



60 Years

IAEA

Atoms for Peace and Development



The Abdus Salam

International Centre
for Theoretical Physics



Radiation Effects in Graphite

Michael I. Ojovan

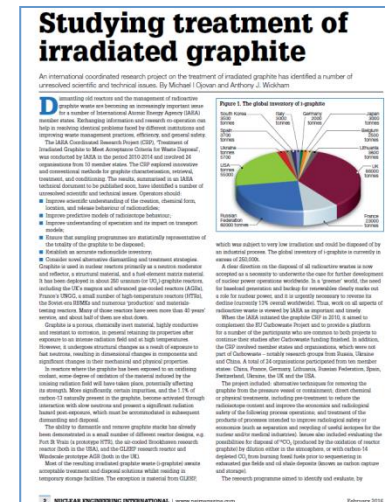
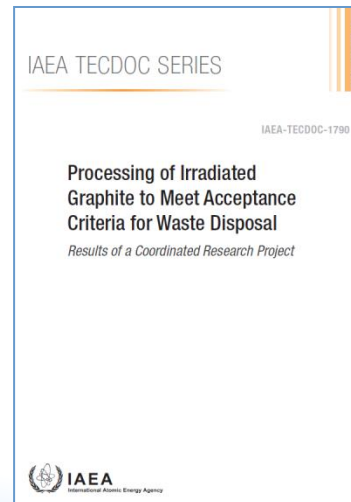
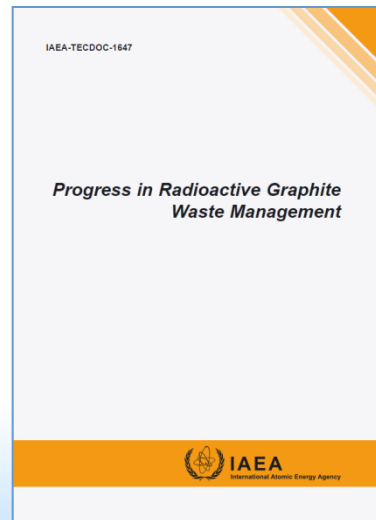
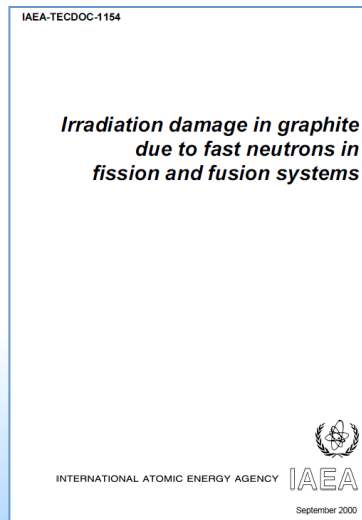
Nuclear Engineer, Department of Nuclear Energy, IAEA, Vienna
Assistant Professor (Visiting), The University of Sheffield, S1 3JD, UK (staff member 2002-2011)

Anthony J. Wickham

Professor (Visiting), Nuclear Graphite Consultancy, Cwmchwefru, Builtth Wells, LD2 3PW, UK and School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester M13 9PL, UK

- Nuclear graphite
- Radiation effects

Research into the subject of radiation damage in graphite began in the early 1950s as a part of the development of nuclear weapons and nuclear power. Since that time many graphite moderated nuclear fission reactors have been built and many varieties of graphite developed.



Nuclear graphite

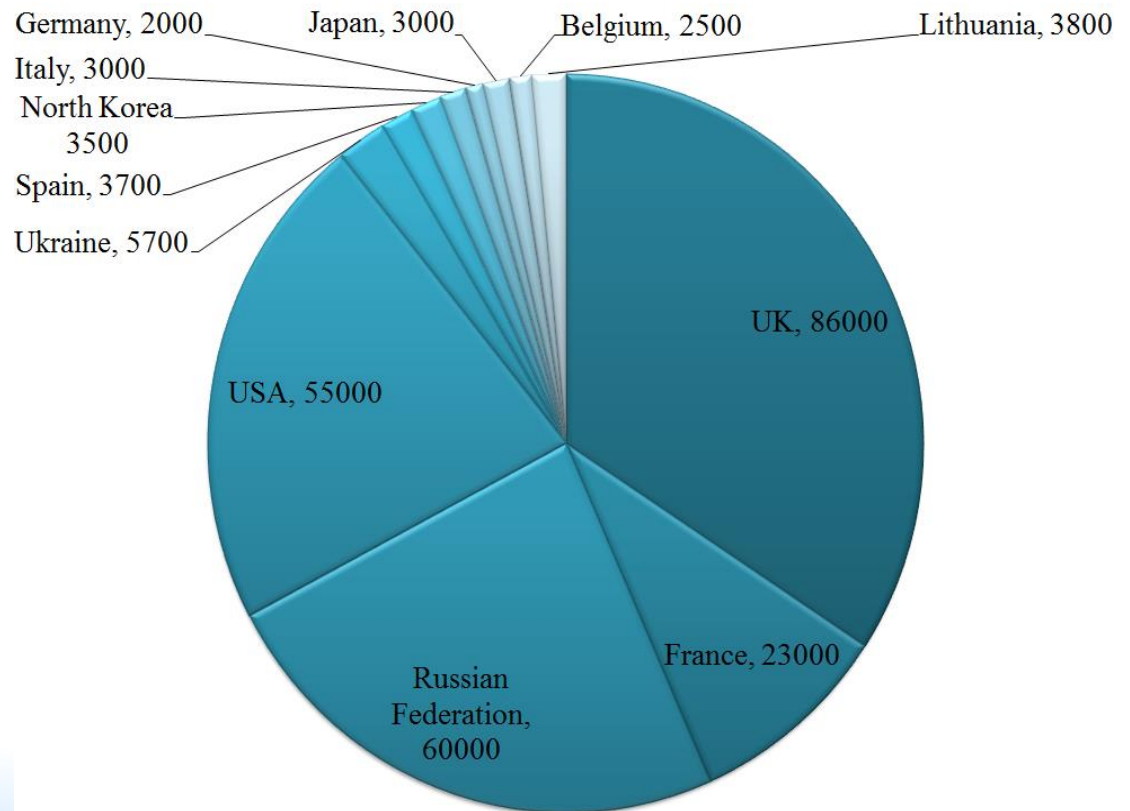
Nuclear graphite is any grade of graphite, usually electro-graphite, specifically manufactured for use as a moderator or reflector within a nuclear reactor. Graphite is an important material for the construction of both historical and modern nuclear reactors, due to its extreme purity and its ability to withstand extremely high temperatures and high irradiation doses (fast neutrons).

Reactor-grade graphite must be free of neutron absorbing materials, in particular boron, which has a large neutron capture cross section. Boron sources in graphite include the raw materials, the packing materials used in baking the product, and even the choice of soap (for example, borax) used to launder the clothing worn by workers in the machine shop.

Boron concentration in thermally purified graphite can be less than 0.4 ppm and in chemically purified nuclear graphite it is less than 0.06 ppm.

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear power plants and in many research and plutonium-producing reactors or piles, in quantities ranging from a few kilograms to more than 3000 tonnes per reactor depending upon the design. In a number of reactor designs it is also used as a fuel sleeving material, leading to the generation of large amounts of less irradiated but still significantly radioactive material.

Many of the older reactors are now shut down, with more approaching the end of their lives, and some **250000 tonnes** of irradiated graphite (*'i-graphite'*) have now accumulated world wide.



UK inventory: Graphite waste represents approximately 30% of the UK volumetric inventory of Intermediate Level Waste (ILW). The largest source of irradiated graphite within the UK originates from reactor moderators and reflector material. The majority of this graphite has been exposed to very high levels of neutron irradiation resulting in activation of impurity radionuclides. There are also other sources of irradiated graphite components, in addition to the moderator and reflector, such as Material Test Reactor (MTR) thermal columns, fuel channel sleeves, graphite plugs, outer circumferential fuel sleeves, graphite boats and side locating struts. Once all the graphite moderated reactors have closed, the UK will have a graphite waste inventory amounting to 86,000 tonnes (... 100,000).

