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Compatibility Problems in the Use of Graphite in Nuclear Reactors

By Robert L. Carter

Summary · *Artificial graphite has long been in use as a thermal reactor moderator medium. Its advantages lie in its low cost, its machineability, its moderate chemical reactivity and its metallurgical stability. It is not exothermically reactive with respect to any common coolant medium except air. Interactions with ordinary structural media begin to be troublesome only as temperatures above 600° C are achieved. It is compatible with a wealth of other moderator media and incidental core materials.*

Zusammenfassung · *Künstlicher Graphit wird bereits seit langem als Moderatormaterial für Reaktoren verwendet. Seine Vorteile liegen in den geringen Kosten seiner Bearbeitbarkeit, seiner geringen chemischen Reaktivität und seiner metallurgischen Stabilität. Graphit zeigt keine exothermische Reaktivität mit irgendeinem gewöhnlichen Kühlmittel mit Ausnahme von Luft. Wechselwirkungen mit üblichen Strukturmaterialien bedingen erst oberhalb 600° C Schwierigkeiten. Graphit ist mit einer großen Zahl anderer Moderatormaterialien und üblichen Core-Materialien vereinbar.*

Sommaire · *Depuis lonvtemps déjà, on emploie du graphite artificiel comme modérateur dans des piles. Ses avantages résultent des frais de traitement peu élevés, de sa petite réactivité chimique et de sa stabilité métallurgique. Le graphite ne présente pas de réactivité exothermique avec n'importe quel fluide réfrigérant usuel à l'exception de l'air. L'intéraction avec les matériaux structurels usuels ne commence à causer des difficultés qu'à partir de 600° C. Le graphite est compatible avec un grand nombre d'autres matériaux modérateurs et des matériaux habituellement utilisés dans les coeurs de piles.*

Introduction

Much well-deserved attention has been devoted to the inherent problems of fabrication and use of graphite in nuclear reactors [1, 2, 3, 4, 5, 6, 7]. Rigorous standards of manufacturing purity are often imposed in an effort to reduce parasitic neutron absorption. The changes wrought as a consequence of energetic particle irradiation of moderator graphite have received especial notice and have been reported in detail [8, 9, 10, 11]. Less peculiar to nuclear reactors *per se*, but of great importance because of its many facets, is the work bearing upon the interactions between the moderator graphite in a thermal reactor and its essential companion materials in a reactor core [12].

The present paper undertakes to survey the character of the interactions with graphite possible in the reactor core. For the sake of organization, interacting materials are classified either as coolants, structural and separator media, fuels, moderators, or control and safety poisons. Materials employed in conjunction with graphite in several important reactor systems are listed in Table 1.

Contact of Graphite with Coolant Media

Water or D_2O

Water has been used as the principal coolant medium in a large number of graphite-moderated reactors. Although it is usually deliberately separated from the graphite by one or more sheaths of metallic tubing, in the event of metal failure, saturation of the graphite will occur. In the case of H_2O, this will result in a ten-fold increase in the macroscopic neutron absorption by the contaminated moderator. While the degree of absorption depends upon the graphite porosity, as a rule about 90% of the void volume is accessible to water penetration. If the graphite temperature exceeds 600°C, the water-gas reaction,

$$C + H_2O \rightarrow CO + H_2 ,$$
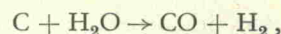
results in rapid oxidation of the graphite [13]. In the presence of ionizing radiation, graphite oxidation becomes appreciable in a moist atmosphere at 500° C. Water can be effectively removed from graphite by conventional drying techniques, although the very considerable internal surface area of the graphite void volume makes the process somewhat tedious [14]. The nuclear consequences of graphite saturation with D_2O are usually not severe, although high temperature chemical problems are nearly identical with those of water.

