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Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors

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CHARACTERIZATION, TREATMENT AND CONDITIONING OF
RADIOACTIVE GRAPHITE FROM
DECOMMISSIONING OF NUCLEAR REACTORS

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FOREWORD

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear power plants and in many research and plutonium-production reactors. It is used primarily as a neutron reflector or neutron moderator, although graphite is also used for other features of reactor cores, such as fuel sleeves. Many of the graphite-moderated reactors are now quite old, with some already shutdown. Therefore radioactive graphite dismantling and the management of radioactive graphite waste are becoming an increasingly important issue for a number of IAEA Member States.

Worldwide, there are more than 230 000 tonnes of radioactive graphite which will eventually need to be managed as radioactive waste. Proper management of radioactive graphite waste requires complex planning and the implementation of several interrelated operations. There are two basic options for graphite waste management: (1) packaging of non-conditioned graphite waste with subsequent direct disposal of the waste packages, and (2) conditioning of graphite waste (principally either by incineration or calcination) with separate disposal of any waste products produced, such as incinerator ash. In both cases, the specific properties of graphite — such as Wigner energy, graphite dust explosibility, and radioactive gases released from waste graphite — have a potential impact on the safety of radioactive graphite waste management and need to be carefully considered.

Radioactive graphite waste management is not specifically addressed in IAEA publications. Only general and limited information is available in publications dealing with decommissioning of nuclear reactors. This report provides a comprehensive discussion of radioactive graphite waste characterization, handling, conditioning and disposal throughout the operating and decommissioning life cycle.

The first draft report was prepared at a meeting on 23–27 February 1998. A technical meeting (TM) was held in October 1999 in coincidence with the Seminar on Radioactive Graphite Waste Management, organized by IAEA in cooperation with the British Nuclear Engineering Society. More than sixty participants from eleven countries discussed various subjects related to radioactive graphite waste management and contributed to substantial improvement of the draft report. After the TM the first edition of the report was finalized at a meeting on 20–24 March 2000. In October 2004, the report was fully revised and updated. Finally, in January–February 2006, a complete technical review was performed by the IAEA for the purposes of resolving remaining issues, ensuring a balanced presentation, enhancing readability, and verifying that the report remains reliable and relevant. The IAEA wishes to express its appreciation to all those, who took part in the preparation and publication of this report. Particular acknowledgement is due to B. Marsden and A.J. Wickham (United Kingdom), the former who chaired the original TM and put great effort into the completion of the first edition of the report, and the latter who performed a comprehensive review and update of the report in November 2004.

The IAEA officer who was originally responsible for this report was R. Burcl from the Division of Nuclear Fuel Cycle and Waste Technology. J.L. González Gómez and J.J. Kelly, from the same Division, finalized the report for publication.

EDITORIAL NOTE

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

The radioactive graphite coming from nuclear installations has different characteristics from other radioactive waste due to its physical and chemical properties. In addition, the graphite waste contains after irradiation a significant amount of long-lived radioisotopes, such as carbon-14 (^{14}C) having a half-life of 5 730 years, and chlorine-36 (^{36}Cl) having a half-life of 300 000 years. Many short-lived isotopes are also important, such as tritium (^{3}H), having a half-life of 12.3 years. All such isotopes may have a significant impact on the dose to the public at different stages of the waste-management process and, therefore, have to be carefully evaluated.

^{14}C is generated in nature by the action of cosmic neutrons on the nitrogen of the atmosphere at a rate of 10^{15} Bq/y. ^{14}C in graphite is generated principally by a similar reaction through interaction of reactor neutrons with nitrogen, which is present in graphite as an impurity or present in the reactor coolant or cover gas. ^{3}H arises from reaction of neutrons with ^{6}Li impurities in graphite, as well as in fission of the fuel. ^{36}Cl is generated in neutron activation of chlorine impurities in graphite.

Even after many years of irradiation, graphite retains relatively good mechanical properties, is insoluble, and is not otherwise particularly chemically reactive. It appears therefore to fulfill most of general requirements for a material suitable for disposal as a solid radioactive waste. However, the evaluation of the radioactive inventory of graphite moderators and other graphite details applied in nuclear reactors, shows that in many cases this graphite cannot be accepted by existing disposal sites without treatment pre-conditioning.

Various options have been studied for management of radioactive graphite waste (see, for example, Ref [1]), but the final and generally accepted solution for its conditioning and disposal remains undecided. Different solutions may be appropriate in different cases. In practice, the most common preferred option applied now is long-term storage (deferred final disposal). Three basic solutions are considered for final disposal of waste graphite:

- Direct disposal after suitable packaging;
- Disposal after incineration with consequent ash conditioning;
- Disposal after chemical treatment (liquid and/or gaseous extraction) and conditioning (impregnation, encapsulation, etc.) and proper packaging.

For direct disposal, near-surface repositories and also deep geological formations have been evaluated.

1.2. OBJECTIVE

The objective of this report is to provide comprehensive information on presently available approaches and technologies for radioactive graphite waste predisposal management. This includes providing a discussion on the relationship between processing and subsequent storage or disposal.

It is intended to provide designers, decision makers, nuclear facilities decommissioning managers and other involved bodies with technologically oriented information on the present state and the recent achievements in radioactive graphite waste management, applicable to planning and realization of decommissioning procedures, processing of radioactive graphite, and its conditioning for final disposal.

1.3. SCOPE

The report covers the most important topics of the radioactive graphite waste management arising in nuclear reactors operation and decommissioning. Available technical information is analysed and good operational practice is summarized and discussed.

The major issues addressed are:

- Review of graphite and graphite components arising in operation of nuclear reactors worldwide;
- Radioactive graphite waste characterisation;
- General approaches to radioactive graphite waste management;
- Radioactive graphite waste treatment, conditioning and transport; and
- Storage and disposal issues are addressed from the perspective of their impact on characterization, treatment and conditioning.

1.4. STRUCTURE

The report consists of six Sections and one Appendix. Following this Introduction, the sources of radioactive waste graphite are reviewed in Section 2. In Section 3, the main graphite characteristics relevant to graphite waste management are presented and discussed. Section 4 is dedicated to the description and analysis of strategic approaches to radioactive graphite waste management. Particular steps for pre-disposal management of graphite waste are described in Section 5. Conclusions and recommendations are summarized in Section 6. The Appendix provides recommended terminology applicable to graphite oxidation in air.

It should be noted that inputs from the United Kingdom, France and the Russian Federation are the predominant references in this report, since these countries have accumulated the most extensive knowledge and experience in the subject.

2. GRAPHITE IN NUCLEAR REACTORS

The majority of irradiated graphite is associated with reactor moderators and reflectors. However, there are a number of other routes from which radioactive graphite components requiring ultimate disposal can arise. These are discussed later.

2.1. GRAPHITE MODERATOR

2.1.1. Types of graphite-moderated reactor cores

The beginning of nuclear power utilization started with the graphite moderated Pile which was built in a squash court at the University of Chicago in 1942. Since then a multitude of designs of graphite moderated reactor have been developed. Most of them are energy-production reactors, others are research and material testing reactors (MTR), and a significant sub-group was specifically designed for the production of plutonium. Graphite moderated reactors include:

— Air-cooled plutonium production graphite piles such as X-10 at Oak Ridge National Laboratory (USA), the Windscale Piles (UK) and G1 (Marcoule, France);
— Light water cooled graphite-moderated piles such as the Hanford reactors (USA), the Russian plutonium-production reactors, and power reactors such as RBMKs and AMB;
— Carbon dioxide cooled reactors such as the British Magnox and French UNGG reactors and the later British advanced gas-cooled reactors (AGRs).
— High-temperature helium cooled reactors such as Dragon (UK, an OECD Project), THTR (Germany), Fort St. Vrain (USA) and the new development reactors in Japan (HTTR) and China (HTR-10) and the planned South African Pebble-Bed Modular-Reactor project.

There were also a small number of experimental reactors. These include prototype molten salt or sodium cooled graphite-moderated reactors, such as MSRE at Oak Ridge (USA), pulse reactor IGR in Semipalatinsk (Kazakhstan), and the USA Sodium Graphite Reactor experiment.

Examples of various arrangements of graphite components found in reactor moderators are given in Figures 1 through 6.

2.1.2. Existing and planned graphite moderated reactors worldwide

Table I is a reasonably comprehensive list of the graphite-moderated reactors worldwide. Besides basic technical data, a recent status is indicated if information is available. However it is difficult to obtain detailed information relating to some of the earlier test and prototype reactors.

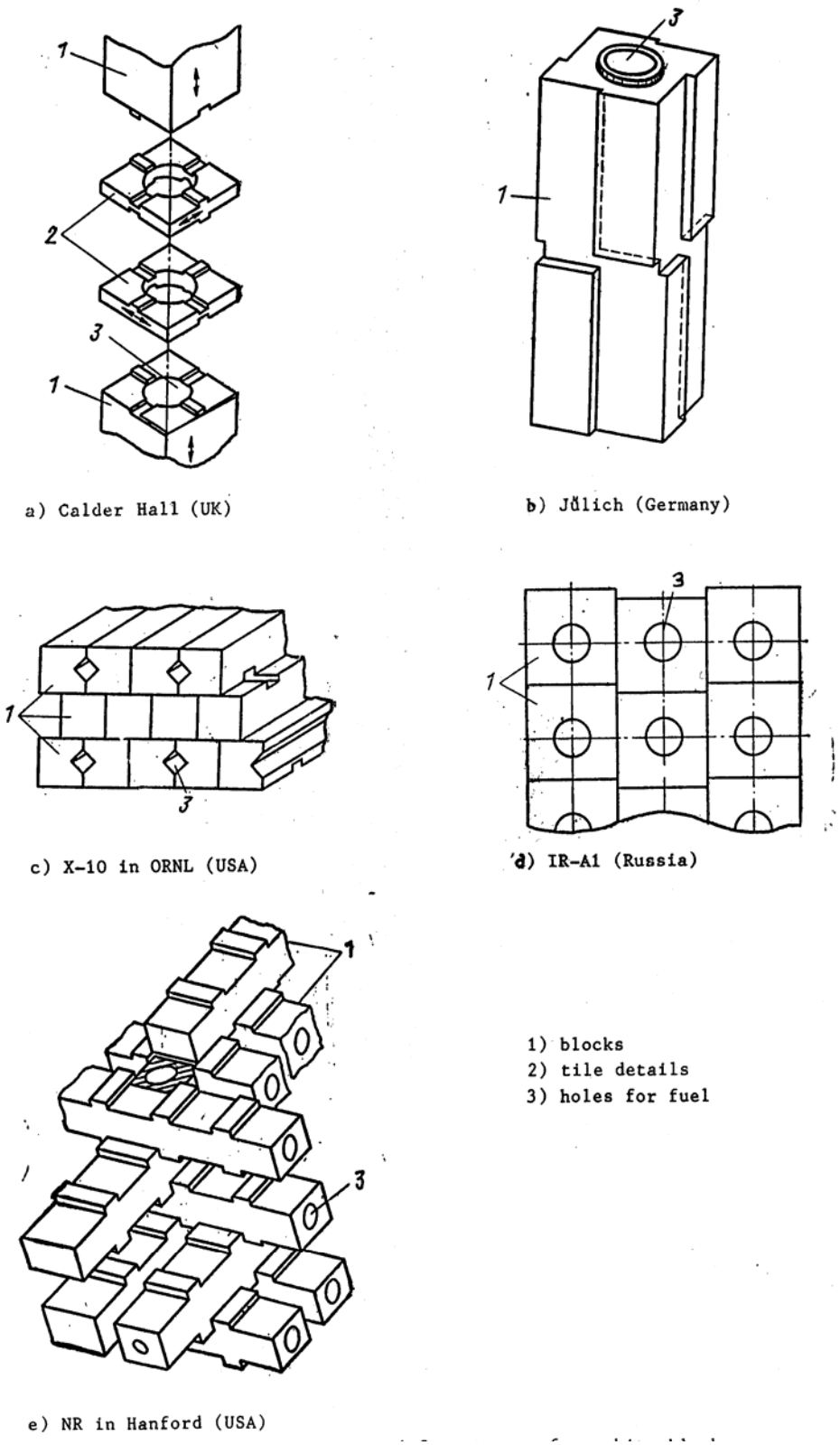

FIG. 1 Selected examples of graphite block arrangements.

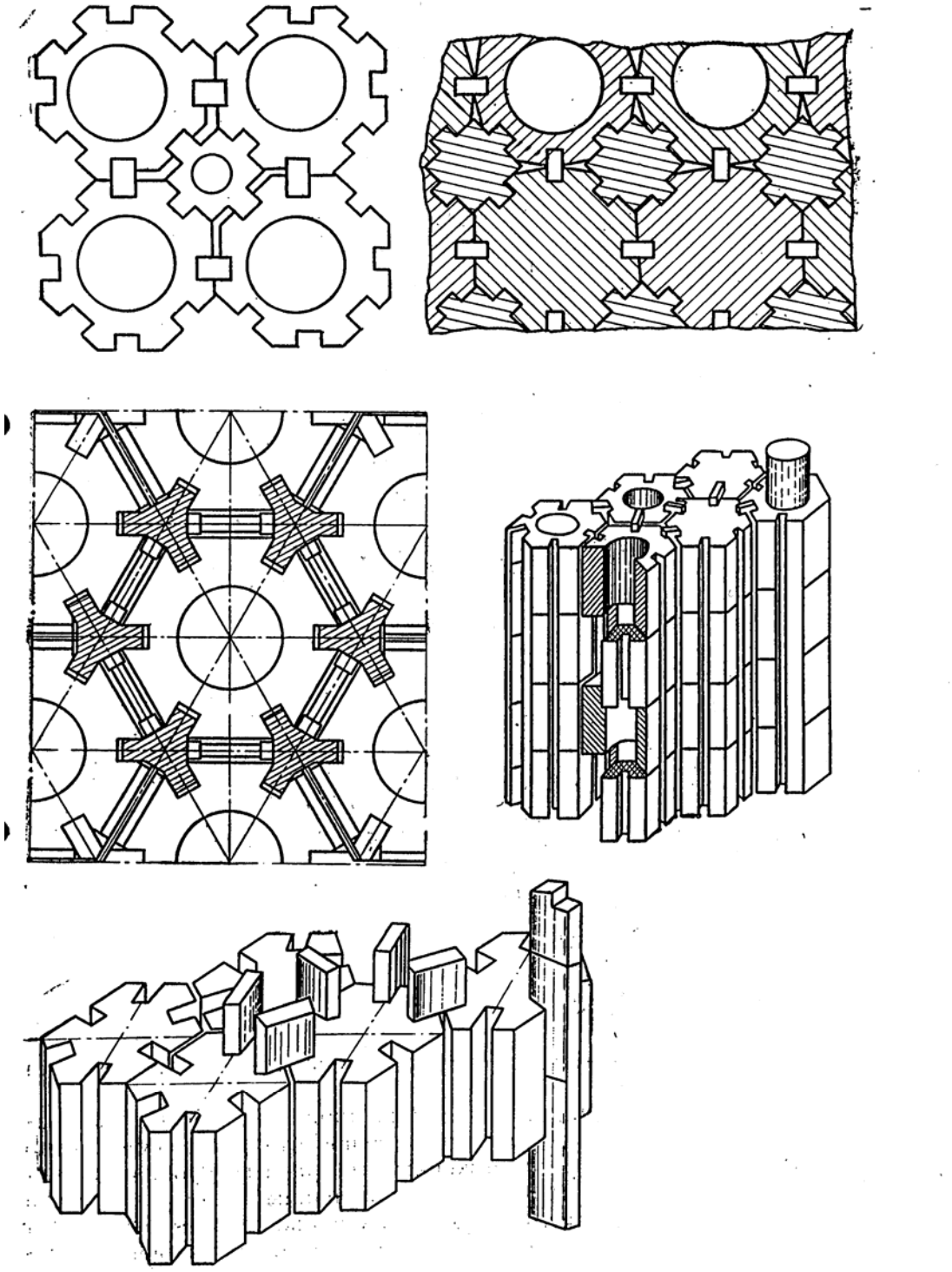

FIG. 2 Graphite block stack schemes.

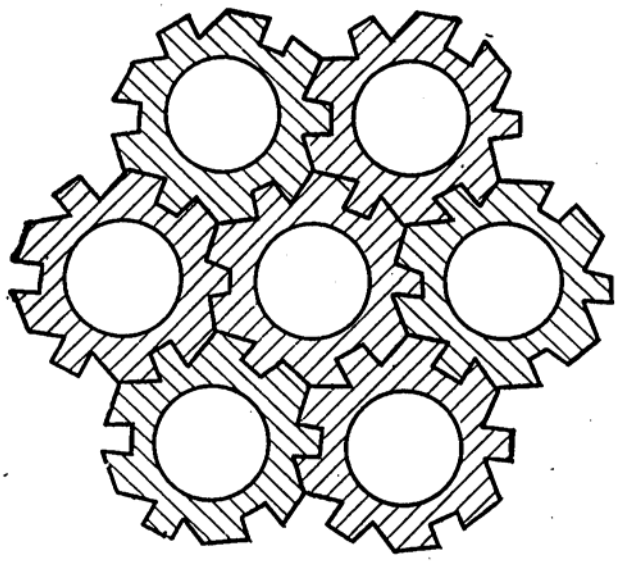

FIG. 3 Graphite stack with vertical rib.

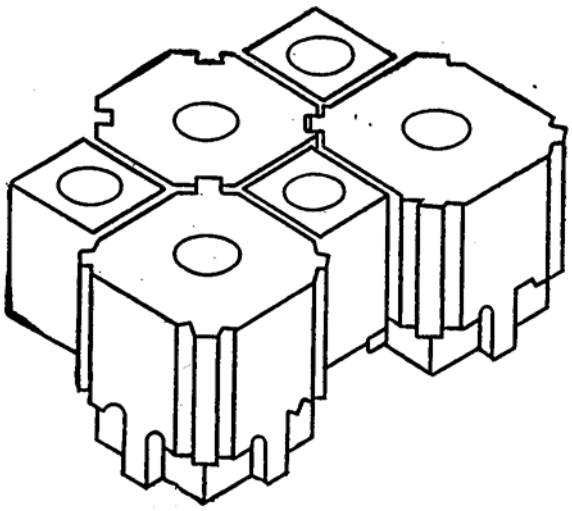

FIG. 4 Stacks of graphite blocks with different cross-sections.