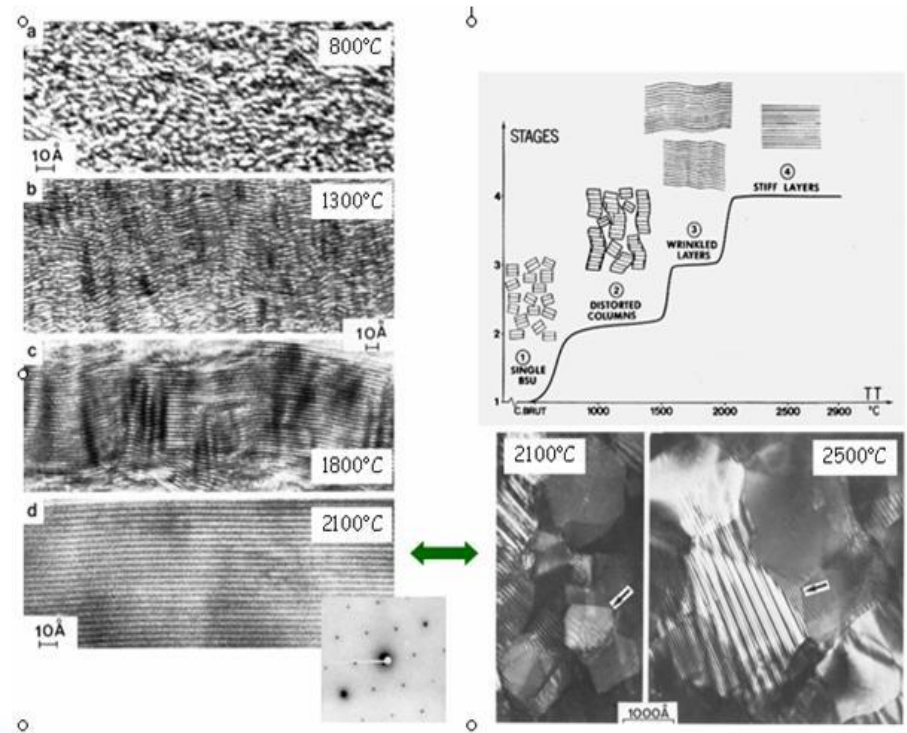
TABLE 1: TEMPERATURES AND FAST NEUTRON DOSE FOR OLDBURY REACTOR 1 (2009) TREPANNED SAMPLES FROM FLATTENED REGION CHANNELS [28]

Sample ID	Trepanned Sample Height (m)	Temperature (°C)	DIDO Equivalent Dose (10^{20} n.cm ⁻²)	Displacement per atom* (dpa)	%wt loss*
1/2	2.66	294	45.56	6.0	33
2/2	3.01	302	48.15	6.3	38
5/2	4.26	329	51.49	6.8	33
6/2	4.70	338	50.95	6.7	33
9/2	5.86	356	45.55	6.0	25
10/2	6.22	361	42.86	5.6	27

* Calculated by the authors

Nuclear reactors use a synthetic polycrystalline graphite. This is essentially a carbon-carbon composite made up of a filler (generally calcined petroleum coke) and a binder (generally coal-tar pitch), screened. The grains obtained are then mixed in suitable proportions to obtain the required density and to help expel the volatile matter from the binder. The coke is then mixed with coal-tar pitch at a temperature of 165°C, before being shaped by extrusion or unidirectional or isostatic compression. It is then baked at 800°C to 1200°C to coke the binder.

The density and mechanical properties of the resulting product can then be enhanced through one or more impregnation stages, generally using a petroleum pitch. Finally, the product is graphitized at 2500°C to 3000°C to obtain the hexagonal (but imperfect) crystalline structure that is characteristic of graphite. Graphitization is carried out using cleaning agents such as NaF, MgF₂ to obtain high-purity nuclear graphite.



Nuclear graphite is manufactured from petroleum or natural pitch cokes. These cokes are baked, blended and mixed with a binder and formed by extrusion, simple or vibration moulding, or isostatic pressing, into blocks known as the ‘green articles’.

These are then baked in the range 800–1200°C forming a carbon block. For moderator and reflector blocks (and fuel element component material) a pitch impregnation may be undertaken at this point: the blocks are then graphitised at ~2800°C and may be further impregnated with binder pitch, re-baked and re-graphitized in order to give a product of higher density, typically 1.6–1.8 g.cm⁻³. This is below the theoretical crystal density of graphite because **pores remain in the material** as the result of gas evolution or entrapment during the processing.

TABLE 2.2. PROPERTIES OF ISOTROPIC NUCLEAR GRAPHITES

Country of Origin	UK	USA	USA	USA	Japan
Designation	IMI-24	H-451	AXZ-5Q1	N3M	IG-110
Coke	Gilsonite	Mixed			Petroleum
Final HTT	~2800°C		>2500°C		1.78
Density (g/cm ³)	1.81	1.73	1.5		4.1 × 10 ⁻⁶
Open pore volume	0.11				
Thermal expansion coefficients (K ⁻¹) (20–120°C)	4.3 × 10 ⁻⁶	4.0 × 10 ⁻⁶	6.7 × 10 ⁻⁶	5.0 × 10 ⁻⁶	
Electrical resistivity (ohm-cm)	0.9 × 10 ⁻³		1.7 × 10 ⁻³		
Thermal conductivity (W/m/K)	131	140	80	180	78
Young's Modulus (GN/m ²)	10.8	8	8	6.5	10.2
Poisson's ratio	0.2	0.1–0.2			0.14
Strength (MN/m ²)					
Tensile	17.5	15	10	41	25.3
Bend	23	20			37.2
Compression	70				76.8
Gas transport properties					
Diffusivity	3 × 10 ⁻³				
Permeable flow parameters					
B ₀ (m ³)	6.5 × 10 ⁻¹⁵				
K ₀ (m)	5.8 × 10 ⁻⁹				

IAEA TECDOC-1154

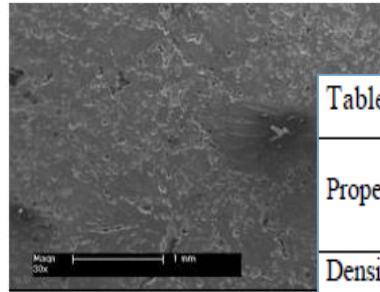
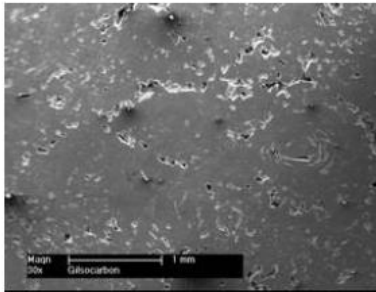
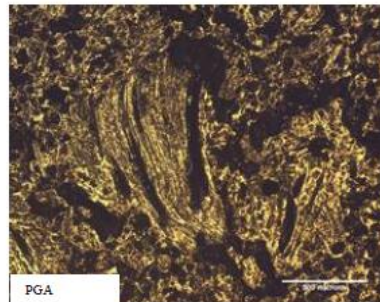
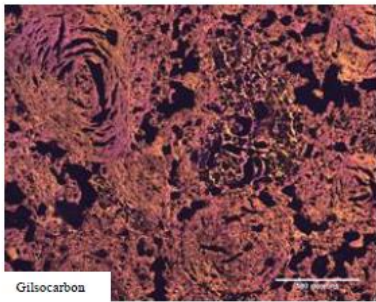


FIG. 1. Cross-polarized optical micrographs (scale bar 500 μm) and SEM images (scale bar 1 mm) of typical Gilsocarbon and PGA graphites used in the UK reactors.

Table 4. Typical virgin properties of Pile Grade A (PGA) and Gilsocarbon nuclear graphites

Property	Units	Pile Grade A graphite (Anisotropic)	Gilsocarbon graphite (Isotropic)
Density	g cm^{-3}	1.74	1.81
Thermal expansion coefficient (20–120°C)	K^{-1}	0.9E6 * 2.8E6 **	4.3×10^{-6}
Thermal conductivity (20°C)	$\text{W.m}^{-1} \text{K}^{-1}$	200 * 109**	131
Young's modulus (20°C)	GPa	11.7 * 5.4**	10.85
Strength tensile	MPa	17 * 11**	17.5
Strength bend	MPa	19 * 12**	23
Strength compression	MPa	27* 27**	70
Electrical resistivity	M ohm cm^{-1}	620 * 1100*	900

* Denotes parallel to the layer planes.