Sodium and Na-K

Liquid sodium and Na-K alloy have been employed in the sodium-graphite reactor concept. As in the case of water cooling every effort is bent toward keeping coolant and moderator on the opposite sides of a metallic separator medium. However, accidental contact is not accompanied by violent chemical interaction. Sodium, like potassium, is believed to form one or more interlamellar compounds with graphite, in which layers of alkali metal atoms are intercalated between graphite layers of carbon atoms [15, 16, 17, 18, 19]. These compounds vary in their average composition with variation of the alkali metal vapor pressure; evacuation at temperatures allowing reasonable vapor transport will remove essentially all alkali metal from the graphite. Graphite crystals dilate in the C_0 direction with metal pick-up, and recover with metal removal. Artifacts made from graphite accommodate with few, if any, minor fractures, the anisotropic expansion of the individual crystallites which accompany sodium adsorption. A small amount of permanent distortion accompanies intercrystalline fracturing of the material. However, the presence of more than 200 parts per million potassium in the sodium leads to graphite decrepitation.
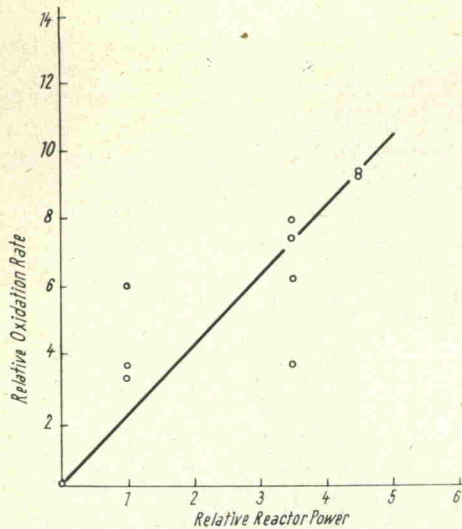
Fig. 1. Effect of reactor power level on oxidation rate of graphite in CO_2 at 250° C

Fig. 2. Schematic diagram of a graphite crystal sheet edge, showing sorption site for CO, CO_2, H and N

Saturation of the graphite pore volume with liquid sodium leads to a 13-fold increase in thermal neutron absorption within the affected moderator graphite. With its larger neutron absorption cross-section, potassium is yet more serious.

Bismuth

Liquid bismuth has been contained in direct contact with suitably densified graphite. The two substances are chemically inert with respect to one another at temperatures below 1400° C [20]. At high pressures penetration of the graphite pores by liquid bismuth or bismuth alloy occurs. Transport of radioactive metal atoms from solution in bismuth into porous graphite has been observed.

Saturation of the entire graphite pore volume with liquid bismuth increases the neutron absorption by only about 55%. However, the negative temperature coefficient of expansion of bismuth near the freezing point makes it imperative that bismuth not be permitted to freeze in a graphite artifact. The Bi-Pb eutectic alloy is free of this problem at temperatures above 130° C, but has a significantly higher neutron absorption cross-section.
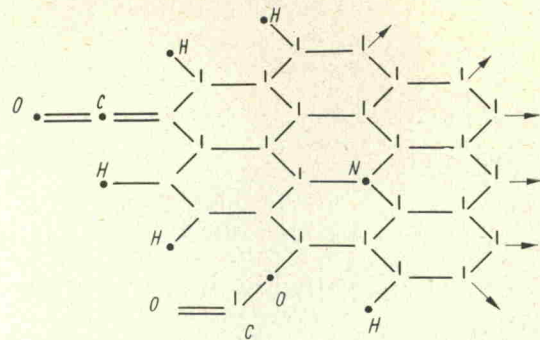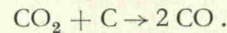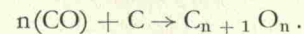
Carbon-Dioxide

Carbon dioxide is compatible with graphite at temperatures below about 700° C [21]. Above this temperature significant quantities of CO are generated by the reaction,

$$CO_2 + C \rightarrow 2\,CO .$$

The resultant CO is reabsorbed on cold graphite surfaces with the formation of graphite suboxides.

$$n(CO) + C \rightarrow C_{n+1} O_n .$$

The character and kinetics of these reactions are altered by the presence of ionizing radiation [22]. Significant oxidation of graphite exposed to CO_2 occurs in a high-level radiation field at temperatures above 500° C (Fig. 1).

The overall appearance of oxidation of carbon in the high-temperature, high-flux region is that of mass transport, and it can result in substantial movement of material away from the higher temperature regions of the reactor core.

Air

If we consider air to be comprised of N_2, O_2, H_2O, CO_2 and A, we should be concerned with the interactions with each separate medium and with combinations of the media. Nitrogen can occupy a carbon site in the graphite lattice, and in a suitable exchange reaction will form molecular compounds with carbon atoms (Fig. 2). Thermally induced interaction of nitrogen with pure

Table 1

Material content of typical reactors containing graphite

Reactor	Coolant	Fuel	Fuel Cladding	Structure	Control and Safety
Oak Ridge Reactor (U.S.)	Air	Uranium	Aluminum	Graphite	Cd Steel Safety, B Steel Control
BEPO (Harwell, U.K.)	Air	Uranium	Aluminum	Aluminum	B_4C in Steel
Brookhaven (U.S.)	Air	Uranium	Aluminum	Aluminum	Boron Steel
MTR (Arco, Idaho, U.S.) *	Water	Uranium	Aluminum	Aluminum	Cd & U in Al
Calder Hall (U.K.)	CO_2	Uranium	Magnox C	Magnox	Boron Steel
NRX (Chalk River, Canada) **	Water	Uranium	Aluminum	Aluminum	Cd or B in Steel
CP-5 (Argonne, U.S.) **	D_2O	Al-U alloy	Aluminum	Aluminum	Cd in Al
SRE (Atomics International, U.S.)	Sodium	Uranium	Stainless Steel	Zirconium	B in Ni

* H_2O moderated, Be reflected with a graphite secondary reflector.