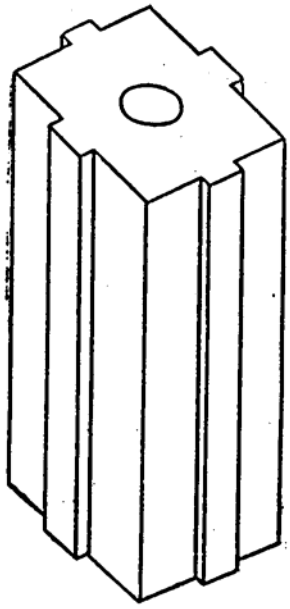

FIG. 5 Graphite block with vertical ribs.

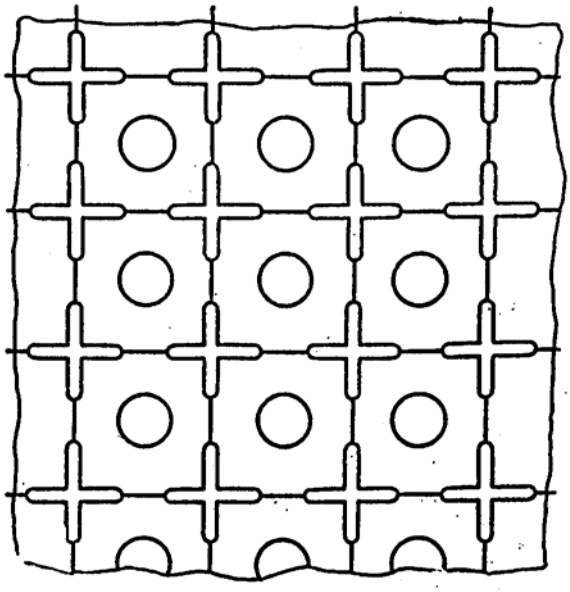

FIG. 6 Graphite stacks with cross-wised cooling holes.

TABLE I: LIST OF GRAPHITE MODERATED REACTORS

Status: S = shut down, D = Decommissioned, D1 = 1st stage of decommissioning (defuelling),
D2 = 2nd stage of decommissioning (peripheral structures dismantling). Note that new construction is not included in the Table.

Country	Location	Reactor	Type	Thermal Power MW(t)	Graphite in reactor tonnes	Graphite total tonnes	Commissioned	S/Down Date
France	Marcoule	G1	Air cooled	50	1200	1200	1956	D2
	Marcoule	G2	Magnox	255	1207	1207	1959	D2
	Marcoule	G3	Magnox	255	1207	1207	1960	D2
	Loyettes	Bugey 1	Magnox	2000	2039	3600	1972	1994 S
	Avoine	Chinon A1	Magnox	300	1050	1060	1963	D1
	Avoine	Chinon A2	Magnox	800	2200	2500	1965	D2
	Avoine	Chinon A3	Magnox	1300	2530	4000	1966	1990 S
	Orleans	St. Laurent A1	Magnox	1570	2572	4240	1969	1990 S
	Orleans	St. Laurent A2	Magnox	1690	2440	4100	1971	1992 S
Germany	Juelich	AVR	HTGR	48	225	ND	1967	1988 S
	Uentrop	THTR 300	HTGR	750	300	300	1985	1989 S
Belgium	Mol	BR 1	Air cooled	3.2	472	472	1956	
Italy	Borgo Sabotino	Latina	Magnox	650	2065	ND	1963	1987 S
Japan	Tokai	Tokai 1	Magnox	585	920	1600	1966	1998 S
	Oarai	HTTR	HTTR	30	ND	ND	1998	
North Korea	Nyongbyon	Nyongbyon 1	Magnox	5	ND	ND		
Lithuania	Visaginas	Ignalina 1	LWGR	4800	1700	2000	1983	
	Visaginas	Ignalina 2	LWGR	4800	1700	2000	1987	
Russian Fed	Kurchatov	Kursk 1	LWGR	3200	1798	2000	1976	
	Kurchatov	Kursk 2	LWGR	3200	1798	2000	1979	
	Kurchatov	Kursk 3	LWGR	3200	1798	2000	1983	
	Kurchatov	Kursk 4	LWGR	3200	1798	2000	1985	

Country	Location	Reactor	Type	Thermal Power MW(t)	Graphite in reactor tonnes	Graphite total tonnes	Commissioned	S/Down Date
Russian Fed	Kurchatov	Kursk 5	LWGR	3200	1798	2000	Exp. 2005	
	Sosnovy Bor	Leningrad 1	LWGR	3200	1798	2638	1973	
	Sosnovy Bor	Leningrad 2	LWGR	3200	1798	1798	1975	
	Sosnovy Bor	Leningrad 3	LWGR	3200	1798	1798	1979	
	Sosnovy Bor	Leningrad 4	LWGR	3200	1798	1798	1981	
	Desnogorsk	Smolensk 1	LWGR	3200	1798	2158	1982	
	Desnogorsk	Smolensk 2	LWGR	3200	1798	1798	1985	
	Desnogorsk	Smolensk 3	LWGR	3200	1798	1798	1990	
	Beloyarsk (Zarechny)	AMB 1	LWGR	286	813	875	1964	1983 S
	Beloyarsk (Zarechny)	AMB 2	LWGR	530	813	875	1967	1990 S
	Obninsk	AM-1	LWGR	10	41	41	1954	
	Chucotka (Bilibino)	Bilibino 1	GBWR	62	133	133	1974	
	Chucotka (Bilibino)	Bilibino 2	GBWR	62	133	133	1974	
	Chucotka (Bilibino)	Bilibino 3	GBWR	62	133	133	1975	
	Chucotka (Bilibino)	Bilibino 4	GBWR	62	133	133	1976	
	Chelyabinsk 40 (Mayak)	A-Anotchka	LWGR	500	1010	1010	ND	
	Chelyabinsk 40 (Mayak)	IR-A1	LWGR	500	146	146	ND	
	Chelyabinsk 40 (Mayak)	AV-1	LWGR	2000	1473	2173	ND	
	Chelyabinsk 40 (Mayak)	AV-2	LWGR	2090	1473	2173	ND	
	Chelyabinsk 40 (Mayak)	AV-3	LWGR	1500	1473	2173	ND	
	Krasnoyarsk-Zelenogorsk	AD	LWGR	2500	1960	3024	ND	
	Krasnoyarsk-Zelenogorsk	ADE-1	LWGR	2500	1960	3024	ND	
	Krasnoyarsk-Zelenogorsk	ADE-2	LWGR	2500	1960	3024	ND	
	Tomsk (Seversk)	I-1 Ivan-1	LWGR	2500	1366	2066	1955	1990 S
	Tomsk (Seversk)	I-2 Ivan-2	LWGR	2500	1366	2066	1958	1990 S
	Tomsk (Seversk)	ADE-3	LWGR	2500	1960	3024	1961	1992 S

Country	Location	Reactor	Type	Thermal Power MW(t)	Graphite in reactor tonnes	Graphite total tonnes	Commissioned	S/Down Date
Russian Fed	Tomsk (Seversk)	ADE-4	LWGR	2500	1960	3024	1985	
	Tomsk (Seversk)	ADE-5	LWGR	2500	1960	3024		
Spain	Hospitalet de l'Infant	Vandellos	Magnox	1750	2440	ND	1972	1990 S
UK	Dungeness	B 1	AGR	1550	850	ND	1983	2013*/
	Dungeness	B 2	AGR	1550	850	ND	1985	2013*/
	Hartlepool	1	AGR	1500	1360	ND	1983	2014*/
	Hartlepool	2	AGR	1500	1360	ND	1984	2014*/
	Heysham	Unit I-1	AGR	1500	1520	ND	1983	2014*/
	Heysham	Unit I-2	AGR	1500	1520	ND	1984	2014*/
	Heysham	Unit II-1	AGR	1600	1520	ND	1988	2018*/
	Heysham	Unit II-2	AGR	1600	1520	ND	1988	2018*/
	Hunterston	B1	AGR	1496	970	ND	1976	2007*/
	Hunterston	B2	AGR	1496	970	ND	1977	2007*/
	Hinkley Point	B1	AGR	1500	970	ND	1976	2006*/
	Hinkley Point	B2	AGR	1500	970	ND	1976	2006*/
	Torness	1	AGR	1555	1520	ND	1988	2024*/
	Torness	2	AGR	1555	1520	ND	1989	2024*/
	Bradwell	Unit 1	Magnox	500	1810	1931	1962	2002 S
	Bradwell	Unit 2	Magnox	500	1810	1931	1962	2002 S
	Calder Hall	Unit 1	Magnox	270	1164	1630	1956	2004 S
	Calder Hall	Unit 2	Magnox	270	1164	1630	1957	2004 S
	Calder Hall	Unit 3	Magnox	270	1164	1630	1958	2004 S
	Calder Hall	Unit 4	Magnox	270	1164	1630	1959	2004 S
	Chapelcross	Unit 1	Magnox	260	1164	1630	1959	2004 S
	Chapelcross	Unit 2	Magnox	260	1164	1630	1959	2004 S
	Chapelcross	Unit 3	Magnox	260	1164	1630	1959	2004 S

Country	Location	Reactor	Type	Thermal Power MW(t)	Graphite in reactor tonnes	Graphite total tonnes	Commissioned	S/Down Date
UK	Chapelcross	Unit 4	Magnox	260	1164	1630	1960	2004 S
	Dungeness	A1	Magnox	780	2150	2237	1965	2005*/
	Dungeness	A2	Magnox	780	2150	2237	1965	2005*/
	Hinkley Point	A1	Magnox	947	2210	2457	1965	2000 S
	Hinkley Point	A2	Magnox	947	3310	2457	1965	2000 S
	Oldbury	Unit 1	Magnox	893	2061	2090	1967	2007*/
	Oldbury	Unit 2	Magnox	893	2061	2090	1968	2008*/
	Sizewell	A1	Magnox	800	2237	2240	1966	2006*/
	Sizewell	A2	Magnox	800	2237	2240	1966	2006*/
	Wylfa	A1	Magnox	1760	3470	3740	1971	2005*/
	Wylfa	A2	Magnox	1760	3470	3740	1971	2005*/
	Berkeley	Unit 1	Magnox	585	1938	1650	1962	1989 S
	Berkeley	Unit 2	Magnox	585	1938	1650	1962	1988 S
	Hunterston	A1	Magnox	545	1780	2150	1964	1990 S
	Hunterston	A2	Magnox	545	1780	2150	1964	1989 S
	Trawsfynydd	Unit 1	Magnox	860	1900	1980	1965	1991 S
	Trawsfynydd	Unit 2	Magnox	860	1900	1980	1965	1991 S
	Windscale	WAGR	AGR	110	285	285	1963	1981 D2
	Winfrith	Dragon	HTR	20	40	40	1964	1976 D
	Windscale	Pile 1	Air cooled	180	<2000	<2000	1950	1957 D1
	Windscale	Pile 2	Air cooled	180	2000	2000	1951	1958 D1
	Harwell	BEPO	Air cooled	6.5	766	766	1962	1968 S
	Harwell	Gleep	Air cooled	0.003	505	505	1947	1990 D
Ukraine	Chernobyl	Unit 1	LWGR	3200	1700	2000	1977	1996 S
	Chernobyl	Unit 2	LWGR	3200	1700	2000	1978	1991 S
	Chernobyl	Unit 3	LWGR	3200	1700	2000	1981	2000 S

	Chernobyl	Unit 4	LWGR	3200	<1700	< 2000	1983	1986 S
	Platteville Col	Fort St.Vrain	HTGR	842	ND	ND	1976	1989 S
	Peach Bottom, PA	Peach Bottom	HTGR	115	ND	ND	1967	1974 S
USA	Hanford	B Reactor	LWGR	250	1080	ND	1944	1968
	Hanford	D Reactor	LWGR	250	1080	ND	1952	1967
	Hanford	F Reactor	LWGR	250	1080	ND	1945	1965
	Hanford	DR Reactor	LWGR	250	1080	ND	1950	1964
	Hanford	H Reactor	LWGR	400	1080	ND	1949	1965
	Hanford	C Reactor	LWGR	650	1080	ND	1952	1969
	Hanford	KW Reactor	LWGR	1850	1080	ND	1955	1970
	Hanford	KE Reactor	LWGR	1850	1080	ND	1955	1971
	Hanford	N Reactor	LWGR	4000	1080	ND	1964	1987
	Savannah River	SR - 305	test	0	ND	ND	1953	D
	Savannah River	SP		0.01	ND	ND	1953	S
	Oak Ridge	8 GR (X-10)	Air cooled	3.5	ND	ND	1943	D
	Brookhaven	BGRR	Test	20	440	ND	1950	1969
	Chicago	CP-1	Test	0	ND	ND	1942	D
	Pacific North West Labs	HTLTR	Air cooled	0.002	ND	ND	1967	S
	Pacific North West Labs	HTR USA		ND	ND	ND	1945	S
	Argonne Nat. Laboratory	CP-2	Graph.pile	0.02	ND	ND	1943	S
China	INET Tsinghua	HTR-10	HTR	10	111		2000	
	Baotou	ND	Air-cooled	20-50?	ND	ND	1963-64	
	Jiuquian	ND	LWGR	400-500	ND	ND	post 1962	
	Guangyuan	ND	LWGR	1000	ND	ND	1973	

*/ - expected shut down
Graphite in reactor - moderator + shielding blocks
Graphite total - graphite in reactor + graphite sleeves + graphite from maintenance/refurbishment
ND – data non-available or classified

2.1.3. Quantities of graphite

Table I provides also the approximate amount of graphite in each reactor, if available. These figures correspond mostly to the amount of moderator and reflector in the reactor. Information on the total graphite inventory at the site, including sleeves and other graphite waste, is provided if such information is available.

2.2. RADIOACTIVE GRAPHITE ARISING IN NPP OPERATION AND MAINTENANCE

During operation, some reactor systems result in a considerable amount of graphite waste being generated. In many cases this waste is associated with always fuel cans, fuel support structures, and in some cases the fuel itself. It may not be possible or desirable to separate graphite from these items, and unique methods for the disposal of some of this type of waste may be needed.

Ref. [2] includes useful descriptions of the graphite usage and structures in fission reactors, which are outlined above. Disposition of materials from fusion reactors (first wall, etc.) is not considered here. Waste of this type includes the following:

— Numerous fuel designs include graphite fuel sleeves. These may have been removed from the fuel elements immediately after discharge from the reactor and retained on the reactor site. The Magnox reactor designs at Tokai 1, Vandellos and Hunterston A, for example, have this feature. Alternatively, they may have been retained with the fuel element when it is returned to the fuel supplier for disposal or re-processing, and thus give rise to a graphite waste stream from the fuel reprocessing plant. The French graphite reactors have fuel with a graphite sleeve and also (except for Chinon A1) a central graphite core (see Fig 7). The central core was retained when the fuel was returned for reprocessing. Fuel elements from the UK AGRs also come into this second category, being returned for processing with intact sleeves. The graphite arising from these fuel elements may therefore have been stored in aqueous solutions for considerable periods before being separated from the fuel element, and may therefore exhibit different chemical behaviour, radioactive inventory, and leaching characteristics compared to graphite from other sources.

— In the UK, the fuel for the Magnox reactors at Berkeley contained additional small graphite items other than sleeves which were removed from the fuel elements along with Magnox struts and braces at the power-station. This feature was not included in any subsequent UK Magnox design.

— The Russian AM and AMB power production reactors at Obninsk and Beloyarsk, and the combined heat and power reactors at Bilibino, contain a unique fuel design where both the fuel elements and cooling tubes are located in a system of graphite sleeves. These graphite sleeves are part of the fuel assembly and are removed with the fuel.