** Denotes perpendicular to the layer planes.

IAEA TECDOC-1647

Radiation effects

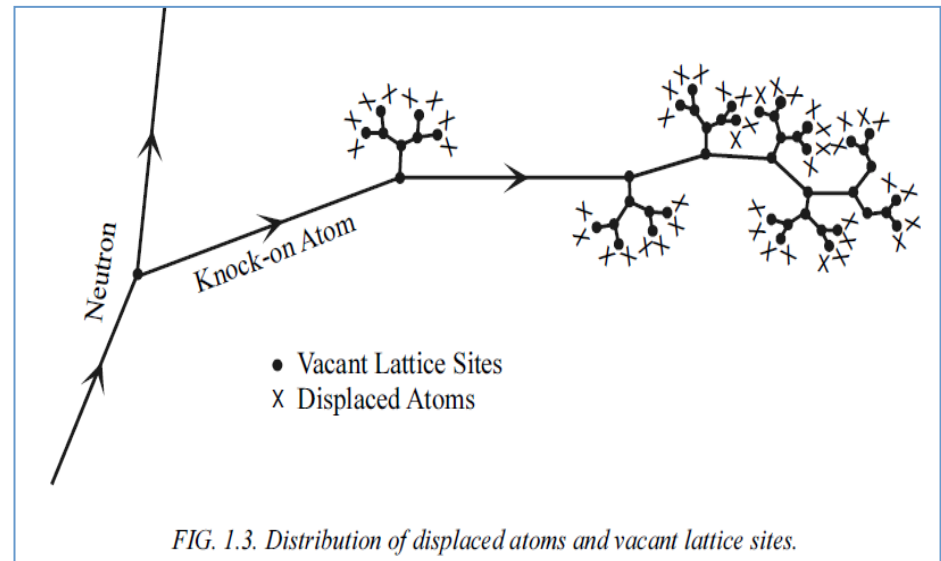
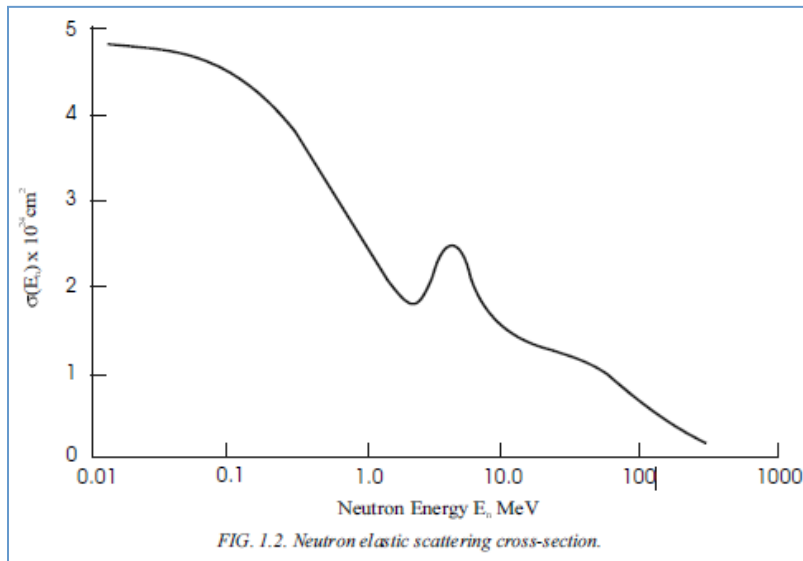
Upon irradiation in a reactor, a number of significant changes take place driven by different components of the radiation field to which the graphite is exposed. The consequence of this irradiation in some cases is temperature dependent, or dependent upon other factors such as the pressure of a coolant gas. In summary, the principal irradiation induced changes are as follows:

- Fast-neutron effects
- Ionizing radiation effects
- Slow neutron effects
- Operational effects and irradiation environment

No two reactor designs will give rise to *i*-graphite with similar properties, since different operational histories will have a bearing on the radioisotope content and possibly on the location (and chemical form) of those radioisotopes.

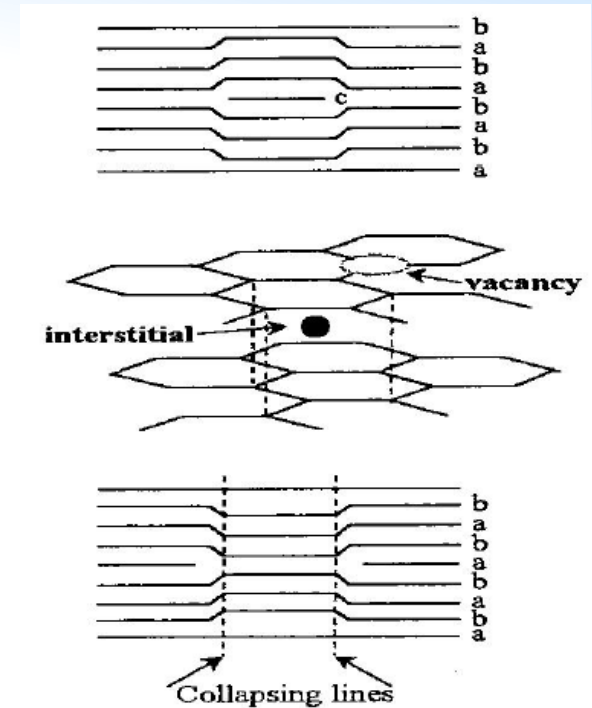
Fast-neutron effects

The purpose of a graphite moderator is to slow high energy neutrons to a lower energy at which capture by further fissionable isotopes in order to maintain the chain fission process is maximised. In the course of collisions between neutrons and carbon atoms cause displacement of the latter from their original lattice positions to form complex structures and dislocations in the original crystallites.

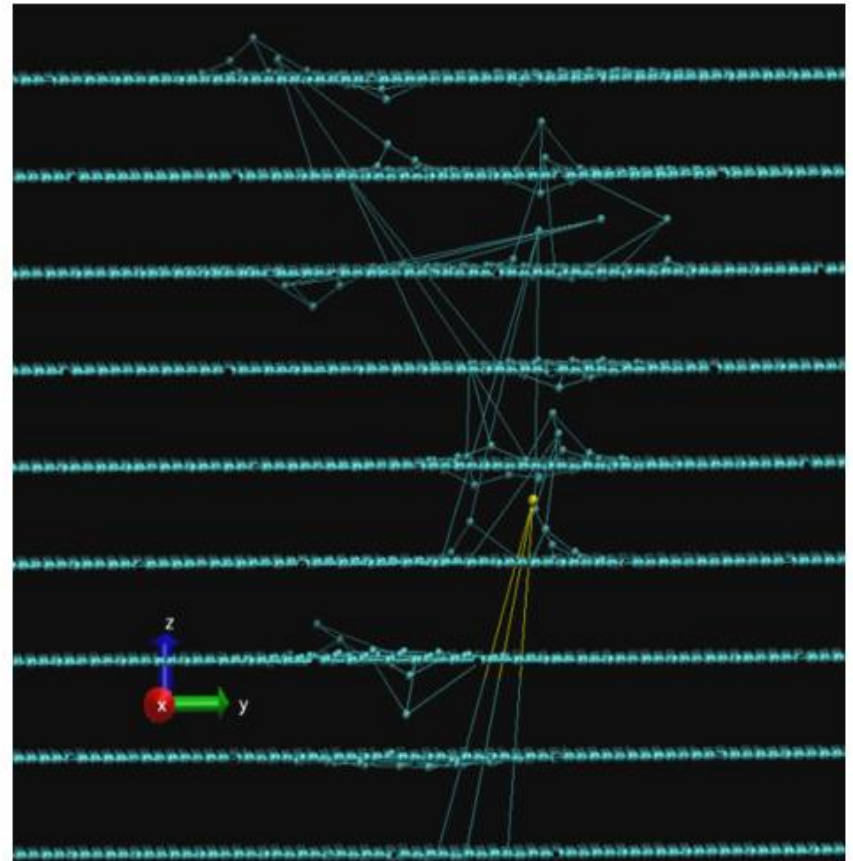
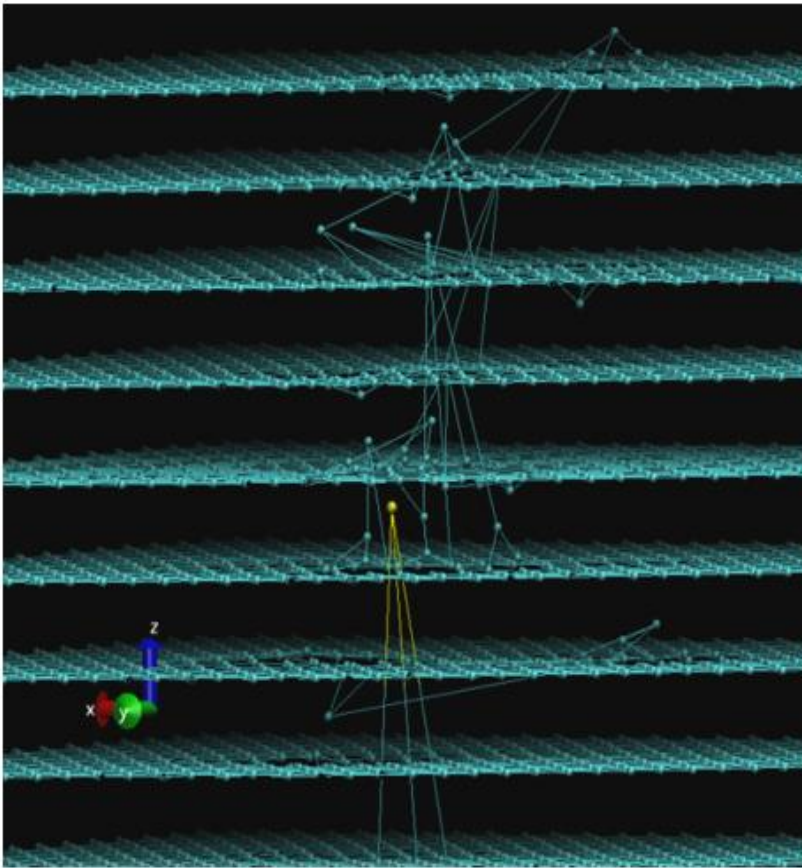