** D_2O moderated with a graphite reflector.

graphite has not been observed, but in the presence of ionizing radiation and graphite lattice damage a slow integration of contacting N atoms into the graphite lattice should proceed.

In a closed cycle system, an initial charge of air will tend to become N_2, CO_2 (or CO, depending on temperature of the graphite) and A. Diffusion losses of H_2 radiolytically separated from H_2O will tend to deplete this species from the system.

Organic Liquids

The use of organic liquid coolants in contact with moderator graphite offers an interesting possibility. Reactor temperatures are limited by the maximum permissable coolant exit temperatures. Under this circumstance the temperature at the position in a graphite artifact most remote from the coolant will be somewhat higher, due to gamma and neutron volume heating. Unprotected artificial graphite will absorb large quantities of organic fluid, and this fluid will subsequently decompose in the internal pore volume of the graphite. This decomposition is accompanied by the release of hydrogen gas and the production of higher molecular weight "polymer". Such decomposition is the consequence of radiolytic and pyrolytic decomposition of the organic fluid [23]. If this process proceeds at a rate which does not lead to physical distortion of the graphite, the end point of such a process is conversion of the graphite into a high density partially graphitized solid.

Hydrogen and Helium

As an inert gas, helium is an obvious choice for use as a very high temperature coolant. However, hydrogen is preferable from the standpoint of availability, thermal energy transport and momentum transfer. There are, of course, many volatile C-H molecular species, some of which have been observed in the product of gaseous hydrogen contact with graphite at temperatures of 600° C and higher. The presence of ionizing radiation is found to produce a chemically active species (probably atomic hydrogen) which react with graphite at temperatures as low as 500° C to form hydrocarbon species [24]. For irradiations of the order of 2×10^{18} thermal neutrons per cm², the hydrocarbon partial pressure rises toward 0.2% of the hydrogen pressure. The evolved gas is about 98% CH_4 with traces of C_2H_6 and C_3H_8. The amount of hydrocarbon product is found to be proportional to the hydrogen pressure and to the exposure time for low exposures.

In a closed cycle gas-cooled system the amounts of hydrocarbon constituents would be expected ultimately to tend toward steadystate levels. In a single-pass system the rate of carbon dissipation through this mechanism must be evaluated.

Interactions of Graphite with Structural and Separator Media

Aluminum

The aluminum-carbon system is inherently non-reactive at temperatures below the softening point of aluminum [25], but limited interactions between aluminum and impurities which may be desorbed from graphite are possible. Among these impurities are CO_2, CO and H_2O, which are rapidly reduced by clean aluminum until a protective Al_2O_3 layer limits the reaction rate.

In the presence of certain metals (for instance, platinum) which will alloy with aluminum, graphite will reduce Al_2O_3, producing CO and metal alloy.

Stainless Steel

Transport of elemental carbon to stainless steel can occur by solid state diffusion at very high temperatures [26, 27], but carburization is more likely to be encountered as the consequence of the presence of an intermediate carbon transport medium. Carbonization of stainless steel by an adjacent carbon-rich medium has been observed to be promoted by the presence of a liquid sodium intermediary at temperatures in excess of 500° C [28]. It has been observed to occur as a consequence of CO transport at temperatures above 600° C [29]. Sacrificial "getter" devices of Ti appear potentially effective in removing carbon from the intermediate transfer medium, providing the getter surface can be maintained at temperatures higher than 900° C [30].

Zirconium and Zircaloy

To the present time no troublesome reaction between graphite and zirconium alloys has been observed. This is largely a consequence of the fact that the physical properties of zirconium alloys thus far investigated have limited temperature considerations to about 600° C. At temperatures above 800° C most zirconium alloys are rather soft. At such temperatures solid state diffusion can result in the formation of a carbide layer on the underlying metal. The carbide layer is tenacious and tends to be protective, unless oxygen is present. In the latter case flaking of the protective layer may produce an unpredictable degree of more severe corrosion.