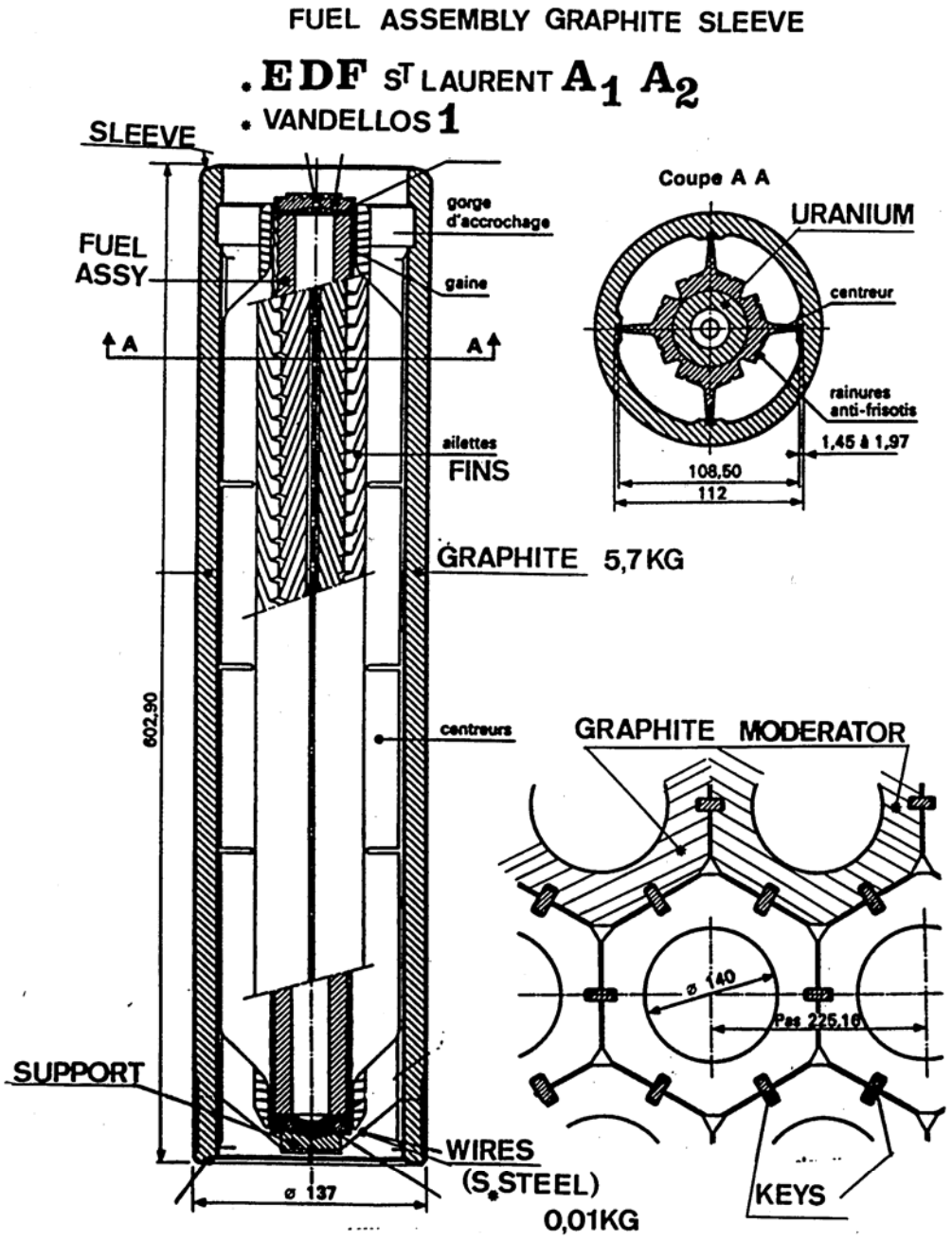

FIG. 7 Fuel assembly with graphite sleeve and central graphite core.

— The coolant in the Russian RBMK reactors flows through a series of zirconium fuel-channel tubes. Thermal contact is maintained between the zirconium fuel channel tube and the graphite moderator bricks by a series of graphite rings. Fuel channel tubes of the RBMK reactors can be replaced during operation. This involves not only removal of the zirconium tubes but also removal of the graphite rings. This will create an additional amount of graphite waste. In addition, there is a small amount of graphite used as displacer elements associated with the control rods. Although this displacer graphite is small in quantity, it is possible that it may contain a significant amount of stored energy owing to the low temperature at which it was irradiated. There are also some graphite blocks from moderator repairs stored near some Russian reactors.

— A special case of graphite wastes arising from the reactor fuel occurs with the fuel compacts of helium cooled high temperature reactors. It appears increasingly unlikely, at least in Europe, that separation will be attempted. Such fuel blocks will probably be disposed of intact as intermediate-level wastes. The possibility to dispose of this fuel without the need for processing gives this type of reactor a distinct advantage. Disposal methods for spent fuel are discussed in [3]. However, in the USA, serious efforts are being directed to investigations of the advantages of separation and volume reduction in the context of finding the most environmentally-friendly solution for disposal of the wastes from Peach Bottom Unit-1 and Fort St. Vrain.

— The graphite/carbon materials associated with the fuel “pebbles” of the German AVR and THTR are a similar case for which the policy remains unclear, although a scheme for milling or peeling off the outer particle-free graphite from the pebbles has been proposed in [4]. It is claimed that 50% of the graphitic material can be removed in a simple first stage, and with the addition of a wire-brushing stage, up to 95% of the carbon and graphite can be recovered without inadvertent inclusion of fuel particles. Reflector graphite blocks from HTR and AVR may be treated in a similar fashion to those from other gas-cooled reactors.

— HTR designs are under development in South Africa, while the HTR–10 reactor in China and the HTTR in Japan are now in operation. For these reactors, decommissioning plans, dealing also with radioactive graphite waste management, were considered at the design stage.

— Special irradiated graphite items exist in some reactors. An example from the UK is the graphite boats and dowels used in the Windscale Piles and now stored in a radioactive waste silo.

— There are also graphite and carbon components which are included in graphite moderated and other types of reactors as a biological protection (biological shield).

2.3. RADIOACTIVE GRAPHITE ARISING IN NPP DECOMMISSIONING

The great majority of the radioactive graphite arising from nuclear plant decommissioning is associated with the bulk moderator and reflector graphite in these reactors, together with shield-wall graphite (or other carbon-bearing material) in certain cases.

In the largest reactors (e.g. later Magnox reactors) this can amount to over 3000 tonnes of graphite per reactor.

Permanent moderator and reflector blocks are present in all the reactor designs already mentioned in this review, including HTR.

In addition, a number of water-moderated reactors including research reactors (like the UK DIDO, PLUTO and DMTR) include graphite reflectors. Some of this graphite contains significant quantities of boron.

The moderator and reflector components will mainly consist of large graphite blocks, e.g. 200 mm x 200 mm x 1500 mm for the earlier Magnox reactors (G2, G3), through 250 mm x 250 mm x (200, 300, 500 and 600 mm) for RBMK reactors to approximately 460 mm diameter x 900 mm long in the AGRs.

The reflectors in some of the high temperature helium-cooled reactors have massive wedge shaped graphite blocks of high-density graphite.

There are also large quantities of small graphite items in some cores, such as the tiles in the Calder Hall type of design, which are about 200 x 200 x 25 mm.

2.4. OTHER CONTAMINATED GRAPHITE

There is also a large quantity of non-irradiated graphite worldwide associated with the production of nuclear weapons, which will need to be addressed using similar techniques as discussed here, with special consideration to contamination by plutonium.

3. GRAPHITE WASTE CHARACTERIZATION

3.1. PHYSICAL AND MECHANICAL PROPERTIES

Nuclear graphite is manufactured from petroleum or natural pitch cokes. These cokes are baked, blended and mixed with a binder and formed by extrusion, moulding or isostatic pressing into various shaped blocks known as the "green article". The "green article" is then baked at about 800^{o}C forming a carbon block. These are used directly for shielding or insulation in some reactors. Blocks intended for the moderator or reflector are then graphitised at ~2800^{o}C and may then be further impregnated with pitch, re-baked and re-graphitised in order to increase the density. Non-irradiated nuclear graphites have initial densities in the range 1.6-1.8 g/cm^3. This can be compared with a theoretical density for natural graphite of 2.265 g/cm^3, the difference being due to internal porosity in the manufactured blocks.

The type and size of coke used and the manufacturing route determine the graphite virgin material physical properties. As an example, Table II gives virgin material properties for the UK Pile Grade A (PGA) and Gilsocarbon graphites. PGA was the graphite used in the early Magnox reactor designs. Gilsocarbon is a more robust graphite developed for the later UK AGRs.

Fast neutron irradiation and radiolytic oxidation radically change the physical and mechanical properties of nuclear graphite. In reactors where the graphite operates in an inert atmosphere, such as the light water graphite moderated reactors (LWGR), or the high temperature helium cooled reactors (HTR), radiolytic oxidation is not an issue. However in gas or air-cooled reactors extensive radiolytic oxidation can take place. For example, French Magnox reactor Bugey 1 has parts of the core which had reached 35% weight loss at the end of life [5] and similar graphite weight losses are now being encountered in some of the UK Magnox and AGR reactors. Methane injection has been used in Bugey 1, Oldbury and the AGRs to reduce the rate of graphite weight loss. Radiolytic oxidation takes place within the accessible graphite pores and does not preferentially attack the graphite component surface. For this reason the component's shape and size will not be greatly affected by radiolytic oxidation during the operational life.

Thermal oxidation is only likely to be of concern in reactors, where accidents have occurred. For example, in the fire-affected zone of the Windscale Piles the thermal oxidation is known to have increased the channel size and weakened some of the components. As an example, there are visible penetrations between certain horizontal fuel channels and vertical shut-down-rod channels [6]. However, it was noticed at Obninsk NPP [7] that the content of carbon dioxide in the gas circuit during periods of reactor operation after "wet accidents" (leakage from coolant tubes) was significant and indicates an intense process of graphite oxidation. In this case, the structure and surface of some graphite blocks were partially destroyed.

The main property changes likely to be encountered during decommissioning of reactor cores are discussed in more detail below.

TABLE II. TYPICAL VIRGIN PROPERTIES OF PILE GRADE A (PGA) AND GILSOCARBON GRAPHITE

Property	Units	Pile Grade A graphite (Anisotropic)	Gilsocarbon graphite (Isotropic)
Density	$g.cm^{-3}$	1.74	1.810
Thermal expansion coefficient (20-120°C)	K^{-1}	$0.9.10^{-6}$ * $2.8.10^{-6}$ **	$4.3.10^{-6}$
Thermal conductivity (20°C)	$W.m^{-1}K^{-1}$	200 * 109 **	131
Young's modulus (20°C)	$GN.m^{-2}$	11.7 * 5.4 **	10.85
Strength tensile	$MN.m^{-2}$	17 * 11 **	17.5
Strength bend	$MN.m^{-2}$	19 * 12 **	23.0
Strength compression	$MN.m^{-2}$	27 * 27 **	70.0
Electrical resistivity	μ ohm.cm^{-1}	620 * 1100 **	900

* Parallel to extrusion.
** Perpendicular to extrusion.

3.1.1. Wigner (stored) energy

Wigner energy (or "stored" energy) occurs in graphite under neutron irradiation because atoms are displaced from their normal lattice positions into configurations of higher potential energy [8]. The quantity of accumulated stored energy is a function of fast neutron flux, irradiation time, and temperature. The higher the irradiation temperature, the lower is the amount of "stored" energy. In all cases, a saturation point may be achieved in terms of the total amount of stored energy for long periods of irradiation. The maximum amount of stored energy ever found in a graphite sample is ~2,700 J/g, which if all released at once could theoretically lead to a temperature rise of approximately 1500°C assuming adiabatic conditions.

Stored energy can be released if the graphite is heated above its irradiation temperature (50K above is typical to achieve a significant release rate), although a temperature in excess of 2000°C is required before all the energy can be released. In the Windscale Piles, with graphite originally irradiated at low temperatures (between ambient and 130°C), a temperature increase can release stored energy at a sufficient rate that the specific heat

capacity of the graphite is exceeded, resulting in potential adiabatic self-heating of the worst-case graphite to ~350^{o}C. Figure 8 gives typical rate of release curves for Windscale Pile graphite. Some of the curves exceed the specific heat capacity of the graphite, and a self-sustaining energy release is, therefore, theoretically possible. If the energy is not dissipated, significant temperature increases could result.

It was a deliberate attempt to "anneal" out some of the Wigner energy accumulated in Windscale Pile 1 which was an initiating event in the fire of 1957 [9]. Consequently, Wigner energy features strongly in the safety arguments being prepared for the dismantling of Windscale Pile No. 1.

Other reactors potentially affected by Wigner energy issues include the Hanford reactors, early Russian and Chinese production reactors and G1 in France. In Soviet-designed RBMK reactors, a small amount of graphite in contact with cool water tubes in control and instrumentation channels is operated at a sufficiently low temperature to accumulate significant Wigner energy.

The potential risk of triggering an inadvertent release of Wigner energy in these reactors while handling and processing individual graphite blocks during decommissioning, along with the potential for releasing energy during any storage period, packaging, conditioning, and even in the final waste repository, is small but requires assessing. In addition, the graphite in some of these early reactors was subject to various incidents which may have resulted in the graphite being potentially more chemically reactive to air as a result of introduced catalysts. Thus, the combination of these effects means that care will need to be taken in such cases to avoid sources of potential heating during the dismantling of the reactor internals.

Such problems do not arise in the UK, French, Spanish, Japanese and Italian Magnox type reactors or the AGR reactors: and, in these cases, the risk of creating a self-sustaining oxidation in bulk graphite during decommissioning activities is negligible, as discussed in Section 3.2. Although at the base of some of the earlier UK Magnox reactors the total Wigner energy in graphite can be higher than in parts of the Windscale piles, the temperature at which this energy starts to be released is over 200^{o}C. In addition the rate at which the energy is released does not exceed the specific heat capacity, and thus self-heating is not a problem. The principal reason for this is the higher inlet-gas temperatures used during operation compared with the early Piles: these have generally been in the region of 140–210°C for the UK Magnox and even higher for the AGRs.

Stored energy is not an issue in HTR because of the very high graphite temperatures involved.

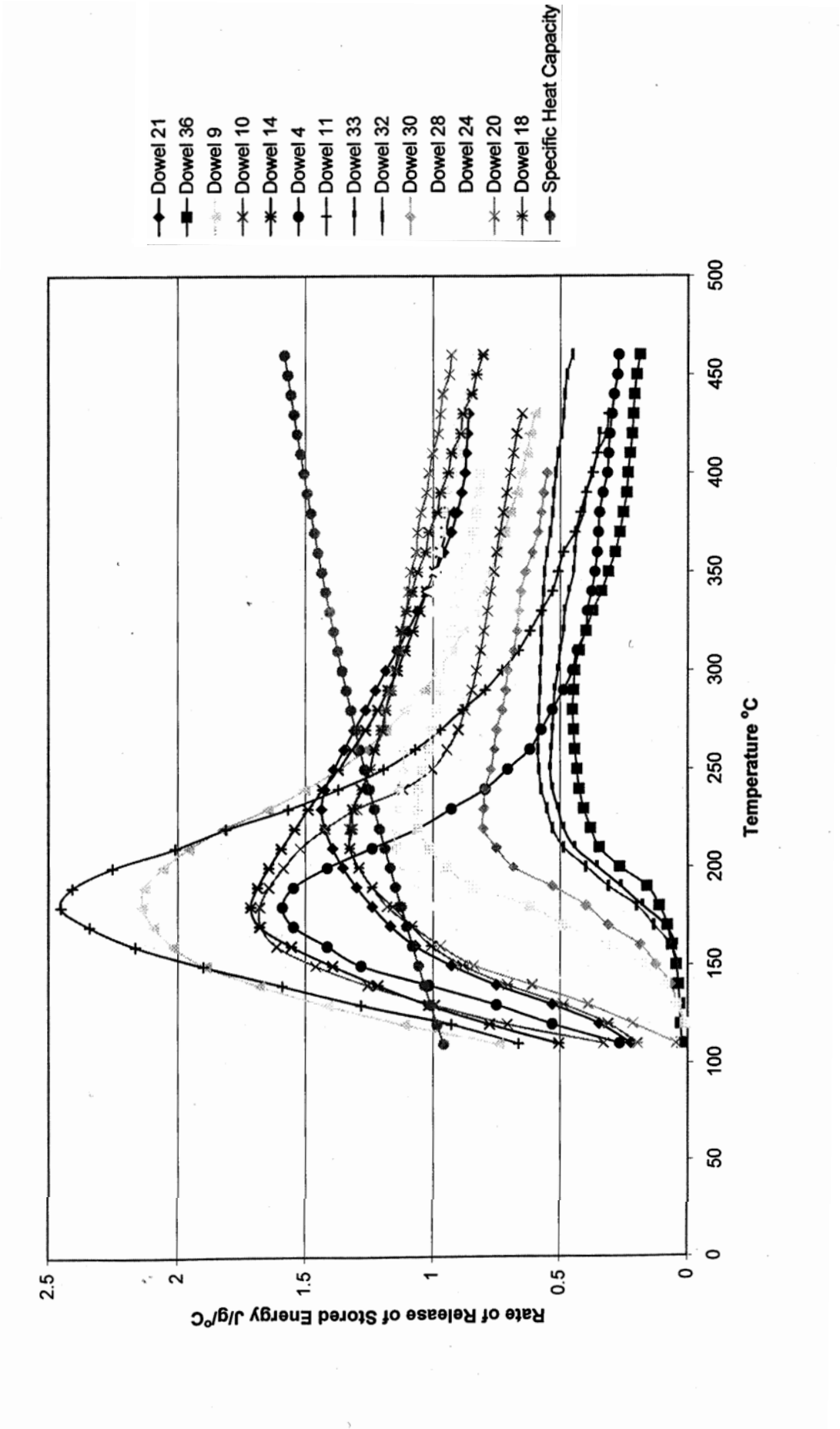

FIG. 8 Rate of release of stored energy from Windscale Pile 2 graphite dowels.

3.1.2. Dimensional change

During reactor operation the graphite components can change dimensions and, in some cases, this can lead to considerable whole core deformations. Up to 200 mm change on core diameter has been measured in some Russian production reactors [10], although most of this expansion was due to brick cracking. Large distortions were also encountered in the Chinese production reactors. A short description of the nature of graphite dimensional changes is given below.

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

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

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

This shrinkage continues until a point is reached when all available “accommodation” porosity adjacent to crystallites (the “Mrozowski cracks” formed on initial cooling from graphitisation) is consumed, and the generation of large crystal stresses and creation of new “bulk” porosity which results causes a phenomenon known as “turn-around.” At this point the graphite start to expand until it reaches its original volume. Irradiation beyond this point can lead to further expansion and degradation of the graphite structure. Some specialists regard the fluence at which the original dimension is regained as the “critical fluence” and an absolute limit to irradiation.

The changes in bulk volume lead to corresponding changes in density.

3.1.3. Modulus and strength

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

Non-irradiated graphite has a non-linear stress-strain characteristic with significant hysteresis. However, a small irradiation dose leads to a much more linear stress-strain characteristic and a significant increase in modulus. With increased irradiation the modulus further increases until at very high doses the graphite structure starts to degenerate and the

modulus falls significantly. The initial increase in modulus is accompanied by an increase in strength, which with continued irradiation follows a similar pattern to the modulus until the graphite degenerates at very high doses. Thermal and radiolytic oxidation also reduces the modulus and strength.

