DOE) and authorities in charge of regulating the safety of cleanup operations at Hanford will determine the appropriate time for launching the disposal phase. Each of the nine cores represents a volume in the order of 10 m^3 and weighs between 11,000 and 16,000 t; they will be buried on site within a trench protected by an engineered barrier.

Table 2: Comparison table of the different dismantling options for the eight reactors and of their impact as indicated in the Final Environmental Impact Statement (DOE 1992)

Alternative	Active Decommissioning Period (years)	Total Cost (in millions, 1990 dollars)	Occupational Radiation Dose (person-rem)	10,000-year Population Dose[a] (person-rem)
No Action (Continue Present Action)	100	$44	24	50,000
Immediate One-Piece Removal	12	$228	159	1,900
Safe Storage Followed by Deferred One-Piece Removal	87	$235	51	1,900
Safe Storage Followed by Deferred Dismantlement	103	$311	532	1,900
In Situ Decommissioning	5	$193	33	4,700

[a] The same population would receive 9 billion person-rem over 10,000 years from natural radiation.

1.5 Japan

The Magnox reactor at Tokai will be dismantled after a 10-year mothballing period. The site will need to be cleaned up in order to build a new nuclear power plant. Studies have already dealt with the associated risks.

Dismantling operations will generate approximately 30,000 stacked graphite blocks. In order to minimise dismantling costs, the density of packages was specifically investigated, including the possibility to cut out components into adequate shapes and sizes.

At Rokkasho-Mura, a project is under review to excavate a subsurface repository for graphite waste as well as low-level and intermediate-level long-lived waste at a depth of 90 m under the current low-level and intermediate-level disposal facility.

1.6 United Kingdom

In the United Kingdom, the dismantling strategy relies on mothballing reactors for a period of about 100 years before deconstruction. That decision derives from the absence of a suitable disposal facility and consists in letting radioactivity decay significantly until it becomes stable. It also has the advantage of expressing costs in actualised values over a 100-year period. However, the Nuclear Decommissioning Authority (NDA), which is newly in charge of dismantling operations, aims at reducing that period to 25 years[7].
The British nuclear industry is mostly equipped with graphite-moderated reactors, 18 of which are currently in service. Radioactive graphite in most Magnox reactors is still contained in the core, although only two of them include also graphite fuel parts. The current dismantling strategy consists in leaving graphite waste in the core for a specific period during which the reactor, emptied of its fuel, will be maintained under mothballed conditions in order to take advantage of radioactive decay.

Former studies have helped to gather a wealth of information on graphite inventories, its conditions throughout the decay period, safety aspects and dismantling. Significant work has been achieved on the management of accumulated fuel fragments, notably with regard to the installation of equipment likely to remove and condition the waste into a form that complies with the future deep geological repository.

Since 1947, the U.K. Atomic Energy Authority (UKAEA) has been responsible for managing research reactors and all facilities dedicated to the deployment of nuclear technologies in the United Kingdom. That responsibility includes the take-over of irradiated graphite from various sources, such as low-irradiation-temperature graphite reactors (Windscale Piles 1 and 2, the British Energy Pile O, the Harwell Low-energy Pile, as well as the Harwell and Dounreay material-testing reactors. To that list of research reactors must be added the AGR graphite-reactor located at Windscale and the neutron-shield graphite from the Dounreay's Prototype Fast Reactor and Fast Reactor). Their dismantling is expected to generate more than 6,000 t of

graphite waste intended for disposal. The first graphite waste is being removed from Windscale's Pile No. 1 and will be followed by those from the AGR.

The UKAEA has undertaken a large number of studies in order to determine the best waste-treatment options, such as the disposal of low-level waste, incineration, coating and the disposal of intermediate-level waste. Several questions associated with each option have been addressed, including Wigner energy, inventory content, graphite-waste coating, soft-steel corrosion due to galvanic coupling, up to public acceptance. The UKAEA is developing conditioning and packaging concepts which should lead to the first waste-certification prescriptions.