Modern technologies have recently suggested that the classical damage configurations should be augmented by more complex structures in which adjacent 'planes' of carbon atoms are 'bridged' by displaced atoms, and in which buckling and shearing of these layer planes can take place.

The displaced carbon atoms recoil through the lattice and produce other carbon atom displacements in a cascade effect. The cascade carbon atoms tend to be clustered in small groups of 5-10 atoms and it is generally satisfactory to treat the displacements as if they occur randomly. However, not all of the carbon atoms remain displaced. The displaced carbon atoms diffuse between the graphite layer planes in two dimensions and a high proportion of them will recombine with lattice vacancies. Others will coalesce to form linear molecules, which in turn may form the nucleus of a dislocation loop – essentially a new graphite plane. Interstitial clusters, on further irradiation, may be destroyed by impinging neutrons or energetic displaced carbon atoms (irradiation annealing).



The irradiation process may also be considered as making the graphite structure increasingly 'imperfect', the planes of graphite within the crystallites and the crystallites themselves becoming less well oriented. Changes also occur in the distribution of porosity, and some new porosity is generated.



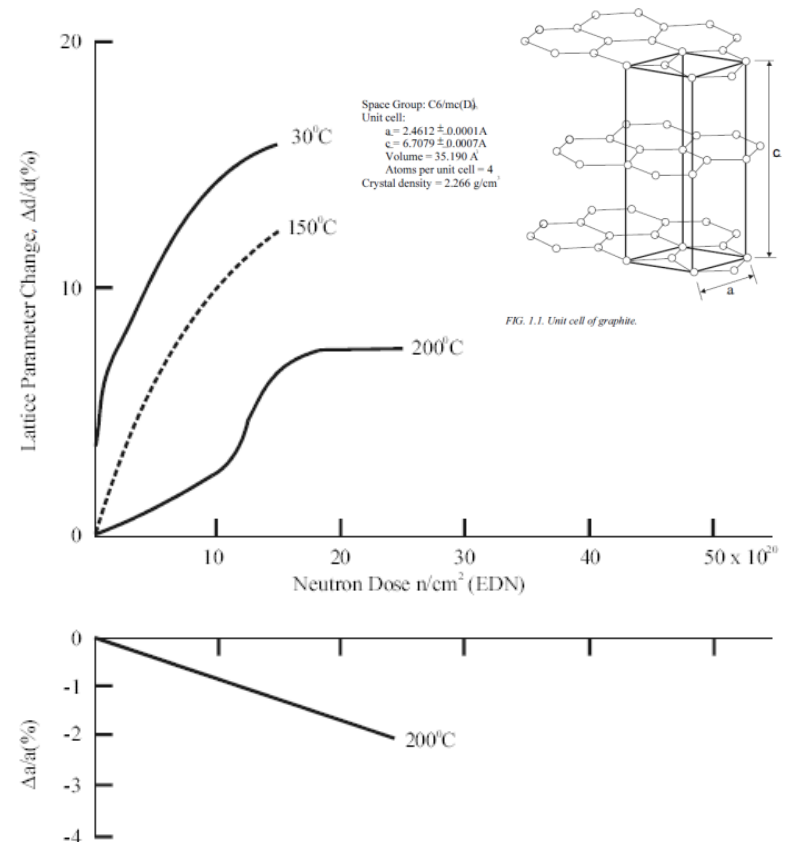
Simulation a cascade in graphite with 1 keV, parallel to z lines indicating the origin of atoms (bonded to neighbouring atoms).

Courtesy R. Nabbi and H. Probst, INBK & Forschungszentrum Jülich, Germany.

Fast-neutron effects have important consequences. The first is to change fundamental physical and mechanical properties of the graphite, leading to dimensional change (*and potential interaction of components in stacks which might result in greater force being needed to dismantle them*), embrittlement and strength reduction, cracking of components, along with changes in thermal properties.

The magnitude of such changes will depend upon the total fluence, to a lesser extent on the flux, and upon temperature, since certain effects are ‘annealed’ (mitigated) at higher irradiation temperature, such that one observes differing change rates and patterns of change in various properties.

An example of the complexity of this phenomenon is seen at the fluences experienced by power reactors such as AGRs and RBMKs at long irradiation times, when an initial shrinkage in the graphite components reverses into an expansion at different times in different regions of the core.



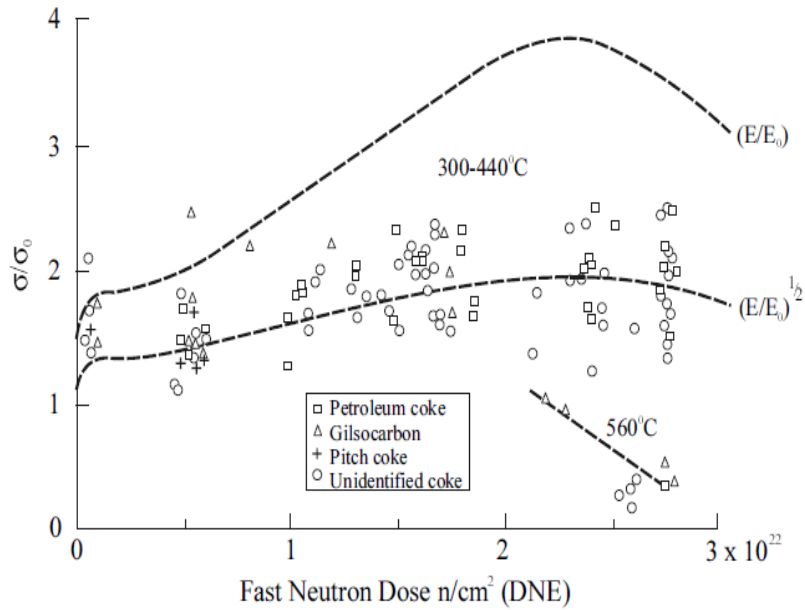


FIG. 5.7. Tensile strength changes with fast neutron dose for near-isotropic graphites irradiated in DFR.