3.1.4. Thermal conductivity

When considering radioactive waste disposal, particularly in deep geological formations, the thermal conductivity of the graphite waste is an important factor, since a small amount of fast neutron damage significantly decreases the thermal conductivity of graphite. With increased irradiation dose the thermal conductivity remains at the low value until, at high doses, the structure of the graphite starts to degenerate. There is then another significant decrease in thermal conductivity. Values as low as 2 or 3 $W.m^{-1}.K^{-1}$ compared with non-irradiated values of around 100–200 $W.m^{-1}.K^{-1}$ can be achieved in graphite irradiated at low temperatures.

Thermal and radiolytic oxidation also reduces the thermal conductivity of graphite as an exponential function of weight loss.

3.1.5. Other properties

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

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

3.2. CHEMICAL REACTIVITY

3.2.1. Oxidation of bulk graphite

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

Chemical reaction in graphite takes place only with extremely powerful reagents. Considering aspects related to safe-storage of graphite cores and eventual decommissioning and disposal, the most relevant oxidation reaction in *solution* which could conceivably occur during storage in moist air in a radiation field — i.e. with the graphite remaining in an air-filled reactor vessel — is with nitric acid. However, in practice, the nitric acid concentrations attainable are orders of magnitude below those which could give rise to exfoliation reactions and structural collapse in the graphite. The reaction is inconceivably slow under storage conditions (either in the reactor vessel or subsequently in a separate storage facility), and the most likely impurities (oxygen and water vapour) are known to inhibit the reaction as does prior irradiation. There are many literature references relating to this reaction; Ref. [11] provides a useful summary and guidance towards the classic literature on this subject.

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

The reaction with air is therefore the only oxidation reaction which needs be considered in detail for graphite-reactor dismantling and storage. There is extensive literature on this subject, which was comprehensively reviewed in 1989–90 [12]. The review covers 130 references. Oxidation of graphite in air is thermodynamically favoured at any temperature below 4000°C. There are three "Modes of Oxidation" which can apply:

— Mode 1, where the oxidation obeys a simple Arrhenius rate law and is characteristic of low-temperature oxidation in which there is an uninterrupted supply of air;

— Mode 2 becomes important at increased temperatures where the potential oxidation rate is high but there is diffusion control on the supply of oxidant imposed by the pore and surface structure of the graphite; and

— Mode 3, at higher temperature, in which the rate of diffusion is no longer limiting and mass-transport limitations apply to the supply of reactant gas.

The larger the graphite component under consideration, the lower the temperature at which the higher oxidation modes become significant.

Many measurements of graphite oxidation rate in air have been made on small samples of moderator and sleeve graphite removed from operating reactors in the UK. Similar measurements have taken place in most other gas-cooled reactors. These have usually been made under Mode 1 conditions and indicate moderate rates of oxidation at 450°C and an activation energy, which effectively precludes significant oxidation below about 350°C. Almost always the measurements have been made at one atmosphere total pressure in ambient air, but it needs to be borne in mind that, for any circumstance where there is a different partial pressure of oxygen, a reaction order of 0.6 is considered to apply, this being the mean average of numerous measurements made and the value accepted within the UK industry.

These measured oxidation rates reveal a radiation enhancement factor resulting from the activation of reacting surfaces by the neutron fluence: this has been approximately quantified and is allowed for in fault studies [13].

Assuming that a similar activation energy applies at low temperatures (as is probable), then there is no significant oxidation at storage temperatures estimated at 30°C for in-reactor-vessel "safe enclosure" and 20–50°C for other storage arrangements: the 30°C value would be eight orders of magnitude below the measured 450°C values allowing for likely changes in the pre-exponential factor of the Arrhenius equation (and a larger factor still if this is ignored). Early work on PGA graphite oxidation using large graphite blocks identified gas-transport limitations (i.e. Mode 3) at temperatures as low as 460°C, which further alleviates the possibility of potential oxidation in air [14].

Measured oxidation rates in irradiated graphite are found also to be elevated as a consequence of modest amounts of inorganic catalysts. The effect of such catalysts is to increase the graphite-oxidation rate above its normal value at any particular temperature. Catalysis is of greatest significance under Mode 1 conditions, and becomes largely irrelevant with Mode 3 where the reaction rate is controlled by the oxygen supply rate. The most potent catalysts are transition-metal compounds and compounds of elements (such as lead), where there is a possibility of transfer between two oxidation states in the oxide form. In [15] there is a useful review of catalytic effects in graphite and carbons, and the same author provides a "merit order" for 21 potential catalytic materials and useful data on substances which could, potentially, be used to inhibit oxidation. Mild catalysts (alkali and alkaline earth compounds) are present in most graphite irradiated in UK reactors but in no case has reactivity in air risen beyond the acceptable limits where the above conclusions would no longer apply.

(Note: Pond-storage of fuel-sleeve material presents an obvious route for contamination with catalysts.)

Graphite cores irradiated in carbon-dioxide-based coolants will also include a proportion of more chemically reactive deposit carbonaceous materials. These tend to be associated with localised areas on the geometrical surfaces of components (e.g. the lower-temperature end of fuel and interstitial channels in which there is a gas flow); they derive from radiolysis of carbon monoxide (which is itself produced by radiolytic oxidation of graphite by the carbon dioxide) to form polymeric materials with a variable oxygen content. Localised concentrations of up to 3% by weight have been found in Magnox reactors, and some typical distributions around a Magnox core are shown in [13]. The formation of this material will be lower in systems where there has also been a hydrogen content in the coolant. The oxidation rate of these carbonaceous deposits (at 450ºC which is the typical measurement temperature because it represents the start temperature for a standard Magnox air-ingress fault study) can be 1000 times that of the underlying graphite.

A related higher-reactivity material, essentially paracyanogen, is found on graphite which has been irradiated while under a nitrogenous cover gas such as in RBMK reactors. In this case, the carbon source in the deposit is from $^{14}N_2$ after neutron irradiation, and is essentially entirely ^{14}C, which needs to be borne in mind when decommissioning.

Oxidation of graphite in air does not present a problem for the disposal of any graphite from most nuclear reactors. However, it needs to be considered more carefully in reactors which have been subject to serious accidents such as Windscale Pile No. 1, where extensive chemical contamination of the graphite has occurred. However, dismantling activities associated with core-restraint structures in any reactor could introduce new catalysts, if appropriate care is not taken; this may also occur if very intense sources of heat are introduced, such as a thermal cutting lance. Under such circumstances, the potential available for poisoning of oxidation sites may well be useful: the methods include gas-phase treatments using, for example, halogens dispersed in nitrogen and even more esoteric compounds, such as phosphorous oxychloride or aqueous treatments involving phosphoric acid.

It is important to set out the circumstances under which significant oxidation of irradiated graphite in air can occur, in order to assist the preparation of decommissioning and storage safety cases. It is easy to find references in the literature to "graphite burning," "graphite fires," etc. and such remarks have attracted the notice of some Regulatory

authorities who have come to regard irradiated graphite as a potential fire hazard. The reality is quite different. The Appendix therefore offers suggested definitions of terms commonly encountered in relation to graphite oxidation, and it is proposed that the industry should refer to graphite *oxidation* which the correct description of the chemical process undergone when reacting with air or oxygen.

There have been numerous convincing demonstrations that nuclear-grade graphite will not "burn" (i.e. demonstrate or sustain a visible flame); recent work from EdF and from SOGIN complements work previously undertaken in the UK and the USA. For example, Schweitzer [16] describes experiments designed to support an operational life-extension for the N reactor at Hanford. 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 supplied 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 confirms a rather simple test previously conducted in the UK to support decommissioning of the WAGR, in which the temperatures attained were rather lower.

Schweitzer has defined the conditions which must be satisfied *simultaneously* before a *self-sustaining* oxidation reaction can take place between graphite and air, based upon research conducted at Brookhaven National Laboratory following the Windscale fire:

(1) a minimum temperature of 900°C
(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 which creates an almost negligible quantity of ash which could otherwise retain heat. Even irradiated graphite, when reheated to temperatures approaching 900°C, exhibits reasonable thermal conductivity so that bulk components are further prevented from attaining combustion by this additional heat-removal mechanism.

More recently, 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 [17]. 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…")*.

Richards' view on these crucial incidents has recently been endorsed again by Schweitzer in a contribution to a recent IAEA specialists' meeting [18]. Both authors now concur that satisfying Schweitzer's criteria for self-sustaining combustion is both necessary and essentially unachievable in realistic situations. Consequently, it is relatively simple to ensure that conditions leading to the simultaneous satisfaction of the Schweitzer criteria cannot be achieved when planning a dismantling, handling, or disposal activity for irradiated graphite. These principles have been successfully applied recently — for example, in the case for utilising flame-cutting equipment during the dismantling of WAGR [19].

3.2.2. Graphite dust explosibility

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

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

It is useful to present the criteria (discussed in detail in [20]), all of which must be satisfied before a dust explosion can be initiated:

- The dust must be combustible;
- The dust must be airborne, implying a need for a turbulent gas flow;
- The particle size must be optimized for flame propagation;
- The dust concentration must fall within an 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; (the use of thermal cutting devices should be avoided);
- The atmosphere in which the dust is suspended must contain sufficient oxygen to support combustion.

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 ignition.

As far as graphite dust is concerned, numerous tests were conducted some years ago on non-irradiated material, including a series of tests at the AEA Technology laboratories at Winfrith in support of a design for a reactor using a carbon-dioxide/suspended-graphite-dust coolant medium. No explosions were observed unless the oxygen concentration exceeded 90% while 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 extremely small particle sizes (e.g. 0.3μm) did any obvious hazard appear — such dusts became self-heating from an initial temperature of 90°C when exposed to air.

Additional tests at the Chapelcross graphite-monitoring laboratory, and further tests commissioned at the former Fire Research Station, failed to find any evidence for inherent explosiveness in graphite dusts except when extremely powerful chemical igniters were present in the apparatus together with an extremely high dust concentration.

It should also be noted that Framatome conducted an assessment of dust explosibility in connection with their pilot-plant design for a crushing and incineration plant for irradiated graphite and concluded that there was no risk [21].

In Spain 1,000 tons of irradiated graphite was crushed without causing any explosion risk with the dust resulting from this operation.

It will therefore be readily understood that graphite dust was originally classified as "non explosible" by the UK's standard Fire Research Station criteria [20] (and other international agencies), and it was not considered that irradiation under Magnox or AGR conditions was likely to affect this.

New studies have recently been conducted in the UK in support of the Windscale Pile decommissioning, by SOGIN on behalf of Latina decommissioning, and by CNPP in Verdon, France, on behalf of the EdF UNGG decommissioning programme. All three studies have utilized equipment following the most modern standards (ISO 6184-1) [22] which also has the status of a European standard (EN 26184-1) and incorporates the British standard BS 6713-1. The standard test employs a 1 m^3 cylindrical chamber and a turbulent air/dust mixture, with a 10 J chemical igniter composed of zirconium, barium nitrate, and barium peroxide: thus, unlike some older methods, there is a deliberate energy input to the system which also generates a pressure pulse in its own right and which must then be accounted for during the analysis of the injected powder.

In all three studies it has been confirmed that unirradiated nuclear graphite dust representative of the source material for each country's reactors is "weakly explosible" if (and only if) a very favourable particle size is present. This is in contrast to the older spark-source equipment and flame tubes which have consistently failed to ignite any explosion in nuclear graphite dusts over a range of concentrations and particle sizes. The combined preliminary findings from all three studies indicate a number of very important factors:

— only very fine particles admit flame propagation; larger particles act as heat sinks;
— the peak overpressure is produced in the range of 440 $g.m^{-3}$ concentration;
— the minimum explosibility limit is at around 100 $g.m^{-3}$;
— ageing of the dusts over a period of weeks significantly reduces the reactivity (and hence explosibility);
— inerting is possible when significant quantities of impurities are present. While this is easily understood if impurities such as mineral oxides are present, it seems that reactor dust removed from cyclone collectors in Latina is also non-explosible and that potential catalysts such as lead oxides (of concern in the Windscale pile because of the presence of lead components in pile) appear also to act as *inerters*.

Further work was underway as of the end of 2004 in both France and the UK; formal publication of the results is awaited. However, dust explosibility should not present significant hazards for reactor decommissioning, provided that obvious precautions are taken to avoid the suspension of dusts where ignition sources are present, and to avoid conditions where smouldering or self-ignition of deposited dust could occur. (See Appendix for relevant definitions).

It has been observed in all Magnox-type reactors that the concentration of graphite dust in the circuit is in any case extremely low. Overall, it is considered that the simultaneous conditions necessary to result in a dust explosion in graphite can readily be avoided and that bulk graphite handling under foreseeable conditions (by whatever route) during storage and decommissioning is not prejudiced by any explosiveness risk arising from any dust generated.

It should be noted that it is possible that other more reactive carbonaceous dust may be present in some reactors due to deposits from oil ingress, fire accidents, or coolant deposition, as discussed earlier. Therefore, due care must be taken if these deposits are present in significant volumes.

3.2.3. Galvanic corrosion

Graphite may react electrochemically with other materials. Acting like a “noble” metal, graphite can promote accelerated corrosion of other metals by electrical (galvanic) coupling, in which local electrolytic cells driven by potential differences lead to increased dissolution and oxidation of less noble metals. Graphite is more electronegative even than stainless steel, so that direct contact between graphite wastes and stainless steel containers can lead to premature penetration and loss of integrity. Experimental studies have shown that corrosion rates can be increased by factors of up to ten [23]. A number of preventative measures have been identified, including use of cement grouts and baskets to isolate graphite from stainless steel waste containers.

3.3. GRAPHITE RADIOACTIVITY

This section examines the potential radioactive material associated with graphite and its implications for the choice of disposal route.

The nuclear graphite in most reactors will have been exposed to very high integral neutron flux (up to 5.10^{22} n/cm^2 [24]) and has a significant radionuclide content arising both from the activation of impurities in the original graphite and from material transported from

other parts of the reactor circuit (e.g. steel-oxidation products) which has also become activated and is held on or within the graphite components. Before disposal of the graphite, the radionuclide content must be estimated in order to determine the most appropriate disposal route. Depending on the graphite source (moderator, reflector or fuel-element components), different quantities of relatively long-lived radionuclides may be present — mainly ^{14}C and ^{36}Cl after a short decay time. Isotopes arising from other sources, such as corrosion products and lesser impurities, include ^{3}H, ^{60}Co, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, , ^{110m}Ag, and ^{109}Cd. In addition to these, quantities of fission products (^{90}Sr, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{113m}Cd, ^{121m}Sn, ^{129}I, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{147}Pm, ^{151}Sm, $^{152, 154, 155}Eu$, etc.), as well as some uranium and transuranium elements (mainly ^{238}Pu, ^{239}Pu , ^{240}Pu, ^{241}Pu, ^{241}Am, ^{243}Am, ^{242}Cm, ^{243}Cm and ^{244}Cm), will arise as a result of fuel failures during operation of the reactor, or just from traces of uranium carried into the core on fuel-element surfaces after fabrication.

3.3.1. Radioactivity, inventory and decay

The radioactivity associated with the graphite components arises both from the activation of the initial impurities and from subsequent contamination arising within the reactor circuit. For items such as fuel sleeves that have been pond stored, the inventory may have been further modified by the immersion in aqueous solution. The contamination may be as solid materials, arising as corrosion products from reactor steel parts, or as a consequence of fuel-element failures, or from gas-phase activation (e.g. ^{14}C arising from activation of ^{14}N in coolant or cover gas) followed by subsequent incorporation into the graphite or into carbonaceous material deposited upon it. The reactor atmosphere may also influence 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 adsorbed compounds containing inactive hydrogen. For instance at Tomsk-7, the significant part of tritium was carried away from the moderator stack by water vapour and cover gas, especially during “wet accidents” (tube leaks) [7].

The initial impurities in various types of nuclear graphite differ significantly. For example, in components, such as fuel sleeves, removed from reactor after relatively short irradiation periods, radioactive inventories may be quite different from those of the moderator. After longer irradiations, such as are experienced by moderator blocks, more isotopes reach equilibrium, and some with short half-lives may even “burn out” entirely. It is not practical to consider all the different graphite types here. In view of this, the following remarks are more general; they are based largely upon calculations carried out for UK materials and upon experimental study performed by a Russian team for graphite stacks from plutonium production reactors [25–27].

A comprehensive analysis of the entire issue of graphite waste disposal is presented in [28], which is a key reference in this topic and utilizes a UK Magnox reactor as a reference case. The estimates of residual radioactivity and subsequent decay are, however, based upon the presumption that the reactors would operate for 40 years at a 70% load factor and that this would be followed by 10 years storage (within the reactor vessel) before the core graphite entered a final disposal route. Sleeve materials, irradiated for much shorter times, are not specifically addressed.

While these assumptions are no longer current, it is worth considering, as an example, the typical impurity concentrations for PGA graphite in UK Magnox reactors and Gilsocarbon

graphite in UK AGRs, given in [28]. ^{14}C, ^{3}H and ^{36}Cl (beta emitters) are the most significant isotopes likely to be present which need to be considered in terms of possible entry to the food chain, while ^{60}Co, ^{94}Nb, ^{152}Eu and ^{154}Eu are the most significant gamma emitters leading to shielding and handling requirements. ^{152}Eu is an exceptional case in that, in a Magnox reactor, most of the activity that remains will be in the outer reflector region because of burnout in regions of higher flux.

The presence of other impurities should also be taken into consideration. For example, stainless steel wires used in fuel assembly graphite sleeves contribute to the total activity. (See Figure 7 in Section 2.)

Uranium impurity in the graphite, although generally below 0.1 ppm, may give rise to fission products and, in a similar way, so can the traces of uranium on the external surface of newly manufactured fuel elements. Generally speaking, radioisotope yields of significant half-life nuclides from fission of these impurities are small compared with the direct activation products, with the exception of the gamma-emitter ^{137}Cs.

In the case of reactors where fuel failures have occurred, significant amounts of uranium may have contaminated the cores, leading to significant amounts of fission products and trans-uranium nuclides. [29].