The first assessments of the management methods for graphite waste resulting from reactor-dismantling operations were published in Report EUR 9232[8] of the European Commission, which states:

- the calculated radionuclide inventory of the graphite waste, resulting from Magnox and AGR reactors (operating for 40 years at a 70% load factor) 10 years after their shutdown shows that the main contribution originates from activated carbon and stable impurities;
- a smaller contribution is due to impurities of uranium fission products in the graphite or on its surface, depending on the design and operation of the reactors;
- several types of conditioning were investigated and estimated. They may be implemented at reasonable costs and show that the conditioning of larger volumes are proportionally the least expensive;
- two different geological formations have been investigated for the disposal of graphite waste: clay, on inland sites, and schist close to the coastline. For a large range of leaching rates and hydrogeological parameters, each of those types of site generates low doses;
- in the case of shallow disposal facilities, radiological precautions will be compulsory until the radiological content of cobalt-60 has decayed considerably. The long-term radiological impact of such a disposal facility requires behaviour studies on carbon-14 in shallow soil and groundwaters. Those studies will need to be completed on specific sites, and

- incineration constitutes an alternative to the direct disposal of graphite. It implies further disposal of residual ashes concentrating the most radioactivity, although it involves some inconveniences, such as carbon releases in the atmosphere.

1.7 Spain

In Spain, Vandellos I is the only nuclear power plant undergoing dismantling, even if it is only in part. It includes a French 480-MWe GCR reactor. Commissioned in 1972; it remained in service until 1989, when the turbine was set on fire due to mechanical deficiencies. The fire did not generate any radioactive release and did not damage any key components. Due to the high repair and retrofitting costs involved, the Ministry of Industry shut down the NPP permanently.

The NPP operator removed the fuel from the reactor and sent it for reprocessing in France; graphite and operating waste were conditioned.

The reactor core consists of a cylindrical graphite pile measuring 15.73 ***m*** in diameter by 10.2 ***m*** in height, and includes 3,072 loading columns.

The fuel assembly and its sleeve were laid out in a slot between pile columns and were removed during fuel unloading. Saddle cables made of stainless-steel alloy were used to maintain the fuel element within its cylindrical graphite sleeve.
During dismantling, graphite stacks were taken apart.

Radioactive graphite waste was contained in three storage silos for graphite sleeves and stainless-steel saddle wires (table 3). Each silo measured 8.7 m in height by 7.2 m in width and 24 m in length, with a concrete wall varying from 0.75 to 1 m in thickness.

Table 3: Radioactive waste stored in silos

Waste type	Silo 1	Silo 2	Silo 3
Graphite sleeves	36,123 sleeves 195.1 t	10,7450 sleeves 580.2 t	43,778 sleeves 236.4 t
Graphite blocks in stack	4,834 bricks 50.7 t	60 bricks 0.7 t	

The waste contained in silos was removed in the framework of an international French-Spanish project (Consortium EQUIPOS NUCLEARES-FRAMATOME).

Graphite sleeves constitute the bulk of the waste and were transferred to a grinder equipped with a high magnetic-field separator that was used to separate the steel cables. The graphite was put in containers.

Graphite sleeves:

- crushed graphite: 1,000 t in 240 6.5- m^3 containers, and
- saddle cables: 2 t in 74 0.35-m^3 containers.

A storage facility for graphite waste was implemented on site within a cell excavated inside the reactor building for a 30-year period.

2. Leaching of irradiated graphite

2.1 Introduction

A number of leaching studies have been carried out in the past 30 years on a variety of irradiated graphite samples by several laboratories for a various radionuclides but with particular emphasis on C-14, H-3 and more recently Cl-36. These studies have been undertaken to support:

1 retrieval of irradiated graphite as part of reactor decommissioning activities;
2 for safe storage post closedown of the reactor;
3 interim storage in silos, vaults, cells etc;
4 potential disposal;

Understanding the fate of radionuclides for [1] will be particular important for Member States considering a wet/underwater retrieval method. This particular approach has been discussed in some detail by the French chapter with particular reference to the Fort St Vrain decommissioning. The US chapter also discusses the decommissioning of this reactor.

Several member States are considering extensive interim in-reactor storage periods i.e. from 25 to 75 years and possibly longer. In such cases the potential for water ingress into the reactor will need consideration as part of any risk assessment. This could be particular valid for climate change when sea levels are predicted to rise by up to 2 metres thus potentially affecting reactors sited in coastal regions. Even in-land stations could be under some threat as water tables could also be influenced by higher sea levels. Possibly to a lesser extent than direct invasion of bulk quantities of water could be the influence of i-graphite being stored for lengthy periods in humid/damp conditions.

Approximately 15% of the i-graphite identified in this review volume is currently residing in solos, vaults, cells etc. With silos these are generally wet storage conditions and hence the leachability of radionuclides from the i-graphite into the aqueous environment will influence the subsequent treatment and disposal of this liquor.

For disposal the compliance with repository criteria will be crucial and hence the leachability of radionuclides under appropriate conditions will be required. At present there is no clear indication of these conditions as few Member States have identified suitable repository sites.