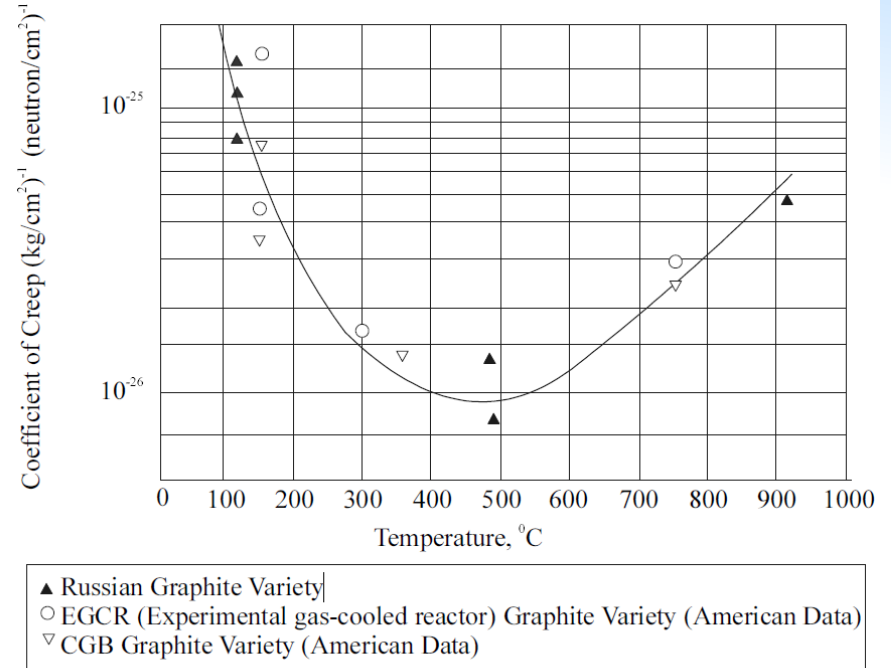
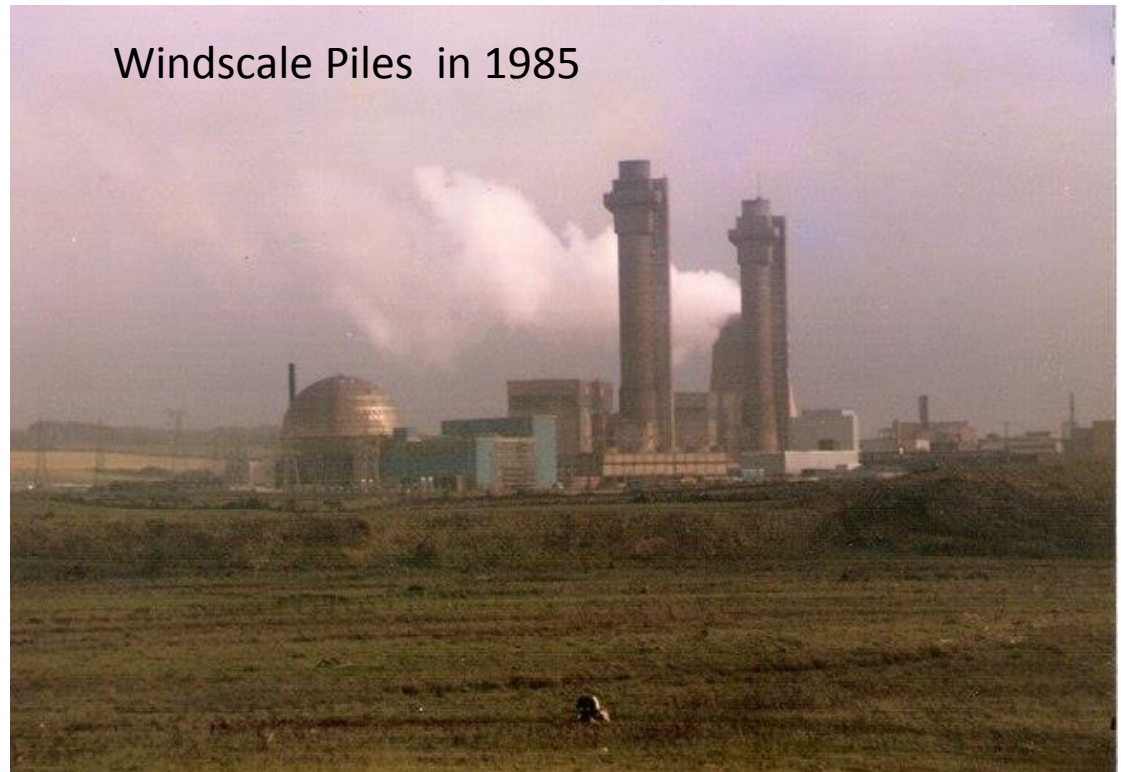


FIG. 5. 2(a). Variation of creep rate with temperature: Russian and American data.

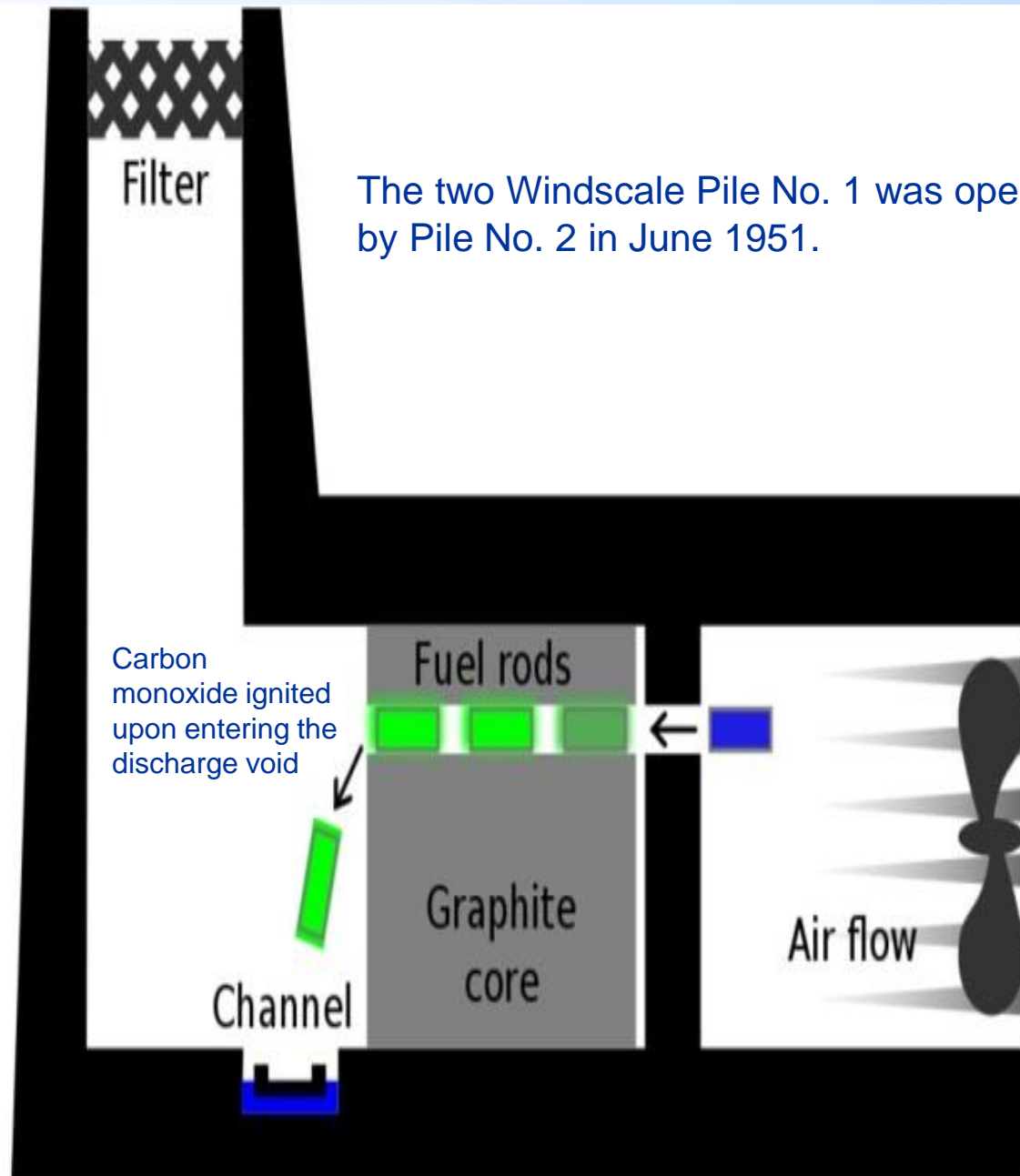
An effect which is specific to low-temperature graphite irradiation ($< \sim 250^{\circ}\text{C}$) is the storage of potentially large amounts of energy within the damaged graphite structures which are capable of being released if the graphite is heated to approximately 50°C above its former irradiation temperature.

This is the phenomenon of **Wigner energy**, the unplanned release of which led to the Windscale Pile 1 accident in 1957.

It should be emphasised that the Windscale fire **was not a graphite fire** but initiated by isotope cartridges and fuel: CO from thermal (chemical) oxidation of graphite at the high temperatures ignited upon entering the discharge void where there was plenty of oxygen in the air space.



The two Windscale Pile No. 1 was operational since October 1950 followed by Pile No. 2 in June 1951.



The Windscale fire of 10 October 1957 was the worst nuclear accident in Great Britain's history, ranked in severity at **level 5**. The accident occurred when the core of the Pile No.1 nuclear reactor caught fire, releasing radioactive contamination into the surrounding area.

The fire burned for 3 days and radioactive material released spread across Europe. Of particular concern was release of ^{131}I .

No one was evacuated from the surrounding area, but there was concern that milk might be contaminated.

Milk from about 500 km² of nearby countryside was diluted and destroyed for about a month.

A 2010 study of workers directly involved in the clean-up found **no significant long term health effects** from their involvement.