Adventitious contamination with additional radioactive material from the reactor circuit (e.g. corrosion products) is also probable. In some cases (e.g. certain AGRs in the UK) this represents a very large contribution, since a large movement of cobalt-containing metal oxides within the reactor circuit is known to have occurred, leading to a large additional ^{60}Co contamination factor in the graphite.

In general terms, when the distribution of the gamma-emitters and their half-lives are taken into account over its assumed 10-year storage period, subsequent graphite handling and shielding requirements will effectively be determined by the ^{60}Co alone in both Magnox reactors and AGRs [28].

After 100 years the position changes significantly. The beta-emitting ^{3}H and the ^{60}Co, with half-lives of 12.3 years and 5.3 years respectively, are then at negligible concentrations. ^{14}C, ^{36}Cl and ^{94}Nb have half-lives of thousands of years and no appreciable decay would have taken place. Hence they now dominate the inventory and the handling/storage requirements of the graphite. Reference [28] should be consulted for a thorough analysis of the relative concentrations of activation products as a function of time.

It is perhaps useful to note here that the assessment of the residual ^{14}C inventory is particularly difficult because of the variety of potential sources. This subject was recently reviewed on behalf of UK NIREX [30], who have placed the report in the public domain *via* their website. In a thermal neutron flux there are three principal reactions of ^{14}C generation, as shown in Table III.

TABLE III. (MAIN) ROUTES OF 14C GENERATION (T1/2 = 5730 y)

Reaction	Abundance of mother isotope in natural element (%)	Capture cross section (barns)
$^{14}N(n,p)^{14}C$	99.63	1.8
$^{13}C(n,\gamma)^{14}C$	1.07	0.0009
$^{17}O(n,\alpha)^{14}C$	0.04	0.235

Taking into account the relative concentrations of precursor isotopes, the order of the importance of these reactions would be expected to be as shown. The averaged nitrogen impurity in a typical Magnox-reactor coolant, taken together with the initial impurity level within the graphite structure itself, leads to 61% of the ^{14}C arising from this source in an example calculation. The corresponding figure for an AGR is approximately 70%. A high proportion from this source is also expected in graphite from RBMK reactors because of the nitrogen content of the cover gas.

Clearly, it would be appropriate to perform a fully comprehensive calculation of the isotopics for any specific reactor under consideration before developing a disposal strategy. The following information, as a minimum, would need to be specified:

— The elemental concentrations of impurities in the graphite and coolant (the latter integrated over the operational lifetime);
— The production and decay routes of important isotopes;
— The reaction cross-sections;
— The thermal neutron flux levels in the graphite; and
— Evidence on additional contamination from circuit materials, coolant and fuel which is already activated or can become activated once in the moderator region, with especial reference to its transport and retention by the graphite.

These data would allow point calculations: a methodology is also required to integrate the results over the whole reactor core.

Interesting experimental data has been provided by Russian scientists [25–27]. They made measurements on a number of graphite samples from the plutonium production reactors at Tomsk 7. It is useful to make a number of important observations relating to residual radionuclide concentrations and distributions from this comprehensive experimental study:

— About 500 samples have been taken from the graphite stack of the I-1, ADE-3 and EI-2 reactors and assayed. Contamination of these samples with radionuclides ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{133}Ba, $^{134,137}Cs$, $^{152,154,155}Eu$, ^{238}Pu, $^{239,240}Pu$, $^{241,243}Am$, ^{244}Cm and some others have been determined;

— It was discovered in this study that the dominant activity in the graphite is ^{14}C, and its distribution in the graphite stack is a reflection of the thermal neutron flux. The concentration of ^{14}C in the graphite from this Tomsk reactor was about 6 times higher

then in the graphite from a similar Hanford reactor. A significant fraction of the ^{14}C activity in reactor graphite was indeed due to the presence of nitrogen in graphite nitrogen cover gas);

— The tritium content in the reactor graphite has been measured, and the content appeared to be very small (about several hundred times smaller) than prediction. ^{3}H is distributed non-uniformly in the graphite stack;

— The dominant fraction of the ^{60}Co concentration in reactor graphite is due to the presence of original ^{59}Co impurity in graphite;

— It was found that actinides and fission products are concentrated on the block surface (within a thickness of 2 mm). The penetration of radionuclides from block surface to its volume is very small. There is the correlation of specific activities between the fission products. Actinide distribution is a reflection of the neutron flux.

Some of these measurements are made by indirect methods and the quality of some of the results in not completely clear. For this reason there is a need for an international benchmark exercise so that standards of measurement technique can be set.

A further potentially useful reference, now unclassified, covers the radionuclide inventory of all the USA Hanford reactors except for the 'N' reactor [24], with comprehensive information for each graphite stack and other reactor components.

3.3.2. Gas-phase activity release

Tests carried out at the Kurchatov Institute [31] have shown that graphite submitted to long range gamma irradiation of up to 2 MGy results in both a gaseous product release and an enhanced potential for radiolytic oxidation in air. However, a cumulative dose up to 2 MGy is unlikely to occur in any of the graphite reactor cores kept in safe storage after closure. The Magnox reactor dose rate is estimated to be 10^{-2} Sv/hr at the time of shut down and tends to decrease to 1μSv/h after 80 years [32]. However, this risk has to be carefully checked regarding the impact on the environment caused by very long deferral in decommissioning graphite moderators.

Gas-phase activity release from irradiated graphite is primarily associated with ^{14}C and ^{3}H. The former will require consideration for time scales on the order of thousands of years (^{14}C half-life of roughly 5730 years), regardless of the route for graphite storage and disposal; whereas the latter will diminish in importance as time passes, because of the relatively short ^{3}H half-life of 12.3 years.

Consider first the potential for release from solid graphite, assuming contact with a gaseous environment. During normal storage and disposal the gas-phase release of ^{14}C and ^{3}H is not a problem. However, under accident conditions (e.g. unforeseen heating during "safe enclosure" or transportation), the possibility of a release should be taken into account. It is known, for example, that it was possible to mobilise (and remove) typically 87% of the ^{3}H and around 63% of the ^{14}C from graphite blocks removed from the Graphite Low Energy Experimental Pile (GLEEP) reactor (Harwell, UK) by calcination at 1150ºC for approximately three hours in an industrial incinerator [33]. This was only made possible by

the very low irradiation achieved by GLEEP, which allowed the blocks to be removed by hand and the total activities to be within the discharge limits for the industrial plant employed.

It is assumed that the majority of the ^{14}C formed close to accessible geometric and pore surfaces since, in order for ^{14}C to be released in significant quantities by exchange with gas-phase species, replenishment of ^{14}C on the graphite surfaces by internal solid-state diffusion would be required. Ref [34] suggests that there is no significant diffusion of carbon atoms within the graphite matrix until a temperature of 1800°C is reached.

According to [35], nitrogen molecules are absorbed on graphite basal plane surfaces with weak interactions. Taking into account the leaching of ^{14}C and distribution of nitrogen on the graphite surface it was suggested that the bulk of ^{14}C activity remained in the graphite matrix which was quite stable, only the ^{14}C localized on the surface of the irradiated graphite was released to the environment.

Tritium in graphite arises from the reaction $^{14}N + n = {}^{12}C + {}^{3}T$ and also from lithium (^{6}Li) impurity in the graphite; but it is also considered that a significant source in Magnox type reactors is from fission. Gas-phase kinetics experiments at the Bradwell and Wylfa reactors in the UK have shown that surface ^{3}H is transferred to gas-phase hydrogenous species with ease. [36, 37] This implies that tritiated species adsorbed on to the graphite surface will have exchanged tritium with atmospheric moisture and that this tritium will have been lost very quickly after reactor operation ceases. Further releases would be dependent upon the solid-state diffusion of tritium within graphite, which is very much slower than the surface exchange rate [38] but remains significant, at least at reactor operating temperatures. However, the activation energy for the process is high (253.7 $kJ.mol^{-1}$), implying a rapid reduction in potential releases with reducing temperature.

The possibility of activity release through biological processes should also be considered for any long-term graphite storage.

The issue of gaseous activity releases during incineration processes is addressed later.

3.3.3. Particulate release

During a storage period graphite may release particulates from:

— Graphite itself;
— Carbonaceous deposits within its pores and upon its surfaces;
— Deposited or entrained contaminants.

The carbonaceous deposits on irradiated graphite are generally closely adherent and are only released under such conditions as would abrade the graphite itself. In order for this to occur there would either have to be mechanical abrasion or other disturbance of the graphite (or of the atmosphere surrounding it), or corrosion (oxidation) of the graphite. Mechanical abrasion could conceivably occur as a result of temperature changes, but it is unlikely that graphite stored either in a reactor vessel or in individual containers would be subject to temperature changes of more than a few degrees. During reactor operation, temperature

swings of several hundred degrees, and the associated thermal movements, which have been monitored, have not given rise to any significant graphite abrasion.

Attention should also be drawn to the observation on some UK samples of irradiated graphite of the presence of metallic-oxide residues, particularly on AGR fuel sleeve samples where red haematite (Fe_2O_3) has been noticed after limited oxidation in air at 450°C. Contamination of moderator graphite with metal oxides, leading to contamination with ^{60}Co in particular, has already been discussed.

3.3.4. Leaching by liquids

Leaching of activity from graphite is primarily a disposal issue, although it is also an issue in "safe enclosure" or any long-term storage arrangement. It is also pertinent to graphite debris stored in vaults or silos.

To prevent activity leaching from graphite waste, many options have been proposed worldwide. These include graphite coating, encapsulation in various matrix materials, sealing graphite into containers, etc. Russian technologists propose that graphite falling into ILW or LLW categories should be impregnated with a sealant (known only as "F preservative") or an inorganic phosphate [39].

It should be noted, however, that some graphite waste has been stored under water in ponds and silos. The original reason for this was to avoid oxidation ("fires")[1], release of Wigner energy, etc. In some cases, some fuel debris may still remain associated with stored graphite, and there may be a risk of criticality due to neutron moderation. For a similar reason, water must be excluded from reactor cores which contain fuel debris to avoid criticality accidents.

The water that might contact the graphite while in "safe enclosure" within a reactor vessel or in surface storage originates as rain water or condensate water. In the case of rainwater, dissolution of atmospheric carbon dioxide may result in a weakly acidic solution. Atmospheric pollutants may further lower the pH. However, if the rainwater interacts with building materials, this could result in a considerable rise in pH to alkaline conditions.

Immediate exchange of surface-bound tritium with the water would be probable. The possibility of desorption of other radioisotopes must be considered, but those chemically bound within the solid are unlikely to be leached until the carbon atoms themselves are leached: this may be by the corrosion processes or by selective dissolution from other minor phases within the graphite. The most important studies on leaching of radioactivity from reactor-irradiated graphite are discussed below:

— The first study indicates that the leaching mechanism for carbon species is a water-catalysed oxidation by dissolved oxygen to form carbon dioxide [40]. There is some evidence that, in the early stages, ^{14}C is oxidised (and leached) at a greater rate than stable ^{12}C. Data are available at 20°C for French graphite and between 20–90°C for the Hanford graphite [41,42]. Values in the range $6.10^{-7} – 5.10^{-13}$ $g.m^{-2}.day^{-1}$ were found for

[1] A perceived but unreal threat, as has already been explained.

^{36}Cl and in the range $1.10^{-10} – 5.10^{-13}$ for ^{14}C, illustrating the importance of obtaining data on representative graphite.

— Another study deals with material from earlier French gas-cooled reactors and covers ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{133}Ba, ^{137}Cs and ^{154}Eu [43,44]. Relationships for normalised cumulative release fractions are given, but as sample volumes and areas are not clearly defined it is not possible to compare the quantitative data with other studies; however, the leach rates decreased in the order ^{137}Cs and ^{133}Ba, ^{60}Co and ^{63}Ni, ^{36}Cl, ^{154}Eu, ^{14}C, with ^{3}H values ranging between those for ^{60}Co and ^{14}C. More recent work in France showed that ^{3}H was not released after 450 days of leaching test on the sleeves from St. Laurent.

— Data from UK Magnox-reactor graphite (PGA) may be found in [28]. Leach-rate data were determined for ^{3}H, ^{14}C, ^{60}Co, ^{133}Ba and ^{134}Cs into de-ionised water, into simulated argillaceous rock groundwater, and into simulated seawater. In this case a standard IAEA procedure for leach tests was followed [45]. Generally, the results were similar (in respect of relative leach rates) to the French work except for Cs; however, the two studies were on different Cs isotopes. The detailed results quoted further illustrate the differences between samples and sample sources, which have generally been found, and further stress the need for data on material specific to the reactor of interest.

Generally, leach rates are initially rather erratic but tend to stabilize within the experimental timescales which have been on the order of 50–140 days. A significant decrease in leach rates for timescales of tens or hundreds of years would be expected. It should also be noted that a computer code exists for calculating leaching behaviour using thermodynamic data for the water compositions and the solid phases (graphite, solid hydroxides, carbonates and amorphous oxides) likely to be the solubility-limiting phases [46].

4. GENERAL APPROACH TO RADIOACTIVE GRAPHITE MANAGEMENT

4.1. GENERAL APPROACH

Over the last twenty years, numerous proposals have been made for management of radioactive graphite waste. These plans include a number of novel chemical or physical treatment procedures for graphite have also been proposed, with the objective to facilitate its subsequent disposal or reduce the environmental impact of the chosen disposal route. A comprehensive review of the general approaches up to 1999 can be found in [1].

The main concerns about the characterization, treatment, conditioning, storage and disposal of radioactive graphite are related to the large quantities involved and to contamination by the long lived radionuclides (^{14}C, ^{94}Nb, ^{36}Cl, ^{110m}Ag, ^{63}Ni, etc.).

After a graphite-moderated reactor has shut down, it is necessary to remove the fuel and the ancillary equipment. It is then necessary to characterize the remaining waste. In the case of the graphite core this not only involves radiochemical analysis but also the structural integrity and chemical properties of the core (including stored energy). In addition, the structural integrity of the core support and the core containment are of paramount importance. The reason for this is that the graphite is likely to be left within the reactor cavity for an extended “safe enclosure”, period which may be more than 40 years before the graphite is removed and disposed.

In the case of other graphite operational waste, sorting, packing, and interim storage may require immediate attention. In deciding on the route to final disposal, a decision will have to be made on final location, the type of packaging and whether treatment (annealing, immobilization, encapsulation, etc.) is required.

The solution to the problem will differ from country to country, due to safety, technical, geological, regulatory and political considerations. The main options and strategies are outlined below.

4.2. GRAPHITE MODERATOR

According to the IAEA recommendations, after defuelling or after dismantling of the peripheral structures, there is the option either to dismantle the moderator immediately or to opt for a “safe enclosure” period which allows significant decay of the shorter-lived isotopes. The second option is preferred in most cases, but there are some special circumstances where the first option is taken. However there is no universal agreement as to the length of the “safe enclosure” period.

Whether a “safe enclosure” period is opted for or immediate dismantling is chosen, the core will have to be removed and the graphite dealt with at some point in time. Graphite should be either sorted to various waste streams (e.g. low level, intermediate level and high level for contaminated graphite), or it may all be classified into a single waste stream. At this point the further processing options are:

— Conditioning of the graphite carried out at this stage by decontamination, surface coating or immobilization (particularly in the case of highly contaminated graphite);
— Packaging the graphite in containers, either encapsulated or not. If the graphite is to be encapsulated, for graphite irradiated at low temperatures and containing a significant amount of stored energy, a decision has to be made at this stage if the graphite has to be annealed or not;
— Incineration of the graphite (possibly with capture of the released ^{14}C) and packaging the highly activated concentrated ash;
— A pyrolysis / steam-reformation process [47].

Having made the above decision, the options for further destination of the packages of graphite which result from the first three options are:

— Store in suitable containers until a decision is made on the final disposal route;
— Intermediate depth disposal;
— Deep geological disposal.

4.3. OTHER GRAPHITE ITEMS

Other irradiated graphite items have usually been stored in dry or wet silos. The construction of many of these silos is not as substantial as the reactors themselves. In addition, some of these silos contained mixed graphite waste. For these reasons these silos will require emptying much sooner that the main reactor core will be dealt with. At this stage, sorting of graphitic and non-graphitic material may be desirable.

The options for annealing or incineration, packaging and disposal may then be the same as for the main moderator.

5. GRAPHITE TREATMENT, CONDITIONING AND TRANSPORT

For moderator and reflector materials, there are earlier “storage” stages which must be accomplished before dismantling of the core and final disposition.

After shut down, the removal of fuel from the site follows, which may take up to several years [48]. During this period, the graphite will normally be subject to an air atmosphere, generally with control of moisture content, at ambient temperature and with a significant but slowly reducing gamma-radiation dose rate. UK safety-case studies relating to the de-fuelling period have considered the implications of chemical reactions, such as the formation of nitric acid. It has been possible to show that the reactor’s metallic structures, including the core restraint, are not compromised by this possibility; the graphite is certainly unaffected and retains the mechanical, physical and chemical properties which applied at the cessation of reactor operations.

The dismantling of structures peripheral to the reactor core follows defuelling, which is then followed by the dismantling of the core and containment itself [48]. During core dismantlement, graphite components should also be dismantled and further processed.

Graphite components from fuel elements, monitoring stringers and other minor graphite components, which have been discharged from the reactors during their operation, are generally retained in vaults while awaiting an ultimate processing and disposal route. In some cases, the graphite has been pond-stored for long periods during fuel element “cooling” and then transported to a processing facility before finally being cracked off from the elements and crushed to a suitable size for handling. Thereafter, the sleeve material can be placed in dry storage in drums in a shielded facility.

The smaller-scale graphite items are expected to be handled for ultimate disposal in an essentially similar fashion to the graphite from core structures. The periods of vault or pond storage, where they apply, are not considered to result in any requirement for special treatment despite the potential differences in isotope content.

Generally, the overall dose achieved by graphite sleeves and other minor graphite items is much less than that of the moderator components, and pond immersion is more likely to reduce the isotopic content rather than to increase it further. While the chemical reactivity of pond-stored material may be enhanced by the uptake of potential oxidation catalysts, it is considered to be unlikely that a change of sufficient magnitude to require different disposal procedures from graphite core components can occur.