It should be emphasised that although a number of leaching studies have been conducted they are small in comparison with the 200,000 tes i-graphite challenge to be addressed and that no commercial reactor has been decommissioned and hence graphite retrieved and no or little graphite has been disposed of. This section addresses these studies in context of the CARBOWASTE project.

2.2 Leaching Studies

Not surprising the major i-graphite problem owners (UK, France, USA and Russia) has undertaken graphite leaching studies. Japan, Italy, Spain and Germany although in comparison owner of smaller quantities has also study i-graphite behaviour in aqueous environments.

It is known that graphite does not react with alkaline solutions. Oxidising acids attack graphite to a different degree depending on the nature and surface area of the graphite under investigation. The reaction with concentrated nitric acid is:

$$C + 4HNO_3 = 2H_2O + 4NO_2 + CO_2$$

Depending on experimental conditions other other products may be formed such as graphitic oxide ($C_7H_2O_4$), mellitic acid ($C_6(CO_2H)_6$) and hydrocyanic acid (HCN).
Other acids such as sulphuric will give rise to similar products as per the equation but SO_2 in place of NO_2.

The above equation represents the attack of graphite by acids and this is more akin to dissolution, unlikely leaching where the matrix (graphite) is largely left intact whilst the target (radionuclide) of interest is removed.
In describing the behaviour of the radionuclides under investigation many of the papers, reports etc describe in detail the virgin and i-graphite structure (porosity, pore structure etc), impurity levels, the diffusivity of radionuclides in graphite as these properties can in many instances provide reasonably good accounts as to the leachability of a particular radionuclide.

It is not intended in this chapter to provide a detailed account of all the leaching studies undertaken but to provide a resume of the key experiments and observations/findings. The following tables identify the type of samples studied, the experimental conditions and the experimentalists i.e. organisation/laboratory, radionuclides of interest etc.

2.3 Graphite samples

Both irradiated and non irradiated samples have been studied. The information in (Table 4) provide a spectrum of samples evaluated but is not an exhaustive list.

The information in Table 4 demonstrates the variability of samples evaluated and thus making comparisons near impossible. Even the French and US studies with G2 reactor samples did not use identical geometries. In some cases samples were selected and treated e.g FZJ and Russian, for specific purposes. The former studies were in aid of understanding the behaviour of graphite under final repository conditions, whilst the Russian workers were evaluating an

encapsulation technique using polymeric materials. Many of the papers lack detailed information of any pre-treatments and/or if the sampling technique influenced the adsorbed radionuclide, in particular for volatile isotopes and when significant heat could be generated by the machining, cutting, crushing and grinding operations.

Table 4: Graphite samples investigated

Organisation/ laboratory	**Origin of graphite samples**	**Pre-treatment/sample preparation**	**Reference**
Toshiba Corporation/ The Japan Atomic Power Company	Nuclear grade unirradiated block supplied by Japan Atomic Power Company.	Block samples prepared using ceramic cutter. Three powder samples of 100 to 500µm, 50 to 100 µm and <50µm prepared by crushing and grinding.	9
RRC Kurchatov Institute, Moscow	Leningrad NPP unit 3	Irradiated samples. Five cubic samples 30x30x30mm of about 47g weight; 4 samples coated with epoxyfurfural resin o.5mm to 0.8 mm thickness	10
FZJ	Unirradiated graphite, MERLIN and AVR reactor samples	Graphite particles >0.8mm and <0.05mm were investigated	11
1. PNL, USA	C reactor Hanford Production reactor.	Irradiated right-circular cylinders 30.5mm long and 30.5mm diameter samples were cut from three retrieved bars. Samples cleaned ultrasonically in deionised	12

		water for 1 to 2 minutes.	
2. PNL, USA	French G-2 reactor	30mm by 30mm samples machined from 3, 80mm dia. by 75mm long blocks supplied by CEA.	13
SERCO, UK	WAGR	Single 9g sample of crushed graphite supplied by NIREX that had been stored for several years in a closed container by AEA Technology.	14
AMEC NNC, UK	WAGR spigot ring	Samples from 3 fragments of a irradiated WAGR spigot ring. One solid sample (~2g) and a crushed sample (~2g) examined.	15
CEA, France	EDF, Bugey and Saint-Laurent A and CEA G2 reactors.	Irradiated samples of powder and of 16 to 80mm diameter by 13 to 80mm in height of 1.5 to 650g in weight evaluated	16
Spain	Vandellos 1	Entire sleeves, smaller samples and grouted samples	17

2.4 Experimental conditions and radionuclides under evaluation

The French and USA studies did attempt to ensure some consistency in methodology by complying with a recognised evaluation technique, Table 5. Even these studies however did deviate in the composition of leachant and in the leachant to solid (graphite) [V/S] ratio. Other

studies lacked compliance with recognised standard procedures and therefore the results can not be regarded as comparable. The use of recognised procedures is discussed later.