Impurities usually present in graphite may react rapidly with zirconium alloys. Among such impurities are CO_2, CO, H_2O, H_2 and N_2. CO_2 and CO form complex flaking surface layers of oxide, carbide and carbon if temperatures of over 800° C exist in the alloy [31]. Hydrogen forms a solid solution, with large composition gradients tending to be established inversely with temperature gradients existing in the system [32]. At high hydrogen contents, a hydride phase precipitates, leading to embrittlement of the metal.

Magnox Alloys

A series of magnesium alloys with aluminum, beryllium and other trace metals has been employed in power reactors in the United Kingdom. The alloys are reported to be unreactive to carbon and dry CO_2 to their melting points. The presence of a trace of calcium prevents attack by moist CO_2 [33].

Integral Coatings

A wide variety of integral coatings for graphite have been proposed to meet various needs. In general, these must exhibit thermal expansion characteristics similar
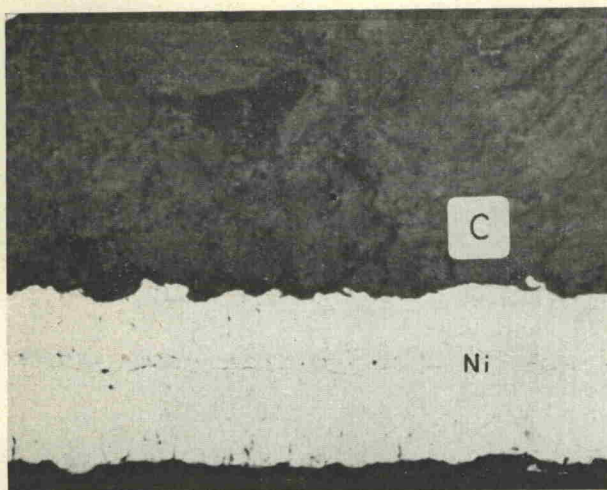
Fig. 3. Section of a coating of nickel upon graphite, showing mechanical „keying" of metal to graphite

to the average of those of the base graphite. Coatings generally adhere because of mechanical "keying" into the intergranular cavities of the underlying graphite (Fig. 3). Some coatings are secured through one or more underlying intermediary substances, which serve to form a graded bond. The purpose of the coating may be to protect against mechanical erosion, or it may be to prevent penetration of the graphite by any trace of a third, fluid medium. In the former case the impermeability of the coating medium is less important than in the latter case.

When an impermeable protective layer is required, the effect of the 5 to 1 anisotropy in the crystalline thermal expansion of graphite becomes a serious problem. Numerous procedures using Ni, Zr, and other metals on suitable under-coatings have been tried with limited success. Small cavities seem invariably to occur in all "protective" layers less than 0.01 cm in thickness. An interesting exception is Si-SiC for use in oxidizing atmospheres. In this case the formation of carbon oxides below coating flaws permits transport of carbon to the surface where further reactions lead to *in situ* formation of SiC and SiO_2. These tend to seal the flaw in the coating.

Interaction of Graphite with Fuel Materials

Uranium metal interacts with graphite to form carbides at temperatures above 1500° C [34]. This reaction is negligible below 1200° C in the absence of a fluid medium to promote transport. Since the carbides exhibit higher melting points than uranium metal, this effect does not lead to material instability. UO_2 is likewise stable with respect to graphite until temperatures of over 1700° C are reached, upon which the reaction

$$UO_2 + 3\,C \rightarrow UC + 2\,CO$$
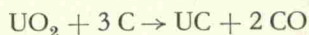
begins to proceed [35]. This reaction will not proceed appreciably at temperatures met in reactors cooled with water, organic fluids or liquid sodium.

The several alloys of uranium considered for use as high stability fuels have generally acceptable properties

with respect to graphite. Many of them are prepared by arc melting in graphite molds. In general, the addition of carbon serves to improve the refractory qualities of the alloy system. The effect of carbon in altering the radiation stability of fuels remains to be explored.

Interactions of Graphite with Other Moderator Materials

Other Graphite

As was pointed out above, there may be gas phase exchanges of mass between communicating high and low temperature regions. If gaseous species containing high cross-section nuclei are in reflector graphite they may be transported through the gas phase or by solution and disolution in intervening liquid or solid media. They may then be redistributed over the core graphite, introducing appreciable changes in the nuclear reactivity of the moderator.