After a graphite reactor has been placed in a “safe enclosure” condition, it is necessary to proceed to the operations listed below, assuming that the decommissioning equipment and the graphite waste treatment equipment are in place and ready to operate:

— Install temporary protection barriers (sealed confinement area) and re-open the reactor to gain access to the core;
— Remove the metallic structures above the core in order to gain access to the graphite stack;

— Remove the graphite bricks with the assistance of dedicated handling equipment; or use a specialist process, such as *in-situ* pyrolysis;
— Transfer the bricks to a waste-conditioning system for performing a suitable treatment, fragmentation, immobilization, impregnation, incineration, etc.;
— Transfer the conditioned graphite or the residues (incineration ash) in proper containers for storage or disposal;
— Continue the operation until the final clean up of the reactor cavity of all the graphite waste, including graphite fragments and dust; and
— Finish dismantling of all the reactor structures, including metallic and or pre-stressed concrete structures.

5.1. INTERIM STORAGE FOR DECAY (SAFE ENCLOSURE)

One of the principal objectives of the "safe enclosure" philosophy — i.e. a delay before dismantling of the cores commences — is to maximise the advantages gained through radioactive decay. There have been numerous studies of the advantages to be gained in this way from the decay of gamma-emitting isotopes present in reactor steelwork (especially ^{60}Co) and graphite. The effective loss of many of the initially prominent beta/gamma-emitters in both graphite and surrounding steelwork, through the lapse of ten or more half-lives, allows the subsequent dismantling to be conducted much more easily, since less shielding and less complex remote handling are required. Provided that it can be demonstrated that radioactive materials can be contained within the reactor vessel with a high degree of certainty, then the long-term economic advantage of "safe enclosure" may be significant.

Other arguments for adopting this philosophy relate to the current unavailability of suitable disposal facilities. If no waste acceptance criteria for waste packages are currently available, early packaging of graphite waste would represent a technical and economic risk that the packaged waste may not be compatible with the repository when it becomes available, thus requiring remedial action which would result in additional cost and further dose uptake. The effective "foreclosure" of disposal options, which early packaging would offer, must be justified in terms of economic and safety benefits.

In order to avoid any impact on the environment, the core containing graphite must be protected using a proper engineered solution, which will depend on the reactor design, on policy of the particular country, and other issues. Sealing the core by filling the free space with a sealing material, as has been performed in at least one Russian plant which has experienced major fuel failures, is a realistic short-term solution. However, it has the major disadvantage that the final dismantling is more difficult, and the volume of the waste is significantly increased.

During the "safe enclosure" period, regular control and monitoring of the core should be maintained in accordance with the particular decommissioning plan.

5.2. GRAPHITE CORE REMOVAL

With or without a "safe enclosure" option, eventually the graphite cores will require removal. The physical and mechanical properties of the core may have significantly changed during operation. Stresses will have developed in the fuel channel bricks, which in a few extreme cases may have lead to a significant amount of failed components. Irradiation growth and shrinkage may have lead to significant channel degradation or even to whole core deformation.

The methodology for core removal will strongly depend on the core design and supporting facilities available. The option of flooding the core to provide a radiological barrier has been effectively used at Fort St. Vrain, where a water-tight containment (pre-stressed concrete reactor vessel) existed [49]. The water circulated in two loops at a rate of about 120 m^3/hour per loop and was filtered at the ion exchange column to ensure water cleanliness and clarity. The use of flooding has also been proposed by the French CEA for G2 and G3 reactors, providing the pre-stressed concrete containments can be shown to resist the water pressure.

However in the case of other reactors, such as the Windscale Piles, there is no water-tight containment, and adapting the present structure to make it water-tight is considered to be non-practical. The options, therefore, are either to dismantle the core remotely in air or, in the case of Windscale Pile No.1 where there is some concern as to the nature of the materials in the fire-damaged zone, either a local or global inert gas blanket has been considered[2].

The core of the Windscale AGR prototype has been completely removed by remote handling in air, but the operation was sealed from the external atmosphere. Consideration was given to core removal underwater; however, as there is no nearby water treatment plant at the reactor site, this option was dropped.

Physical removal of a graphite core may have been complicated by irradiation growth or shrinkage. Cores which have operated at low temperature may have significant growth that may exert forces on the core supports, restraints and fuel channel tubes. These forces may make it difficult to remove graphite components, and the large removal forces that may be required could lead to debris production.

If the reactor core is to be removed in air, in reactor cores containing high amounts of Wigner energy or large amounts of carbonaceous dust, the use of burning torches to remove ancillary equipment should be analysed and appropriate safety procedures developed as previously discussed.

Also as previously discussed, the strength of the graphite will be influenced by the irradiation dose and, in the case of graphite irradiated in an oxidising atmosphere, by the weight loss. The strength of highly irradiated or thermally damaged graphite may be significantly reduced and a significant amount of debris may be created during decommissioning operations.

[2] This is under review again (2004) following improvements in the understanding of potential hazards, such as the likelihood of problems from pyrophoric UH_3, which appear to reduce the risks involved in decommissioning compare with past expectations.

5.3. TREATMENT AND IMMOBILIZATION INTO AN INERT MATRIX

5.3.1. Treatment of Wigner energy

Perhaps the most significant graphite property in terms of the implications for package performance and the potential effect on the overall disposal performance is that of Wigner energy. As previously described, for graphite waste arising from irradiation temperatures between ambient and around 130°C, a temperature increase above the irradiation temperature can potentially release sufficient energy to result in self-heating to 350°C in a few minutes if conditions approach adiabatic [8]. It may prove difficult to demonstrate that such a temperature increase cannot occur during normal handling and processing operations for such graphite wastes, and certainly not for potential fire accident conditions during handling or transport operations in which the release of Wigner energy could result. In addition, this risk may be increased for graphite containing contaminants, such as lead, which have been shown to increase the oxidation rate of graphite at a given temperature; irradiation of graphite has also been shown to increase the oxidation rate. Graphite wastes arising from irradiation at temperatures higher than 130°C, such as Magnox and AGR graphite waste, are much less at risk from uncontrolled Wigner energy release during normal conditions of management, although there is clearly some potential for small releases during fire accident conditions.

As an example, the total stored energy in Windscale Pile 2 has been estimated as 2×10^{12} J and for a typical Magnox reactor 3×10^{11} J. However, for safety cases it is the *rate* at which this energy can be released that is important and not the total amount of energy.

To assess the risk, related to significant amount of stored energy accumulated in graphite, during long term “safe enclosure”, handling during dismantling or core sampling, processing, packaging and final disposal, it is necessary to carry out calculations using theoretical models based on experimental data [8]. These models balance external heat input and energy released from the graphite against heat lost due to convection and conduction. In the case of graphite handling in the air atmosphere, a heat generated due to thermal oxidation also needs to be accounted for. It is also important to take account of the large reduction in thermal graphite conductivity (down to 2–3 W/m/K). However, there would be an increase in thermal conductivity by a factor of 2 or 3 as the energy was released.

There is a considerable amount of literature dating from the 1950s and 1960s on the release of stored energy in operating graphite reactors. The experiments carried out at that time and the theoretical models developed were aimed at modeling the release of stored energy due to temperature rises over relatively short time periods (minutes). In the case of packaging or storage in the repository, the temperature increases of concern are much longer range. If the packaging material and backfill are cementitous, there could be a significant temperature rise due to curing of the cement.

In the case of packaging the temperature rise due to curing of the encapsulating material may be over several hours. In the case of a deep geological repository the temperature may rise extremely slowly due to the temperature buffering effect of the surrounding rock and the curing of the backfill. The assessment of the significance of Wigner energy for deep geological disposal in the UK has been presented by UK NIREX [50]. They suggest that graphite with the potential of rapid release of Wigner energy should be annealed prior to final packaging up to a sufficient temperature which would exceed that ever likely to be

encountered in storage. However, the theoretical assessment of the behaviour of graphite, containing Wigner Energy during packaging and disposal is complicated and requires the use of theoretical models based on measurements of Wigner energy release from real graphite samples.

Various models for the release of stored energy exist mainly based on work carried out in the 1950's. These models are summarized in [51]. The most difficult problem is to assess the potential for very low rates of release in a storage facility, since no data exist on release rates at such temperatures, and they cannot be obtained from contemporary instrumentation. An attempt has been made to model this problem [52], and it has now been partially validated using graphite samples taken from the Windscale Piles.

Unfortunately, there is not enough information to calculate precisely the potential rate of release of Wigner energy in irradiated graphite from its operational history, either at low ambient temperature or at higher temperatures. For this reason, it is difficult to separate out graphite requiring annealing from that which does not require annealing, taking into account only the position within the reactor core. This poses a logistical problem for those involved in dismantling the older low temperature reactors.

It is therefore important that, for graphite irradiated at low temperature, representative graphite samples should be taken and measurements made of:

— Total stored energy;
— The rate of release of stored energy;
— Thermal conductivity;
— Air reactivity (oxidation rates in air).

This information can then be used to model the graphite behaviour during the "safe enclosure" period, dismantling, processing, packaging and disposal.

Since it is not acceptable to store or dispose of graphite containing significant releasable stored energy, such graphite should be annealed to remove the energy which could cause self-heating. An annealing temperature in excess of 250°C should be adequate to protect against any subsequent excursion in ambient temperature during transportation and storage.

To solve the need to anneal Wigner energy from Windscale Graphite, an annealing plant has been designed by RWE Nukem [53]. This process involves heating the graphite to 250°C using induction heating. Investigations of the release of ^{3}H have been carried out, which show that in the temperature range of the annealing process only 0.5% of the total tritium content is expected to be released for this particular graphite [54]. However no final decision has been taken on the deployment of such a plant.

An alternative approach is to mix the graphite with other materials or mix with graphite with a lower amount of stored energy in order to increase the thermal capacity of the package. It may be possible to utilize this approach to develop a package which is robust to foreseeable events, but this would impose a considerable burden to characterize the graphite and to demonstrate its performance.

Some graphite and carbon shields are impregnated by boron. It is known that boron enhances radiation damage in graphite. However, there is no data on the accumulation of stored energy in boron-doped graphite irradiated at low temperature.

5.3.2. Immobilization, matrices and packaging

The development of suitable packages for direct disposal of radioactive graphite wastes after their conditioning, surface decontamination, and coating will be dependent on 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; heat output and surface contamination; and package radioactivity release under normal and accident conditions of handling, transport, and disposal. In addition, for graphite wastes, there are a number of specific properties of the material which need to be considered in the development and demonstration of packaging options.

In design of the packaging container the possibility of galvanic corrosion should be considered (see Section 3.2.3). British Nuclear Fuel Limited (BNFL) commenced a development programme in the UK in 1982 to assess the packaging options for each of their intermediate level wastes arising at the Sellafield site [55]. These wastes include graphite fuel element sleeves remaining from reprocessing of AGR fuel assemblies. The sleeves arise in the form of fragmented pieces, which are cracked and crushed after removal of the fuel element pins from the fuel element assemblies. The development programme initially assessed a wide range of possible encapsulation matrices, covering cement, polymer-modified cement, polymer, resin sand, bitumen, glass, low melting point metal, and ceramic. A summary of the process and product considerations identified by BNFL for each of these matrix types for application to AGR graphite waste are shown in Table III (based on [56]). It is of note that no mention is made of the potential application of incineration or other volume-reduction techniques as a graphite waste-management tool.

Of the eight potential matrix materials identified, three were selected for further, more detailed, study: cement, polymer-modified cement, and polymers. Further studies [57] evaluated the performance of these three preferred matrix types using a multi-attribute decision analysis technique. This technique provided a methodology for scoring and ranking alternative options and evaluating any risks associated with an option.

The basic process identified for the cementation of the graphite waste consists of pre-mixing of the cement grout in an inactive area, followed by transfer of the grout into the waste-containing drum. Detailed evaluation work on the process and product properties of AGR graphite waste, encapsulated with cement, has been performed [55], with the preferred matrix being three parts of blast furnace slag (BFS) to one part of Portland cement (PC) [57]. The preferred container type is a stainless steel 500 L drum (the actual volume of the container is of the order of 560 L and “500 L drum” being the common name for the container). This container is the principal ILW container type developed by BNFL. The drum is not designed to provide any radiation shielding and has to be transported to the repository within a re-usable shielded transport container. The transport container will carry four drums located in a handling stillage, and will comply with the requirements of the type B container specified by the IAEA regulations for the transport of radioactive materials [58].

The product properties assessed by BNFL in order to demonstrate the acceptability of the product include mechanical strength, dimensional stability, chemical properties, radiation stability (using accelerated alpha and gamma irradiation tests to simulate 100 year doses), thermal conductivity, thermal stability and impact performance. The use of a cementatious encapsulation matrix is consistent with the cement-based backfill material designed by UK NIREX and intended to surround the waste packages in the repository. This backfill is designed to fulfil a number of requirements [59]:

— Long term maintenance of alkaline pore water chemistry in order to suppress dissolved levels of key radionuclides;
— Long-term maintenance of a high active surface area for sorption of key radionuclides;
— Relatively high permeability and porosity to ensure homogeneous performance, in order that localized concentrations of material in wastes do not exhaust the desired chemical conditioning and thereby locally reduce the containment performance.

It is noted that BNFL's overall strategy for the management of its intermediate level waste, including graphite from all the Magnox reactors following a "safe enclosure" period, is to encapsulate it in a cement based matrix with the resulting solidified wastes being held onsite in engineered retrievable stores until such time as a suitable disposal route is available.

Of the remaining graphite wastes within the UK which are intended for disposal, the majority will not be retrieved and packaged until dismantlement of the reactor core for commercial and research and development facilities. These wastes include reactor reflector and moderator assemblies.

There are a few circumstances where decommissioning or retrieval of graphite waste is to be performed at an earlier stage than detailed above, with consequent packaging of the waste in preparation for disposal. These activities are presently the direct responsibility of UKAEA Nuclear Decommissioning Authority and may be summarised as:

— **Windscale advanced gas cooled reactor (WAGR).** As a part of this demonstration decommissioning project, graphite moderator waste has been packaged in shielded concrete boxes, with a cementatious encapsulation matrix. The WAGR box and infilling grouts have been the subject of extensive development programmes: however, this is considered in the UK to be a non-standard design. Since the packaging plant had already been built, it has been decided to continue with its use for WAGR only.

— **Windscale Pile graphite boats and dowels (from silos) and Pile-1 graphite core[3].** To improve existing safety arrangements, the fire-damaged pile is intended to be completely dismantled. The future management route for the graphite has yet to be decided, with disposal as favoured option at present.

— **GLEEP:** The entire graphite core of this low-energy, low-irradiation reactor has been dismantled, essentially "by hand," with the majority of the graphite crumbled to facilitate calcinations treatment as described earlier. It is intended that this will facilitate

[3] Pile 2 is intended to continue in "safe enclosure;" no further programme presently exists for its dismantling.

eventual disposal of the graphite as LILW-SL to the Drigg shallow-burial site in suitable containers.

— **BEPO:** This air-cooled pile has been closed since 1968 and samples taken through the core to establish activity levels. No firm disposal plan for this reactor currently exists.

A further special case, which remains a BNFL issue, concerns the Berkeley operational graphite fuel-element debris. As part of the ongoing decommissioning operations at the Berkeley site, it is intended that miscellaneous fuel element debris, comprising Magnox, graphite, zirconium and steel, will be retrieved from the existing bunkers and packaged/cemented in the UK NIREX 3 m^3 LILW-LL box in preparation for disposal. The 3 m^3 box is essentially of the same design requirements as the 500 L drum, i.e. designed for transport in a reusable shielded transport container, but it is intended for larger items of waste which will not fit in the 500 L drum.

An additional UK graphite-bearing waste which has been described earlier, but for which management plans are not finalised is that of Dragon fuel and reflector-graphite waste. One option under consideration for the compacts remaining from the fuel elements is packaging in a 500 L drum in a form suitable for disposal, presumably deep geological disposal. The UKAEA Nuclear Decommissioning is currently considering the issues.

EdF CIDEN (Centre d'Ingénierie de la Déconstruction et de l'Environnement), based in Lyon, France, has been established to decommission nine French reactors, including UNGG graphite moderated reactors. EdF CIDEN has established a joint graphite specialist committee with CEA (Commissariat a l'Energie Atomique), which is advising EdF management on appropriate procedures. A UK specialist attends their meetings, along with representatives of SOGIN (Società Gestione Impianti Nucleari SpA) and ENRESA (Empresa Nacional de Residuos Radioactivos S.A.), with the objective of pooling knowledge and experience to arrive at the most appropriate solutions. The current position is best described as "recovery of graphite knowledge." Extensive sampling of the shutdown reactors has been made to establish current physical and mechanical properties, chemical reactivity, isotopic content, etc, in order to support modern computer models which are being developed to assess the whole inventory and thus determine the disposal strategy most suitable for France.

SOGIN, in Italy, is also making significant progress in its planning for Latina dismantling. Again, an underground repository is seen as the favoured solution, and much work is in progress to achieve this aim against the Italian waste-management rules which differ somewhat from those of other European countries in terms of categorisation.

An interesting simple immobilization method for graphite contaminated with uranium and actinides has been proposed in the Russian Federation [60]. After milling the graphite, powders of Al and oxides of Y, Ce, Ti are added; then, after some initial heat, a self-propagating high temperature synthesis is produced in hermetic steel containers. This process is similar to that of the thermite process. The resulting product (of density 2–4 g/cm^3) has a structure $TiCa_{0.9}N_{0.1}+Al_2O_3+Y_3Al_5O_{12}$. During high temperature synthesis, atoms of Y can be replaced with uranium and actinide atoms. The product is a stable carbide-oxide composite material, ready for disposal. ^{14}C has also been successfully locked into this structure. This technology is claimed to be fully ecologically safe.