Table 5: Experimental conditions and radionuclides studied

Organisation/ laboratory	Experimental conditions	Radionulides evaluated
Toshiba Corporation/ The Japan Atomic Power Company	Alkaline leachant, composition not specified. Results for C-14 compared with $H_2SO_4/KMnO_4$ leachant. Temperature of experiment not specified but duration was for 720 days.	C-14
RRC Kurchatov Institute, Moscow	Distilled water (150ml) temperature not specified but aqueous samples were withdrawn from the reaction vessel at 30, 60 and 90 days. A control sample, i.e. no coating of polymer was also investigated.	α β and γ-activities measured. α for determining Pu-239, β for Sr-90 and γ for Cs-137
FZJ	Experiments involved water, $MgCl_2$-rich brine (brine-2) and NaCl-rich brine (brine-3) solutions at 900C under argon, oxygen and air atmosphere. Some experiments were performed in the presence of γ-irradiation sources under argon atmosphere.	Co-60, Eu-154, Eu-155, Cs-134, Cs-137, Ba-133
1. PNL, USA	The leach test procedure based on ANSI/ANS-16.1-1986 but modified for ease of analysis. Two leachants used deionised water and Hanford ground water. Both leachants sparged with clean air for 10 to 15 minutes prior to use.	

	Leachant to graphite sample ratio specified (V/S = 9.25). Temperatures of 90, 50 and 20^{0}C evaluated for deionised water and the upper and lower temperatures for Hanford ground water. Leachates were changed weekly over a period of 8-weeks. 10^{-2} M and 10^{-4} M Na_2CO_3 used as blank experiments.	C-14 and Cl-36
2. PNL, USA	Conditions generally as above but for deionised water only with a V/S ratio of 9.27 and a temperature of 20^{0}C. Leachates were changed at intervals of 1, 2, 3, 5, 7, 9, 11, and 13 weeks.	C-14 and Cl-36
SERCO, UK	Highly alkaline solution of pH 13, containing calcium hydroxide, potassium hydroxide and sodium hydroxide. This leachant simulated water that had been equilibrated with a typical waste encapsulation grout. V/S ratio of ~28, temperature of 25^{0}C and duration of 336 hours.	C-14 and H-3
AMEC NNC, UK	Leachant was saturated solution of calcium hydroxide with the pH adjusted to 13 with a mixture of potassium and sodium hydroxide. V/S ratio of ~110, leachate samples removed weekly for first month thereafter monthly for the next six.	C-14 and H-3
CEA	Three leachants evaluated, pure water, water saturated with $Ca(OH)_2$ and industrial water of pH 7.2 containing ppm levels of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-} Cl^-, $NO3^-$ but higher concentration of HCO_3^-. V/S ratios of 0.33 to 1.26 and temperature of 20 and 40^{0}C. Duration of experiments 90 to 455 days.	Cl-36, C-14, H-3, Co-60, Cs-137, Cs-134, Ba-133, Eu-154,

		Eu-155 and Ni-63,
Spain	Distilled water (pH 5.5 to 10.5) and pond water (pH 11.6 to 12.4), mass of sample from 28g to 1200g with experiment duration of 238 to 385 days at 40^0C.	H-3, C-14, Cs-137, Co-60

2.5 Conclusions from the leaching experiments

It is difficult to drawn some definitive conclusions for the work reported in this section. This is largely due to the paucity of information, diversity of experimental conditions, lack of consistency, and the relative small number of samples studied. Some conclusions are made in Table 6

Some general comments are made in the next section (2.6).

Table 6: Experimental conclusions/observations

Organisation/ laboratory	**Conclusions**
Toshiba Corporation/ The Japan Atomic Power Company	These studies were undertaken in an attempt to understand the leaching mechanism for C-14 from i-graphite. The majority of the study investigated morphology and impurity of nuclear grade graphite and emphasis was directed at N-14. The degree of C-14 leaching rather than kinetic information was quoted and the researchers concluded that '*only a little amount of C-14 was released into the leachant and that the leaching ratio of C-14 was* 10^{-5} *for 720 days'*.
RRC Kurchatov Institute, Moscow	The release of any radionuclide from coated samples was absent even after 90 days of testing. For the uncoated sample Cs-137 the release rate was calculated to be $4.7x10^{-13}$ Bq/g/cm^2 the total Cs-137 released over the 90 days testing was estimated to be $6.4x10^3$.