Releases (TBq)

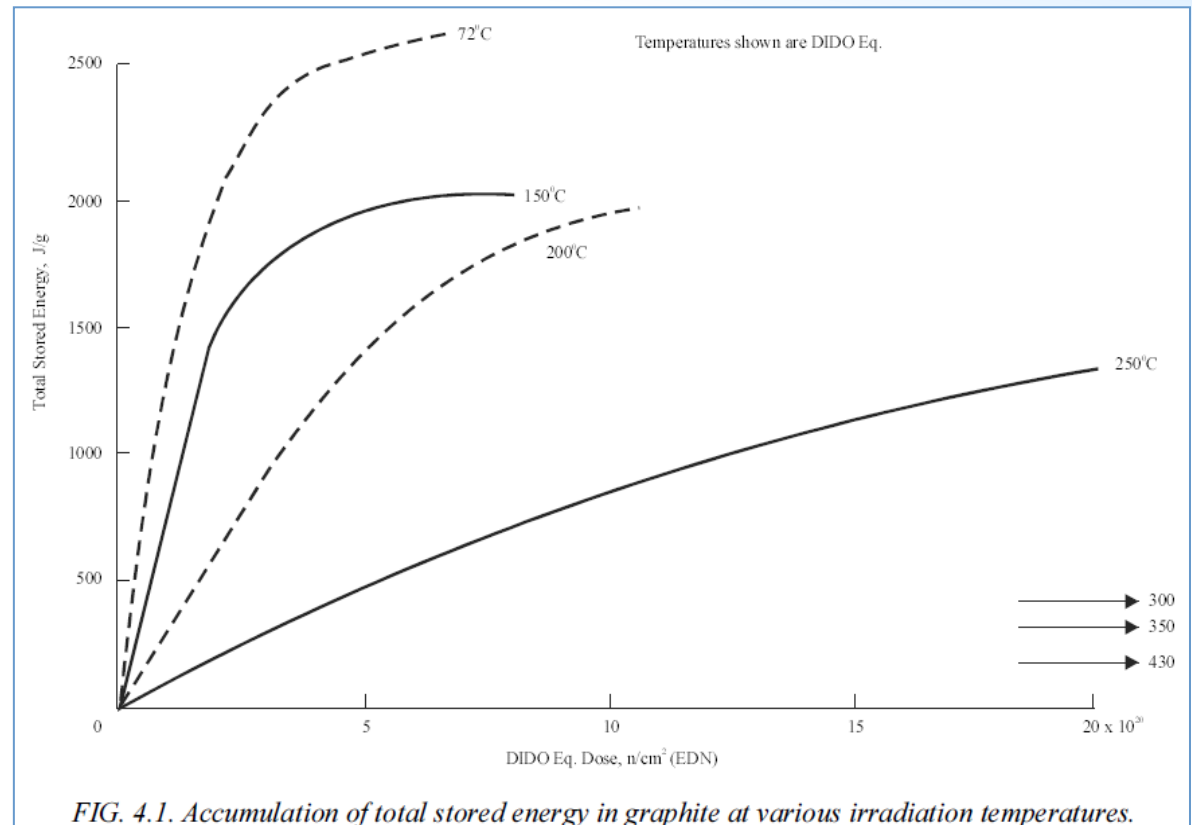
R/n	Windscale	Chernobyl	Fukushima Daiichi (atm.)
^{131}I	740	1,760,000	130,000
^{137}Cs	22	79,500	35,000
^{90}Sr		80,000	

Decommissioning works in 2013



Wigner energy is successfully controlled by regular annealing and can be kept well below any threshold for release.

The important parameter in this case is the rate of release of energy as a function of increasing temperature, which has the same units as specific heat capacity and relates to the rate at which the graphite will heat up in response to an external source of energy.



Monitoring of the stored energy in power reactor graphite moderators is routine practice where the operating temperature is low, because of the effects it has on the thermal capacity of the moderator in accident situations. The saturation levels of stored energy for irradiations above ~300°C is too small to be of practical importance.

Wigner or stored energy release is potentially present in graphite derived from such reactors as the Brookhaven Graphite Research Reactor (BGRR, USA, now dismantled), BEPO in UK and G1 at Marcoule in France, along with production reactors elsewhere.

Wigner energy in many cases was successfully controlled by regular annealing and remains well below any threshold for release.

Modest amounts of **Wigner energy** are present in the cooler regions of Magnox-type reactors, but the levels have saturated well below those at which they are likely to present a decommissioning or storage hazard. Other designs may contain limited amounts in particular **regions of the stacks** (e.g. RBMK).

Ionizing radiation effects

γ - and β -radiations (both defined here as ionizing radiations) are present in the graphite of the reactors, the flux primarily arising from fuel fission-products (gammas) with contributions also from local emitters (activated structural components). These ionising radiations do not affect the graphite structure directly but interact with coolant gases to generate species from the gas phase which may then interact with graphite.

TABLE A1.1 G-VALUES FOR VARIOUS IRRADIATING PARTICLES IN CO₂

Particle	G (ion pair)	Ref.
Electrons 18 keV	3.05	Jesse and Sadauskis (1955)
67 keV	3.04	
Protons 1.83 MeV	2.91	Larson (1958)
α -particles (Po ²¹⁰)	2.94	Widder and Huber (1958)
Recoil ions Th C 117 keV	0.98	Stone and Cochran (1957)
Th C 168 keV	1.01	
C ¹³ 1.64-2.92 MeV	2.38	Leake (1967)
O ¹⁶ and C ¹² 0.1-1.5 MeV	1.47-2.56	
O ¹⁶ 30 keV	1.45	Boring and Woods (1968)
40 keV	1.52	
50 keV	1.58	

In reactor irradiation the max G value (pure CO₂) is 3.0 which is reduced by the inhibiting action of the CO produced and (in AGRs) by added methane.

A significant proportions of the secondary electrons which cause the ionisation come not from gammas but from inelastic collisions between fast neutrons and carbon atoms in the graphite.

(A.J. Wickham)

G-value: the number of a particular species produced **per 100 ev** of energy loss.

The most important effect is oxidation of the graphite by oxidizing species generated in carbon dioxide or air coolants. Such effects are proportional to the ionizing radiation fluence, the gas density, the open-pore volume of the graphite (and its size/shape distribution), along with the concentrations of any oxidation inhibitors present in the gas.

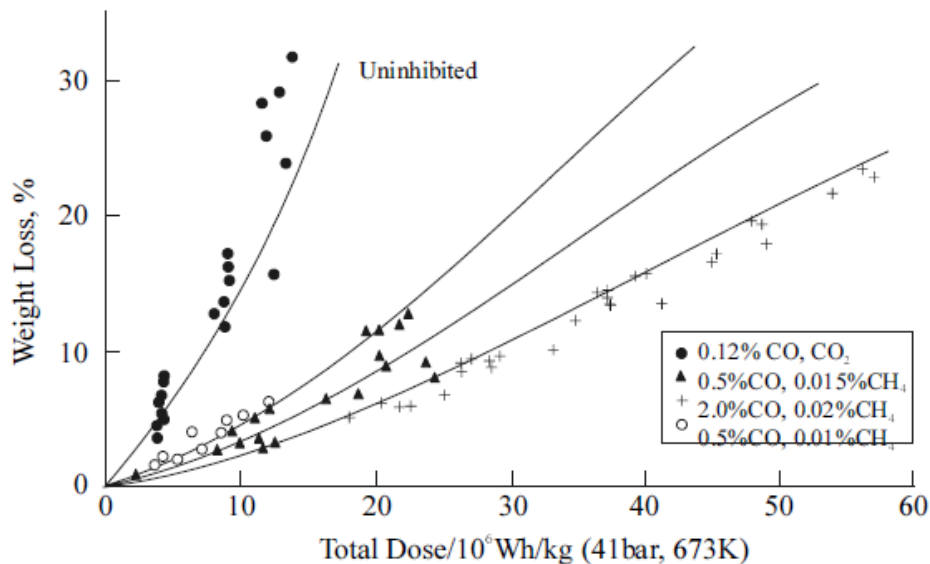


FIG. A1.4. Moderator weight loss against dose in different coolants.