TABLE III. INITIAL EVALUATION BY BNFL OF PROCESSING OPTIONS FOR GRAPHITE IN THE UK

ENCAPSULANT	PROCESS		PRODUCT	
	Advantages	Disadvantages	Advantages	Disadvantages
Cement	• Simple process • Proven technology • Low temperature process • Removes residual water • Inexpensive • Non-Combustible	• Low initial strength • Potential for presetting in pipework • Hydrophobic properties of graphite	• High strength product • High radiation stability • Good self shielding • High pH matrix • Non-combustible product • Self-supporting matrix	• Relatively permeable • Increase the volume of waste to be stored • Leaching rate may not be acceptable
Modified cement	• Simple process • Proven technology • Low temperature process • Removes residual water	• Potential fire hazard • Increasingly expensive as polymer content increases • Organic solvents required for plant wash down • Short setting times	• Improved strain resistance • Reduced permeability • Good self shielding • High pH matrix • Self-supporting matrix	• Reduced radiation stability • Organic components may enhance equilibrium leaching
Polymer	• Relatively simple process • Proven technology • Low temperature process	• Potential fire hazard • Expensive • Organic solvents required for plant wash down • Less tolerant to residual water • Probably toxic	• High Strain resistance • Low permeability • Self-supporting matrix	• Potential fire hazard • Reduced radiation stability • Organic components or filler may enhance equilibrium leaching • Life of polymer may be much less than ^{14}C
Resin sand	• Potentially simple process • Curing and dewatering • combined	• May prove difficult to infill wet waste • Requires high temperature for curing • May require drying	• High strength produce • Self-supporting matrix • Good self shielding	• Potential fire hazard • High porosity product • Probable poor leaching characteristics • Reduced radiation stability

TABLE III. (cont'd) INITIAL EVALUATION BY BNFL OF PROCESSING OPTIONS FOR GRAPHITE IN THE UK

ENCAPSULANT	PROCESS		PRODUCT	
	Advantages	Disadvantages	Advantages	Disadvantages
Bitumen	• Incorporates dewatering	• Potential fire hazard • High temperature process • May result in poor grouting	• Good leaching resistance	• Potential fire hazard • Low radiation stability • Non-self supporting • Low self-shielding • Deforms on heating
Glass	• None	• High temperature process • Very expensive • Highly complex process • Complex off-gas treatment • Probably require pre-drying	• Good self shielding • Non-combustible • High radiation stability	• Probably fractured due to thermal incompatibility • Low thermal stability • Fracturing may result in low leach resistance
Low melting point metals	• Probably use proven casting technology	• High temperature process • Very expensive • Probably toxic • Probably require pre-drying	• Good self shielding • Non-combustible • Self supporting matrix • Good leaching properties • High radiation stability • Good thermal conductivity	• Probably toxic following disposal • Melt under fire conditions • High density may make transport difficult
Ceramic	• None	• Requires high temperature and pressure • Expensive • Highly complex process	• Good self-shielding • Non-combustible • Self supporting matrix • High radiation stability	• Probably sustain thermal stress damage on heating • Uncertain performance on drop testing

If graphite is to be encapsulated in concrete, the density of the graphite compared to the concrete should be taken into account, as the graphite components, and dust, may float in the mixture of grout.

5.3.3. Coating and impregnation

The aim of coating and impregnation is to immobilize radioactive waste or to protect it from impact from the environment, e.g. from oxidising gases or from moisture. The difference between surface coating and impregnation is as follows:

— **Impregnation** clearly has potential for improving the quality (non-permeability) of a graphite waste surface for long-term storage by covering the surface with a thin layer of impregnation material. The advantage in comparison with another methods (such as cementation) is that if it is eventually decided later to process the graphite in other ways, such as by incineration, then the presence of the additional materials (cement) could give rise to technical problems. Impregnation materials can include ultra-fine grouting, bitumen, polymer and modified polymers.

— The **surface coating** methodology was an unsuccessful attempt to protect graphite from the effects of radiolytic oxidation during reactor operation in a carbon-dioxide-cooled plant using a deposited silica coating. A vapour deposition method involving the pyrolysis of silane/CO_2 mixtures was investigated, but proved less than 100% effective in providing an impervious coating, and the idea was abandoned. However, for graphite waste, and with improvements in coating technologies on irregular large objects, the process is perhaps again worthy of investigation.

French research into immobilisation of radioactivity on bulk graphite has concentrated upon impregnation rather than surface coating [44, 61]. Studies were carried out on cylindrical samples (outer diameter 74 mm) removed from the G2 reactor at Marcoule. Following the leaching tests already discussed, investigations of immobilising the radioisotopes using epoxy resin and/or bitumen were carried out. The technique with epoxy resin requires a preliminary evacuation to around 10^{-2} mm Hg followed by immersion at a pressure of up to 10 bar. A cure of the resin at 150°C follows. An increase in mass of around 12% indicates successful impregnation of the internal pore structures down to diameters of approximately 0.1μm, confirmed by X-ray tomography.

A number of bitumen products were also tested, with a direct distillation product classified as 80/100 chosen because of its fluidity. Again, the graphite was evacuated before impregnation, with care being taken to avoid carbonisation of the bitumen. A pressure of about 2 bars was applied at 200°C for 30 minutes to ensure full penetration. Retention of the bitumen was between 3.5–7.0%.

A tar/epoxy mixture was considered superior to the individual materials, with curing over a number of days at ambient temperature avoiding the need for a heat-treatment stage. Tests of compressive strength indicated an improvement of a factor ~1.7 compared with pure graphite, a useful feature for the avoidance of handling damage in storage.

Leaching tests were carried out after impregnation, demonstrating reduction in leaching rate by water of up to two orders of magnitude for the principle isotopes. The authors [44, 61]

consider that the procedure is capable of effectively immobilising the great majority of the radioisotopes present, and therefore offers environmental protection against the possibility of subsequent rupture or corrosion of the storage containers.

5.3.4. The Russian "SHS" process

Russian technologists are developing a special procedure for dealing with graphite which is classified as high-level waste as a result of contamination with fuel and fission products following fuel failures in its production reactors and also at the Beloyarskaya NPP reactors [39]. This involves the so-called **S**elf-Propagating **H**igh Temperature **S**ynthesis process similar to the classical "Thermit" process, in which graphite is intimately mixed in stoichiometric proportions with aluminium and titanium oxide according to the equation

$$3C + 4Al + 3TiO_2 = 2Al_2O_3 + 3TiC$$

The reaction is initiated electrically and is thereafter self-propagating. It has been demonstrated on the laboratory scale and it is planned to build a plant, presumably at NIKIET Sverdlovsk (adjacent to Beloyarskaya NPP). It has the advantage of immobilising all significant isotopes present in the oxide and carbide matrices (including ^{14}C in the latter) and results in a highly unreactive and insoluble product with very good leaching characteristics.

5.4. INCINERATION

5.4.1. General considerations

The prospect of incinerating graphite waste in order to reduce the volume of waste for disposal raises four major issues:

— Difficulty of burning graphite, especially the very pure form used for nuclear purposes;
— Release of radioactive gases, particularly ^{14}C, ^{36}Cl and residual ^{3}H;
— Processing and disposal of the residual ash, in which other radioactive isotopes are concentrated; and
— Graphite has to be crushed into small pieces prior to incineration.

The disposal options (for both near surface or deep geological disposal, incineration, and the subsequent fate of high-activity incinerator ash) were comprehensively reviewed in the 1980s [28]. For a typical incineration process, it considered that the ratio of graphite to ash is approximately 160, so the overall volume of material to be disposed of by immobilisation, canning and burial would be considerably reduced compared with the original graphite, although this material would be of a higher waste category.

To avoid the discharges of the residual radioactive gases, it is necessary to equip the graphite incineration system with an efficient filtration system consisting of a pre-filter, a back flushable filter, and a HEPA (High Efficiency Particulate Air) filter in order to trap all the radioactive particles and aerosols.

For ^{36}Cl contamination, the incineration system should be also equipped with a wet scrubber in order to neutralize the hydrochloric acid formed and to perform an abatement of

chlorine release in the off gas. An additional filtration system should be constructed to retain some other gaseous pollutants (e.g. NO_x).

Collective and individual doses should be also calculated, especially for the ^{14}C and ^{3}H effluents from incineration. A key study from the UK CEGB examined the effects of incinerating the equivalent of one Magnox graphite moderator and reflector per year for 20 years [62]. This showed that the effect on *global* dose was small compared with the natural production rate in the atmosphere arising from cosmic neutrons interacting with $^{14}N_2$. However, the local dose around the incineration plant, together with consideration of the surrounding population density and local meteorological and geographical factors, are of rather more significance.

To compare the environmental risk of incineration and other graphite waste conditioning methods a detailed calculation has been made by Framatome for both of G3 reactor at Marcoule, France, and also for all the EdF reactors [21]. The calculation of maximum individual dose for the incineration of G3 graphite is extremely close to the figures quoted from [28]; a figure three times greater is quoted for the continuous EdF reactor programme. A typical internal and external dose to the population living near the incineration plant in the Marcoule area in between 5-40 μSv/y, which is lower than the admissible dose to the public, which is set at 1000 μSv/y according to the ICRP-60 [74]. (With regard to discussions on graphite, the focus of the Marcoule facility was on graphite in fuel assemblies rather than on graphite reflectors/moderators.)

Note: The International Commission on Radiological Protection is in the process of revising its radiation protection recommendations. Draft recommendations were distributed in 2005 and, when finally published, will replace Publication 60 (ICRP-60) in its entirety.

In order to mitigate the impact of the CO_2 release containing ^{14}C on the environment, in the Russian Federation and in France, an idea is in consideration on the possibility to localize a small fluidized bed incinerator for burning low contaminated graphite waste in the vicinity of a large thermal power plant burning oil or coal, which creates a depleted zone of ^{14}C due to rejection of large quantities of CO_2 depleted by ^{14}C. For instance a 10 kg/h fluidized bed burning of low contaminated graphite should have no measurable impact on the ^{14}C concentration if the off-gas is ejected (mixed) with the off-gas of a 600 MWe plant burning coal. In this case, the average concentration of ^{14}C in the environment will not alter background levels.

Further alternatives, albeit costly solutions, are available to avoid release of most of the ^{14}C from incineration of irradiated graphite. These are cryogenic separation processes reliant upon exploitation of the mass difference between ^{12}CO and ^{14}CO. Canadian patents exist for such a process [63], while the process is also currently under investigation in Japan with the objective of incineration of fuel sleeves from Tokai 1, and possibly also the reflector blocks [64]. The latter method involves a number of cycles of pressure-swing absorption but, in the opinion of the present reviewers, remains unproven.

5.4.2. Furnace incineration

It is well established that it is extremely difficult to burn nuclear grades of graphite because of its chemical purity, and little assistance is generally afforded by catalytic

mechanisms (although deliberate contamination with, for example, lead salts, is a possible route). Also, the relatively high thermal conductivity means that heat is conducted away from surfaces into the bulk of the material, and the high emissivity (black-body radiation) provides a further route for efficient heat loss. These factors all contribute to the lack of combustibility.

The earliest research into this subject appears to have been carried out in France; the first experiment performed at CEA consisted of placing pieces of graphite into a coal stove, which was unsuccessful. This basic experiment was followed by more realistic tests performed at Cadarache, Marcoule and Saclay. Along with German tests at pilot-plant scale, they demonstrated that conventional burning was possible but technically difficult. A very high proportion of carbon monoxide is expected in the off gases unless considerable care is taken in designing the delivery rate of oxygen and the combustion temperatures for the plant. Relevant thermochemical data are reviewed in [28]. This initial work led to the realisation that more complex technologies should be developed.

The initial conceptual design for a conventional graphite incinerator envisaged crushing of the material into cubes of approximately 2.5 cm on a side (i.e. 15.6 cm^3 each) before combustion in a batch process dealing with a bed volume of around 2 m^3 at a temperature of around 1000°C. A propane burner was planned for start up, with an excess supply of hot air constantly blown in to maintain the combustion. With a throughput of around 10 tons per day, a complete reactor core could be incinerated within one year.

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 and then introducing a ceramic thermal lance to provide oxygen to the combustion zone. Selective burning of the sections of the fuel compact which contain the fuel particles has been considered in order to release them to a separate HLW stream. The crushed graphite burning in shaft furnaces has been demonstrated both at the General Atomics facility in the USA and at KFA Jülich in Germany.

NGK Insulators Ltd. in Japan have patented an incineration plant design whereby pulverised graphite wastes are burned at temperatures between 800-1200°C in which there appears to be provision to recover the ^{14}C and ^{3}H as CO_2 and H_2O. The potential to recover a high proportion of the radioactive products otherwise exiting via a stack is currently considered to be the most significant feature of incineration processes and requires further development. Specific examples of incineration designs with commercial potential, which have been developed to a pilot-plant stage, are considered in the following Sections.

The Pacific Northwest Nuclear Laboratory (PNNL) in the USA has also proposed the use of closed-chamber incineration for nuclear graphite [65]. At present, US DOE facilities rely on “cocooning” (a type of safe enclosure) for graphite wastes.

For completeness, an unusual approach to nuclear graphite oxidation from the Ukraine should be mentioned. This was first published in 1995 [66], whereby the oxidation/ combustion of graphite materials is assisted by prior “expansion” or “exfoliation.” The process involves separation of the individual layers of the graphite crystallites, partially destroying the graphitic structure and enhancing considerably the reactive surface area [67]. Historically, exfoliated graphite, produced *via* intercalation compounds, has required the use of strong oxidising acids at low temperatures, followed by decomposition of the products.

The Ukrainian process is a “dry” process, although small portions of fuming nitric acid, perchloric acid, magnesium perchlorate, or oleum (sulphuric acid) are used at ambient temperature. This is followed by heat treatment at 600°C for a few minutes without prior separation of the graphite and acids. The subsequent oxidation rate of the product in air is stated to be between 4 and 27 times higher than before the treatment, dependent upon the reagent used.

This process clearly would require considerable development before it can become a significant contender for a commercial radioactive graphite waste processing technology and a number of research groups worldwide are investigating the properties and potential exploitation of exfoliated graphite materials.

5.4.3. Fluidised-bed incineration

Framatome in association with EdF and CEA have developed the incineration concept based on the use of a fluidised bed technology. The design studies [21, 68] provide details of the latest developments in fluidised-bed incineration, for which pilot-plant tests have been successfully completed. It covers not only the actual incineration, but the facilities necessary to recover spent fuel sleeves, crush them so that the graphite is reduced to particles not greater than a few millimetres across, separating the stainless-steel seating wires which are a feature of the French fuel design with a magnetic separator, and compacting them along with other materials from the waste storage silos. The graphite is then drummed prior to incineration.

Framatome has accumulated extensive knowledge of crushing of irradiated graphite through its experience of crushing graphite sleeves retrieved from storage from Vandellos 1 silos. The total number of irradiated sleeves which have been crushed into small pieces is about 200 000 corresponding to a total mass of irradiated graphite of about 1 000 tons.

Framatome has also made careful assessment of the oxidation characteristics of graphite fragments under the three modes of oxidation, and has also taken into account the small amount of additional energy release during combustion which arises from the Wigner-energy content of some irradiated reactor graphite. The process design requires particle sizes with a maximum diameter of 1 mm in order to ensure a large enough surface area to give a reasonable combustion rate at practical temperatures. It is considered important that the proportion of dusts less than about 100 μm remains low, otherwise carry over of dust from the primary bed would be excessive, and also bed efficiency could be compromised by coagulation. It is intended that this specification will be achieved in the initial pulverisation in the case of sleeves, therefore avoiding a need for double handling. Core blocks would be dealt with using automatic hammers and cylindrical roller crushers. For graphite from cores operated at low temperatures and having, therefore, a very high strength, this part of the process may present additional difficulties. Milling also increases the volume of material which must be handled at this point in the process.

The crushed graphite is fed into a circulating fluidised-bed combustor, whose features include a powerful pre-heating burner, a powdered refractory material as the basis of the bed, a high fluidisation air-flow rate, and high turbulence in the combustion region. Solids are separated from the combustion gases by a cyclone separator and recycled in a loop, which works without further moving parts to eliminate problems of abrasion. However, some dust consisting of fly ash, unburned graphite particles, and fine refractory particles arising from

wear of the fluidised bed are carried over and enter a further combustion chamber. This is followed by a dust and ash separation system before the product gases are discharged to atmosphere through HEPA filters (Fig. 9). As the ash includes residues from the refractory bed, its final volume will be greater than from other combustion systems.

The fluidised-bed technology for incineration of graphite provides for graphite combustion at a relatively low temperature (~1075°C), which minimizes the formation of pollutants such as NO_x. The resulting efficiency of combustion is rather high at more than 99.8% for nuclear grade graphite. Filtration systems and routes for ash disposal are the same as for other incineration methods.

The pilot fluidised-bed incinerator at Le Creusot has been operated successfully. More than 20 tons of graphite was incinerated with a combustion efficiency of 99.8% and an average feed rate of 30 kg/hour. Combustion was reported as "complete and perfectly controlled" [21]. Prior to operating the pilot plant, a full safety analysis was carried out which included an assessment of dust explosibility. The safety analysis focused on both the incinerator and the crushing room.