FZJ	Slow corrosion rate was influenced by dissolved oxygen in aqueous solutions in the absence of irradiation. Corrosion rates in aqueous solutions under pure oxygen and air atmosphere decrease in the order water>brine-3>brine-2. Γ-irradiation accelerated graphite corrosion in brines.
1. PNL, USA	The steady-state fractional leach rates for C-14 in deionised water and Hanford ground water were respectively $1.5x10^{-6}$/day and $0.25x10^{-6}$/day, for Cl-36 these rates were $2.6x10^{-6}$/day and $1.3x10^{-6}$/day. The investigators concluded that '*the use of the so-called steady state leach rates quoted here for predicting long-term leach rates is subject to considerable uncertainty because not enough is known about the leaching mechanisms*'.
2. PNL, USA	Data obtained on the French graphite support the idea that the leach rate of C-14 from irradiated graphite initially exceeds the leach rate of C-12. This supports earlier work. Since leach rates of C-14 and Cl-36 tended toward common values with both French and Hanford graphite, it supports the premise that both are controlled by some common factor such as the leach rate of C-12 following depletion of active or readily accessible portions of the C-14 and Cl-36. The investigators did note the large differences in results between the different French samples, and this requires more information, post manufacture to try to explain this observation.
SERCO, UK	3.6Bq of C-14 was released as C-14 containing hydrocarbon gas or carbon monoxide over the 336 hour period. In addition 11Bq of H-3 as $^{3}H_2$, $^{3}HCH_3$ or other tritiated hydrocarbon gas was released from the 9g sample. Around 60Bq of $^{3}H_2O$ was also released. The investigators also state '*the behaviour of the crushed material in the experiment reported here may not be analogous to that of intact irradiated graphite in waste packages in the repository, as the act of*

	crushing may increase the availability of potentially reactive material and promote faster rate of reaction. It is also possible that volatile species may be released from graphite, on crushing, prior to the start of the experiment'.
AMEC NNC, UK	For H-3 the crushed and intact samples exhibited different behaviours, i.e. initial release of H-3 for intact sample only (700Bq in first week) For C-14 0.7Bq released in first week for intact sample this dereased to <0.44Bq for subsequent samples. An initial release was not apparent for the crushed sample.
CEA	Some of the comments made from this study were: 1. The size of the sample and the S/V ratio is a parameter that should be taken into account; 2. good repeatability of the experiments that used samples from a single graphite core; 3. the release of Cl-36 into solution depends on physical and chemical processes; 4. the fractions of Cl-36 released varied from 10 to 90% depending on the experiment for Bugey 1 samples 5. for G2 samples more than 80% of the Cl-36 leached during the first month, thereafter more slowly; 6. release into solution of C-14 and H-3 was very low in all cases; 7. Co-60 was released little into solution, except in the case of leaching experiments on powder; 8. lime saturated leach solutions inhibit Co-60 and Ni-63 release; 9. Cs-137 leached at significant levels
Spain	Suggestion that more alkaline conditions (pond water) appear to suppress the release of C0-60 and Cs-137. Up to 40% of Cs-137 released into water.

2.6 Standardisation and modelling

A wide variety of experimental methodologies have been employed in the acquisition of leaching data. This has largely resulted in extreme difficulty in comparing data as experiments have been devised for a specific objective such as testing encapsulation techniques and hence the transferability of data is not always possible.

Both the PNL and CEA studies employed the ANS leach-test standard. This standard It was proposed more than forty years ago to develop a standard leaching method under the IAEA guidance. This has not found favour as formal standards such as ASTM, ISO or DIN are already in existence, although was accepted for vitrified waste.

2.7 Implications of the leaching studies for CARBOWASTE

A critical account of the leaching data has already been provided[17] and therefore the following are generalised comments not assigned to anyone study:

- Overall the leaching data suggest that the results are strongly influenced by the nature of the graphite under examination;
- The rate of leaching of radionuclides from graphite is likely to be governed by:
  [a] the rate of corrosion of graphite itself;
  [b] selective dissolution from other phases within the graphite core;
  [c] desorption from the graphite;
  [d] complexation in the leachate solution.
- The ability to predict long term leach rates with confidence can be improved only through enhanced understanding of the leach mechanisms involved.
- Uncertainties due to variations in graphite grades used in the various nuclear reactors could be reduced by more representative sampling within a given reactor environment and by taking samples from different reactors;
- Carbon -14 may be present in different chemical forms in i-graphite and mechanisms for its release are uncertain
- It is also proposed, to explain the release of Cl-36, the existence of two forms of chlorine
- Releasing radionuclides from i-graphite into the leachant depends on several physical and chemical processes.

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