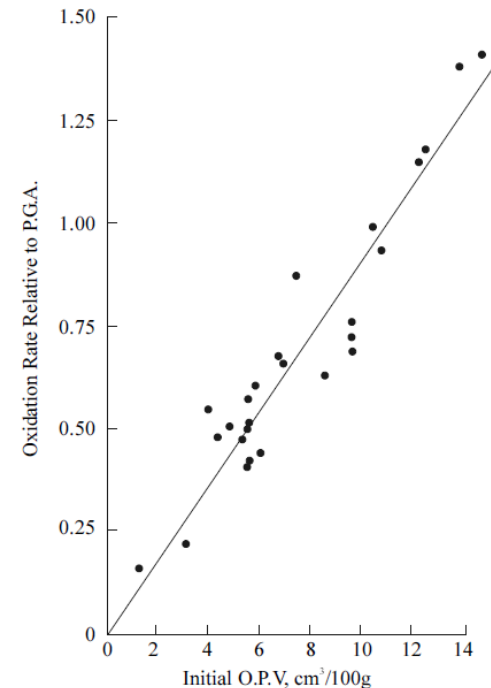


FIG. A1.2. Oxidation rate of graphites relative to PGA as a function of open pore volume.

In carbon dioxide or air cooled plant, radiolytic oxidation will lead to changes in graphite properties including reductions in strength and elastic moduli: in UK AGRs and in the Bugey I UNGG plant in France, regions in excess of 40% weight loss are known to exist.

Typically there is no thermally induced graphite oxidation, except in plants which have sustained accidents: this cannot occur with significance at temperatures below about 400°C in carbon dioxide. In the hottest reactors using this coolant (AGRs), a system of re-entrant flow maintains the moderator stack at a sufficiently low temperature to avoid thermal oxidation. Some thermal oxidation of fuel-element sleeves occurs in these reactors, but the dwell time of sleeve graphite is seven years rather than the full 35+ years of the moderators.

➔ Reaction between air and pure nuclear graphites is generally not measurable below about 350°C and only becomes significant in the region of 400°C. The rate of reaction is typically of the order of $3-8 \times 10^{-10} \text{ kg.kg}^{-1}.\text{s}^{-1}$ at this temperature (historically expressed in $\mu\text{g/gh}$; $1\mu\text{g/gh}$ being $2.78 \times 10^{-10} \text{ kg.kg}^{-1}.\text{s}^{-1}$). The chemical regime then extends typically up to 550-600°C.

The special cases are Windscale Pile 1 in the UK which sustained the fuel fire: in the fire affected zone the air oxidation during the fire is known to have increased the channel size and weakened the graphite components, and there are penetrations (locally 100% oxidation) between certain horizontal fuel channels and vertical shut down rod channels resulting from 'chimney effects' during the fire.

In Obninsk NPP, 'wet accidents' led to the production of carbon dioxide and a high rate of graphite oxidation as a result, damaging the surfaces and structure of some graphite components.

In the helium coolant in an HTR environment, there is no thermal or radiation-induced oxidation either, except through the introduction of impurities, when radiation energy absorbed in the helium can be transferred to the impurity molecules and contribute to their reaction rate. The most likely oxidants in the pebble bed HTR design are water and air introduced with the fuel pebbles, but only accident scenarios could lead to any significant amount of graphite oxidation.

A separate potential issue in CO₂ based systems is the production of various forms of adherent carbonaceous deposition, which is found on both fuel-element and moderator graphite (as well as on metallic structural components). In the coolest part of Magnox reactor moderators, such concentrations can be locally very high, and there have been concerns about the potential 'sticking' of components during dismantling.

Slow neutron effect

From the dismantling and waste disposal point of view, slow neutrons may represent the most important feature of graphite irradiation. A number of impurities within the graphite have significant capture cross sections for activation to radioactive isotopes. Depending upon their half-lives, these radioisotopes may be important during the dismantling phase and the 'operational' period of a repository (e.g. ^3H , ^{60}Co) or present a very long lived presence and therefore a containment issue (e.g. ^{14}C , ^{36}Cl , ^{41}Ca).

Inventory ^a (TBq)	Core graphite	Other graphite
chlorine-36	2.31E+01	5.52E-01
carbon-14 (2004 Inventory)	1.27E+03	7.65E+02
carbon-14 (revised estimate) ^{b (2)}	6.07E+03	2.33E+02
cobalt-60	2.97E-01	1.36E+06
Tritium	3.82E+01	2.47E+05

^a All activities are undecayed activities reported in the 2004 Inventory for stocks and future arisings, with the exception of C-14 (revised estimate).
^b Carbon-14 (revised estimate) is the current best estimate from Nirex.

Associated with these effects is the physical location of these newly created isotopes within the graphite structure: in addition to the source location, recoil-energy effects may be important in changing the position and chemical form of the newly-created species.

Table 5. Types of radiation and half-lives for the radionuclides in nuclear graphite

Radioisotope	Radiation energy				Half-life (years)
	α	B	γ	E	
^3H		√			12.3
^{14}C		√			5730
^{36}Cl		√			300 000
^{41}Ca				√	130 000
^{60}Co		√	√		5.3
^{85}Kr		√			10.8
^{94}Nb		√	√		20 000
^{95}Nb		√	√		0.096
^{133}Ba			√	√	10.5
^{134}Cs		√	√		2.06
^{137}Cs		√	√		30.2
^{152}Eu			√	√	13.3
^{154}Eu		√	√	√	8.5
^{155}Eu		√	√		4.96
^{238}Pu	√				87.75
^{239}Pu	√				24 390
^{240}Pu	√				6537
^{241}Am	√		√		433
^{241}Pu	√	√			14.89

RBMK1500 data

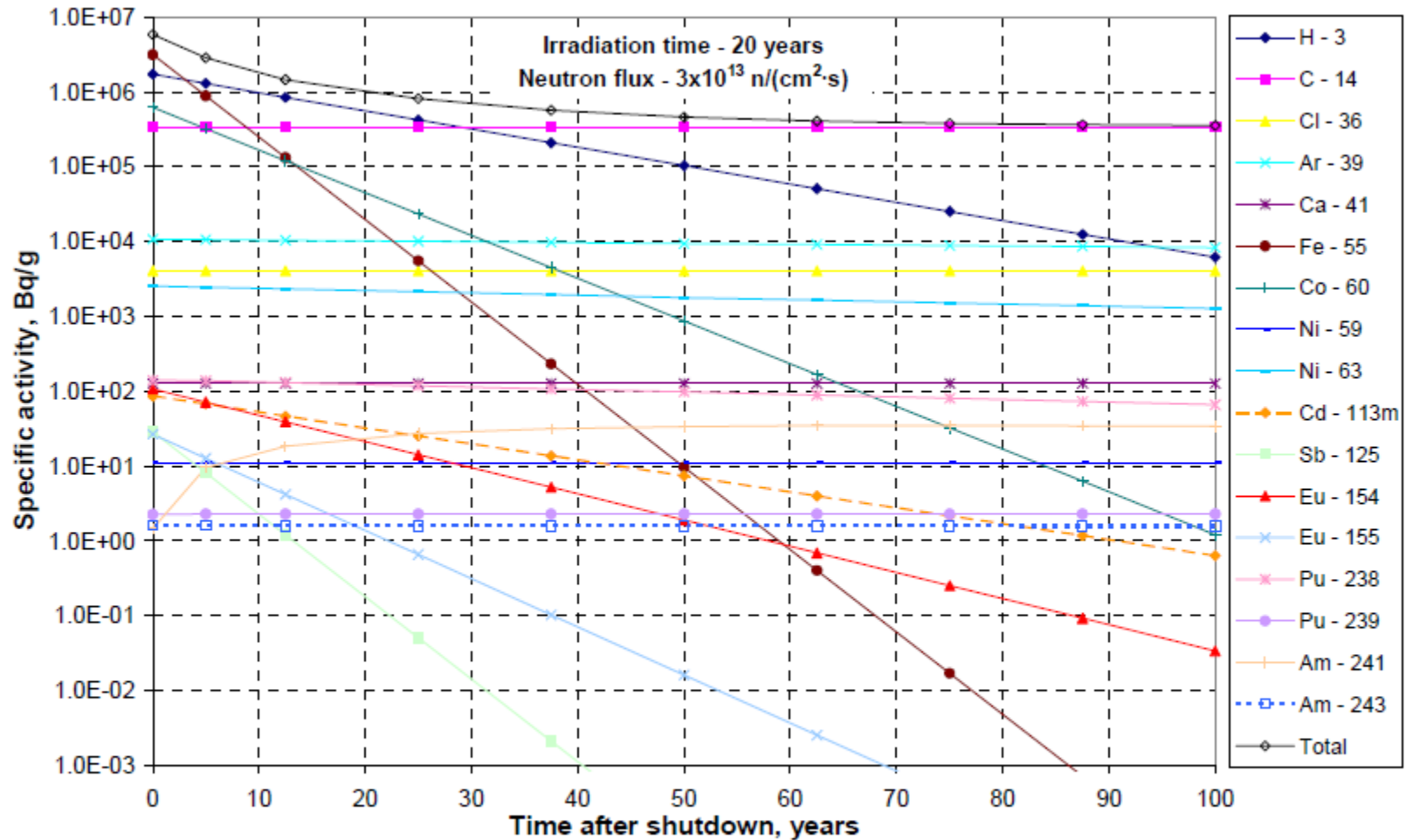


FIG. 5. Induced activity dependence on cooling time for the main nuclides.