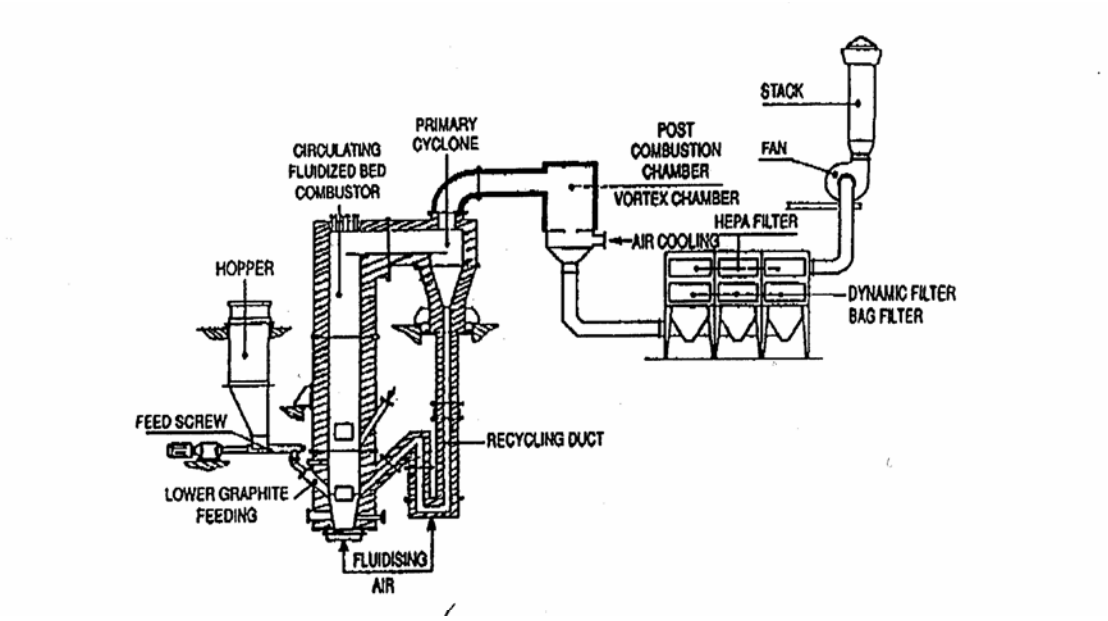

FIG. 9 Fluidised-bed incinerator.

5.4.4. Laser incineration

Laser technology for graphite incineration has been investigated at CEA at Bagnols-sur-Cèze, France. The potential advantage of this alternative approach is that the graphite components are incinerated directly, without prior crushing or other pre-treatment, using a high-powered laser to ignite and sustain combustion at the geometrical surfaces.

This process has been developed to pilot scale, following initial laboratory experiments and comprehensive modelling of the heat-transfer parameters. These parameters include the thermal conductivity of the graphite, strongly influenced by reactor irradiation and also by the temperature increase effected by the laser [69]. The pilot furnace consists of an internally polished stainless-steel vessel designed to reflect the radiation from the hot graphite and

covered with mineral-wool insulation. The plant size would be optimised to the size of the graphite blocks. A reciprocating laser beam from a CO_2 power laser (trials have been made with powers between 5 and 22 kW, with a beam diameter of approximately 35 mm) enters from above and impinges upon the graphite, capable of raising its temperature to 1100–1200°C in the illuminated zone. Oxygen is then admitted to the furnace (mixed with air) resulting in combustion with a blue flame (indicating the oxidation of CO to CO_2). The temperature rises further as a result of the combustion heat: Combustion rates of up to 14 $kg.h^{-1}$ were readily attained.

Further computer simulation, combined with the experimental observations, has permitted the design of a commercial furnace. A 7 kW laser is considered sufficient for a well-insulated and internally reflective system. This would typically be located in an adjacent room with a suitable beam transport system incorporating water-cooled mirrors. Zinc selenide windows will admit the beam to the furnace without significant attenuation. The final mirror would be motor driven to allow movement of the beam on the graphite blocks. The graphite would be heated by the laser until it reaches the stated "self-ignition" temperature of 1800°C in the oxygen-rich atmosphere, which is supplied through four nozzles directed at the graphite. An operator controls the laser beam according to the geometry of the material within the furnace, and it is calculated that continuous irradiation will not be necessary while the oxidation remains self-sustained. Remote-handling facilities would allow the graphite components to be re-oriented.

A commercial throughput of 10 $kg.h^{-1}$ graphite was intended for the above plant, with daytime operation only. The furnace would remain hot overnight to facilitate re-start the next day. Ash would be removed by vacuum transfer after a week-end cool down. Advantages claimed for this process over other methods of incineration include:

— Prior milling of the material is unnecessary;
— Easy temperature control via the laser beam;
— Steel wires and other contaminants need not be separated first;
— Once combustion has started, oxygen addition should not be necessary; and
— Remote monitoring of the progress of combustion is possible via infra-red monitoring through the optical windows.

5.4.5. Steam pyrolysis

A graphite treatment process based on steam pyrolysis has been proposed by Studsvik and Bradtec [47]. In this process, the graphite fragments are transformed by high temperature interaction with steam into two combustible gases (hydrogen and carbon monoxide). The gas treatment at the outlet of the reformer consists of a quencher, a scrubber, and a water condenser. After oxidation and transformation into CO_2 and H_2O, the gas is released to the atmosphere through a HEPA filter.

The contamination species, except for ^{14}C and ^{129}I are collected at the scrubbers and various filters. The separation options have already been described for collecting at least the ^{14}C off gases.

The CO_2 can be transformed into insoluble carbonate, but there is a large increase in the volume of waste. For instance, 1200 tonnes of graphite would be transformed into 10 000 t of calcium carbonate or 20 000 t of barium carbonate, which is very insoluble and prevents the release of radionuclides into the environment.

6. CONCLUSIONS

The great majority of the radioactive graphite waste arising from nuclear plant decommissioning is associated with the bulk moderator and reflector graphite in such reactors. This can amount to over 3000 tonnes of graphite per reactor. Permanent moderator and reflector blocks are present in all of the reactor designs discussed in this publication.

The difficulties in managing radioactive graphite are highlighted by the huge volumes of graphite waste involved (more than 230,000 tonnes worldwide) and the presence of significant quantities of ^{3}H and long-lived radionuclide contaminants or impurities, such as ^{14}C and ^{36}Cl. Improper management can have dangerous consequences, and the mitigation considerations in this publication are important imperatives. On the positive side, graphite waste retains its good mechanical properties and will remain stable for considerable periods of time. In addition, the leaching of isotopes is low even from unconditioned graphite waste.

This section summarizes the most important conclusions and considerations related to managing graphite waste through the characterization, treatment and conditioning phases. Due consideration is given to dangerous characteristics of graphite waste and to storage and disposal considerations which impact characterization and processing.

Pre-dismantlement conclusions

Prior to dismantling or retrieval of graphite moderators, reflectors or other graphite components from a reactor or from interim storage, the following considerations apply:

— Each repository and the appropriate licensing authority must establish repository-specific waste acceptance criteria (or generic waste acceptance criteria if a repository has not been selected) and identify long-term safety considerations, including those applicable to disposal of graphite waste. These acceptance criteria, when combined with the waste characterisation, are the key elements for selecting appropriate treatment and conditioning processes, as well as packaging specifications for storage and disposal.

— A good radiological characterization of the graphite waste is needed before proceeding with treatment or conditioning. This characterization could be obtained through knowledge of the operational and irradiation history, fuel failure channel blockages, and significant operating incidents. Radiological characterization also relies upon historical documentation and knowledge of graphite chemical impurities or contamination at the time when the graphite was installed in the reactor.

— Calculations used for radiological characterization should be verified by sampling representative graphite blocks. The results of the sample analyses should be validated by experimental radionuclide measurements. The sampling method must be chosen and conducted carefully—especially in the case of low temperature irradiated graphite—in order to avoid a sudden release of Wigner energy during the trepanning operation of graphite samples.

— Safety assessments and environmental impact studies should be conducted for conditioning operations by the organization responsible for treatment and conditioning (as well as for subsequent storage and disposal). These studies need to be carefully reviewed by the Safety authorities, and they should take into consideration the national

and international regulatory requirements and recommendations as critical elements of each related decision-making process.

Critical characteristics of graphite affecting waste management

After a graphite-moderated reactor has shut down, it is necessary to remove the fuel and the ancillary equipment. It is then necessary to characterize the remaining waste. In the case of the graphite core this involves radiochemical analysis of the graphite, along with analyses of the structural integrity and chemical properties of the core (including stored energy). In addition, the structural integrity of the core support and the core containment are of paramount importance. The reason for this is that the graphite is likely to be left within the reactor cavity for an extended "safe enclosure" period which may be more than 40 years before the graphite is removed and disposed. The following conclusions focus on the critical characteristics of graphite applicable to waste management.

Stored energy characteristics of graphite waste

The release of stored (Wigner) energy in graphite from operating reactors could lead to unexpected and dangerous results during processing, storage and disposal. If the energy is not dissipated, significant temperature increases could result. Early experiments and theoretical models focused on the release of stored energy due to temperature rises over relatively short time periods (minutes), which demonstrated the most significant reactions. In contrast, for conditioning, packaging, storage or disposal, the temperature increases which might otherwise be of concern occur over much longer periods, thereby mitigating the danger of sudden release of stored energy. However, if the packaging material and backfill are cementitous, there could be a significant (potentially dangerous) short-term temperature rise due to curing of the cement. This may also occur if using conditioning (immobilization) technologies which generate heat (e.g. cement encapsulation).

It is unacceptable to store or dispose of graphite containing significant releasable stored energy. Such wastes should be annealed during or prior to the treatment and conditioning phase if the characterization analyses indicate significant Wigner energy. Modern techniques are discussed in this publication for controlled dissipation of Wigner energy.

Fire versus oxidation of graphite waste

It is important to set out the circumstances under which significant oxidation of irradiated graphite in air can occur, in order to assist the preparation of decommissioning and storage safety analyses, including handling, packaging, characterization, etc. It is easy to find references in the literature to "graphite burning," "graphite fires," etc., and such remarks have attracted the notice of some Regulatory authorities who have come to regard irradiated graphite as a potential fire hazard. It is a conclusion of this publication that the reality is quite different. There is little evidence for self-sustaining combustion of graphite, even in the Windscale Accident and at Chernobyl.

Self-sustaining combustion would almost always require an artificially-sustained supply of air, without which the available oxygen would quickly become exhausted. It is proposed that the industry should refer to graphite *oxidation*, which is the correct description for the chemical process when graphite reacts with air or oxygen. This publication describes the conditions which must be satisfied *simultaneously* before a *self-sustaining* oxidation reaction can take place between graphite and air.

Explosive characteristics of graphite waste

When characterizing graphite for waste processing, safety analyses, etc. graphite dust must be distinguished from other impure carbonaceous dusts (like coal dust) which are explosive. There has never been a recorded dust explosion in a graphite manufacturing or machining plant; in contrast, dust explosions in coal mines have been relatively common. Nuclear graphite dusts are found to be much less reactive, and it is a combination of chemical purity and particle size which is primarily responsible for the difference in behaviour between graphite dust and other impure carbonaceous dusts. It should also be noted that an explosion would require that the dust suspension occur within a confined space, which inhibits the relief of the pressure rise resulting from ignition.

Nevertheless, this may not be the case for reactor graphite in the presence of large amounts of stored (Wigner) energy. As discussed above, the presence of stored energy needs to be determined early in the planning process and resolved as appropriate before or during the treatment and conditioning phase.

Changes in radioactive characteristics over time

As discussed earlier, the main challenges related to managing radioactive graphite are related to the large quantities involved and contamination by the long-lived radionuclides (^{14}C, ^{94}Nb, ^{36}Cl, ^{110m}Ag, ^{63}Ni, etc.). In general terms, the half-lives and distribution of the gamma-emitters present in contaminated graphite impact the treatment and conditioning options depending on the period of decay prior to processing. For example, if dismantling, treatment and conditioning occur after a relatively short decay period (e.g. 10 years), subsequent graphite handling, shielding, contamination control, and processing requirements will effectively be determined by ^{60}Co and ^{3}H.

However, if dismantling occurs after 100 years of decay, the characterisation situation changes significantly, since ^{3}H and ^{60}Co are then at negligible concentrations. In contrast, ^{14}C, ^{36}Cl and ^{94}Nb have half-lives of thousands of years, and no appreciable decay would have taken place even after 100 years, and they become the primary nuclide drivers for treating and conditioning graphite waste.

Treatment and conditioning considerations

If waste acceptance criteria for waste packages are not available, the treatment and conditioning of graphite waste would represent a technical and economic risk because the packaged waste or waste form may not be compatible with future disposal criteria. This is one of the primary reasons that some Member States are pursuing the “safe enclosure” decommissioning option. Eventually, all graphite waste will need to be treated and/or conditioned.

Once a decision is made to process graphite waste, it should be either segregated into multiple waste streams based on contamination levels (e.g. low, intermediate and high contamination levels) or classified into a single waste stream which bounds the most restrictive radiological characteristics. At this point the further processing options are:

— Treatment for control of contamination by decontamination or surface coating;

— Conditioning for immobilization, particularly for highly contaminated graphite;

— Packaging for storage or disposal, recognizing that packaging might serve as the immobilization process.

If the graphite is to be encapsulated — which could result in a rapid temperature increase — and if the graphite was irradiated at low temperatures and contains a significant amount of stored (Wigner) energy, a decision must be made as to whether the graphite needs to be annealed prior to immobilization, just as such a decision is necessary for storage or disposal.

Table III in this report provides an evaluation matrix of common conditioning methodologies used for immobilizing graphite wastes in the UK. As a result of that evaluation, the overall UK strategy for the management of its intermediate level waste, including graphite from all the Magnox reactors following a "safe enclosure" period, is to encapsulate it in a cement-based matrix. Other countries are examining important alternative graphite waste immobilization methodologies, including:

French immobilization processes

French research into immobilization of radioactivity on bulk graphite has concentrated on impregnation rather than surface coating. Investigations of immobilising radioisotopes using epoxy resin and/or bitumen were carried out. For both techniques, the graphite was evacuated before impregnation, with care being taken to avoid carbonisation of the bitumen. A bitumen/epoxy mixture was considered superior to the individual materials, with curing over a number of days at ambient temperature avoiding the need for a heat-treatment stage. Tests of compressive strength indicated an improvement of a factor ~1.7 compared with pure graphite, a useful feature for the avoidance of handling damage in storage.

Leaching tests were carried out after impregnation, demonstrating reduction in leaching rate by water of up to two orders of magnitude for the principle isotopes. The researchers concluded that the procedure is capable of effectively immobilising the great majority of the radioisotopes present and, therefore, offers environmental protection against the possibility of subsequent rupture or corrosion of the storage containers.

Russian Federation immobilization processes

Russian Federation technologists have developed a special procedure for dealing with graphite which is classified as high-level waste as a result of contamination with fuel and fission products following fuel failures. The reaction is initiated electrically and is thereafter self-propagating. It has been demonstrated on the laboratory scale and has the advantage of immobilising all significant isotopes present in the oxide and carbide matrices (including ^{14}C in the latter) and results in a highly unreactive and insoluble product with very good leaching characteristics.

Another interesting but simple immobilization method was evaluated by the Russian Federation for immobilization of graphite contaminated with uranium and actinides. After milling the graphite, powders of Al and oxides of Y, Ce and Ti are added. Next, after some initial heat, a self-propagating high temperature synthesis is produced in hermetic steel containers. This process is similar to that of the thermite process. The resulting product is a stable carbide-oxide composite material, ready for disposal. ^{14}C has also been successfully locked into this structure. This technology is claimed to be fully ecologically safe.

Special packaging conclusions related to graphite waste

The development of suitable packages for direct disposal of radioactive graphite wastes after their conditioning, surface decontamination, and surface treatment will be dependent upon the overall waste acceptance criteria of the repository. A number of generic criteria will be applicable for each disposal facility regardless of the waste type, including container size

and weight, package surface dose rate, heat output and surface contamination, package radioactivity release under normal and accident conditions of handling, transport, and disposal.

Consideration of electrochemical reactions (galvanic corrosion) is also an important aspect of the design of graphite waste packages. In addition, metallic packages should be avoided due to the high probability for deformation from rock pressures in intermediate and deep geological repositories. If metallic packages are to be used, they should be placed in a thick-walled overpack designed to resist such deformation. In addition, for graphite wastes, there are a number of specific properties of the material which need to be considered in the development and demonstration of packaging options. These considerations are addressed in this publication.

Other conclusions related to storage and disposal of graphite waste

The challenges imposed for radioactive graphite waste management are numerous and complex. There are no universally accepted decisions on treatment and conditioning methodologies at present, although it is clear that disposal will be either in an intermediate depth repository or a deep geological repository. The depth of disposal impacts the waste acceptance criteria, which in turn impacts the waste form, treatment and conditioning methodologies, including package selection and specifications.

Similarly, the approach used for, and the duration of, interim storage pending an available disposal repository has an impact on any pre-storage characterization, treatment and conditioning considerations and criteria. For these reasons, this publication addresses storage and disposal, but only in terms of their relationship to characterization, treatment and conditioning. In most cases, design, construction and licensing of a disposal repository for radioactive graphite is still pending, and at present, the most common approach is to rely on “safe enclosure” of graphite in existing facilities.

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APPENDIX
RECOMMENDED TERMINOLOGY APPLIED TO GRAPHITE OXIDATION IN AIR

Burning

It is proposed that the term "burning" should be strictly be restricted to the oxidation of the material *in the vapour phase* and this is not possible with graphite below around 3770K, the lowest temperature at which it has a significant vapour pressure. More frequently, "burning" or "fire" are general descriptive terms for an uncontrolled conflagration in which flames are present. Except for the external ignition of the flammable oxidation product of graphite formed in a limited supply of air (carbon monoxide), this situation does not arise with graphite either.

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. The process has been employed in the UK for mobilizing isotopes in the very weakly-irradiated graphite from the GLEEP reactor.

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 auto-catalysis) 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.

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.

Incineration

"Incineration" is defined in the IAEA Radioactive Waste Management Glossary [73] as "a waste treatment process of burning combustible waste to reduce its volume and yield an ash residue." For the purpose of this report, further discussion is appropriate. 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 the main body of the report.

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 in the main body of the report.

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. no visible flame exists). 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.

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) 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 with any external ignition source. Thus, while 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.

Wigner energy

Wigner energy is created inside nuclear reactors that use graphite as a neutron moderator. When the graphite is bombarded with neutrons from the reactor core, crystalline

dislocations occur as a result of the Wigner effect, causing the graphite rods to swell and begin storing the energy. This energy is problematic for nuclear reactors, because it can be spontaneously and rapidly released from the graphite in the form of heat, and unplanned excess heat is not a desirable situation within a nuclear reactor.

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