One issue which arises with respect to slow neutron irradiation is the perceived need for **radiation shielding** during the dismantling process. WAGR was successfully dismantled in air in the UK, as was BGRR in USA. Fort St. Vrain (USA) utilised underwater dismantling as a radiation shield because of highly activated metallic components and the residual presence of fuel element compacts.

Whilst France plans to dismantle later UNGGs under water to provide shielding, the UK sees no case to do this for Magnox reactors or AGRs. **Underwater dismantling** will result in the leaching of isotopes from the graphite into the water, and a consequential need to retain these on ion exchange resins, with the additional complication and cost of disposing of this material, the associated plant, and the water.

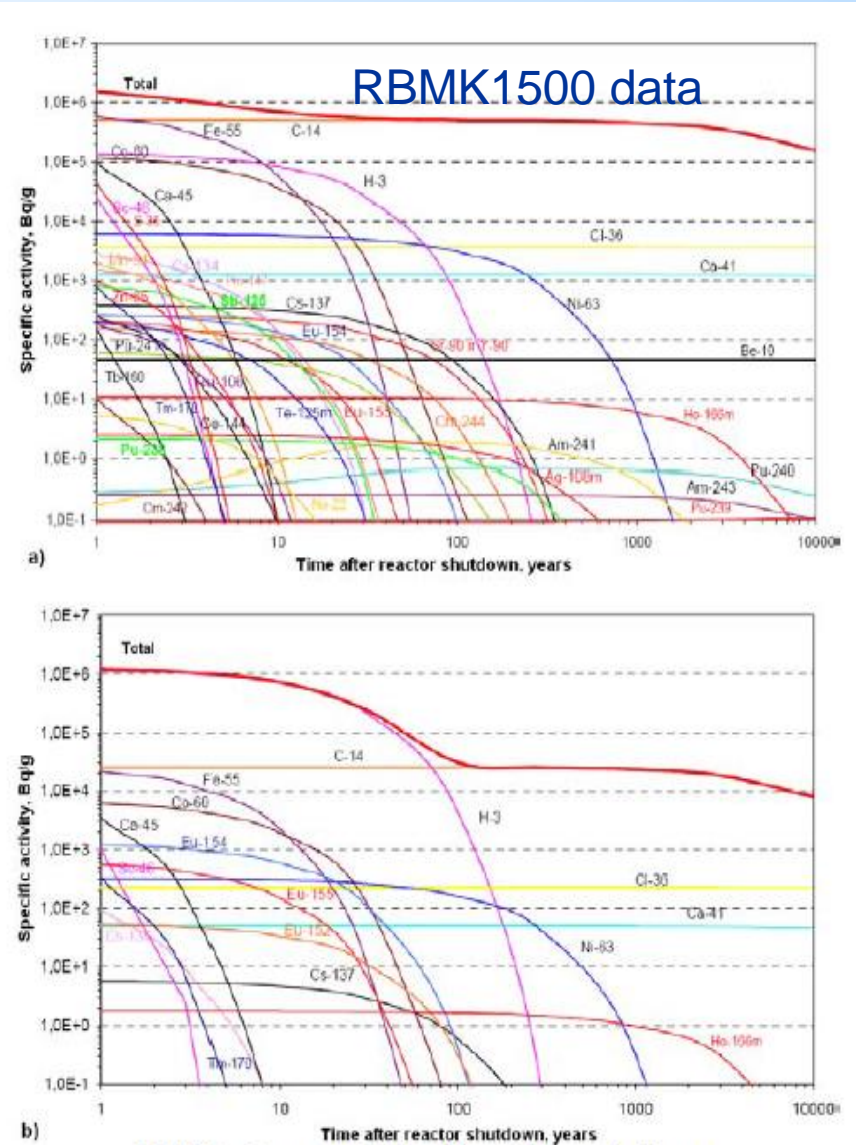


FIG. 14. Specific activities of radionuclides as a function of cooling time: a — in the moderator; b — in the corner reflector.

Operational effects and irradiation environment

Attention must also be paid to the nature of the environment in which the graphite has been irradiated. As an example, the graphite in the RBMK design is irradiated (usually) in a helium/nitrogen mixture which is essentially static. This environment can give rise to the formation of a high concentration of ^{14}C from the reaction $^{14}\text{N}(n,p)^{14}\text{C}$, with the ^{14}C located on accessible graphite surfaces.

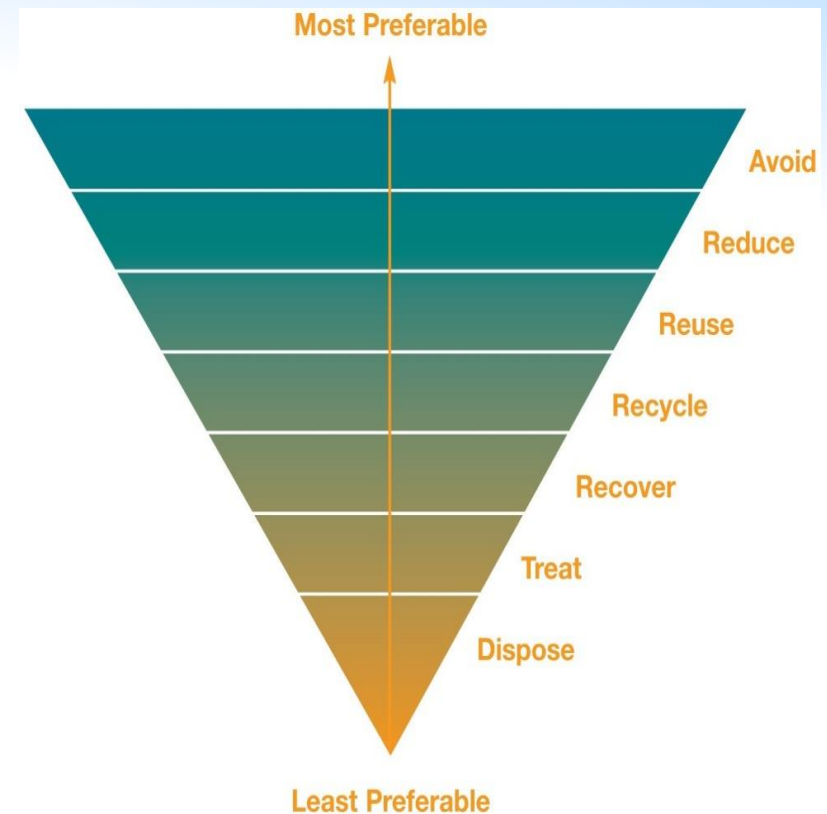
A secondary effect in this environment is the creation of a new chemical compound, paracyanogen $(\text{C}_2\text{N}_2)_n$ with essentially all of the carbon atoms being ^{14}C ; this was first described not in the graphite waste context but as an unwanted by-product in the annulus gas space of CANDU reactors when nitrogen was used as the annulus gas. The significance of the potential existence of this compound on graphite surfaces requires careful consideration.

Conclusions

Upon irradiation in a reactor, a number of significant changes take place driven by different components of the radiation field to which the graphite is exposed.

The consequence of irradiation is dependent on many parameters such as temperature, pressure of a coolant gas.

No two reactor designs will give rise to *i*-graphite with similar properties.



References:

1. IAEA TECDOC-1154. Irradiation damage in graphite due to fast neutrons in fission and fusion systems. IAEA, Vienna (2000).
2. IAEA TECDOC-1647. Progress in Radioactive Graphite Waste Management. IAEA, Vienna (2010).
3. IAEA TECDOC -1790. Processing of irradiated graphite to meet acceptance criteria for waste disposal. IAEA, Vienna (2016).
4. M.I. Ojovan, A.J. Wickham. Studying treatment of irradiated graphite. *Nuclear Engineering International*, 16-18, February 2016. <http://www.neimagazine.com/features/featurestudying-treatment-of-irradiated-graphite-4818534/>



IAEA

60 Years

Atoms for Peace and Development

Thank you!