BeO

Under certain circumstances it may be desirable to utilize BeO and graphite as moderator materials in a single core. BeO can be readily formed into complex shapes. Graphite is less expensive as a bulk moderator material and can be readily machined to shape. In applications where BeO can be used unclad it may be economical to avoid complex graphite cladding sheath shapes by utilizing BeO filler shapes (Fig. 4). The reaction

$$BeO + C \rightarrow Be_2C + CO$$
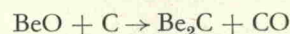
has been reported [36], but only at temperatures in excess of 2300° C. It is thus unlikely to be of real concern in reactors of prosaic design.
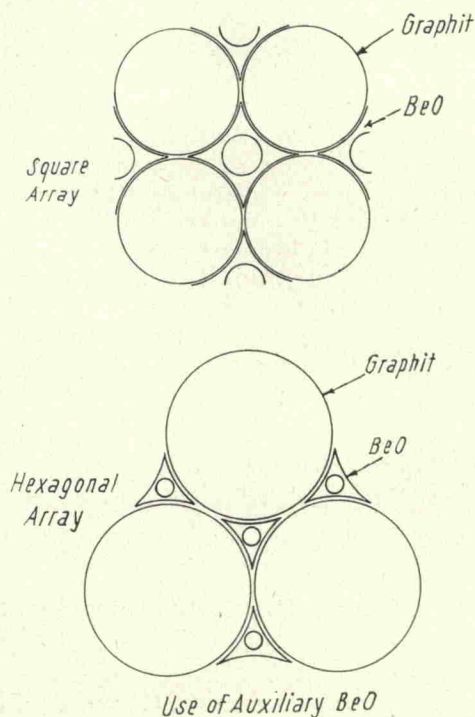

Fig. 4. An economical mixed moderator structure for an SGR

Beryllium Metal

In certain instances it may be desirable to utilize Be metal in a compact core with graphite as a reflector. Limitations set by softening of Be metal tend to preclude approach to temperatures where Be-C reactions proceed. However, the Be surfaces react rapidly with any CO evolved from the graphite with the creation of a powdery layer of BeO and carbon on the Be metal surface. The finely dispersed state of this product leads to expression of the full degree of potential toxicity in the event of subsequent exposure of personnel to the corroded surface of the Be.

Hydrides and Deuterides

A wide range of chemical properties is exhibited by this family of compounds [37, 38]. Of greatest potential interest for reactor use are those of metals having low nuclear cross section and exhibiting reasonable chemical stability. Among these are hydrides of magnesium, yttrium, zirconium, niobium and cerium. Most of the transition metal hydrides are "interstitial" compounds, with a wide range of composition ratios, exhibiting approximate stoichiometry only insofar as limiting compositions are concerned. As temperatures are elevated, near-stoichiometric hydride compositions are maintained only by provision of high back-pressures of H_2 gas. This situation may be further aggravated by the presence of a reaction between the metal species and adjacent carbon. This will occur at likely temperatures only if the transport of the metal or carbon species be rendered rapid by the presence of a soluble intermediary species, such as CO or CH_4. The latter mode of transport will occur at sufficiently high temperatures in the presence of excess H_2. Inadequate data exist to establish the threshold temperature for this reaction, which nets

$$C + MH_{2x} \rightarrow MC + x\,H_2 \,.$$
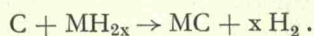
It is probably in excess of $900°C$ for the metals listed.

Organic Liquids

The use of graphite with organic coolants was discussed above. A similar class of fluid materials has been utilized for moderating purposes [39]. Rather extensive polymerization with accompanying production of H_2 has been observed. Graphite moderator saturated with an organic liquid will gradually become densified with occasional minor fractures occurring as a consequence of pressure build-up in enclosed pockets of H_2 gas. Such fractures "heal" spontaneously with the filling of the fissures with polymerized organic fluid. The mixed moderator mass gradually becomes completely solid and very hard, requiring diamond-edged tools for cutting.

Interaction of Graphite with Control and Safety Poisons

Boron Alloys

In the event of an extreme temperature excursion, it is conceivable that interactions may occur yielding carbide compounds of boron and the carrier metal. These will generally remain localized at the point of contact and must be removed mechanically.

Boron Trifluoride

BF_3 has recently been given attention as the poison constituent in a family of self-activated safety elements for use in reactor cores [40]. It is conceivable that malfunction could lead to contact of this substance with reactor graphite. It will thereupon penetrate the graphite core structure and at moderate temperatures will react with metallic impurities in the graphite, yielding volatile metal fluorides and a local deposit of boron metal or B_2C, depending upon local temperatures. This event is undesirable, leading to a severe rise in the macroscopic neutron absorption cross-section of the moderator graphite.

Cadmium and Cadmium Alloys

Cadmium metal is volatile at moderate temperatures (above $500°C$) and it can be transported in the gas phase into the pore volume of graphite if not separated by an intervening barrier. Alloyed cadmium may be placed in contact with graphite at temperatures consistent with compatibility between the carrier metal and graphite. The same general comment may be applied to chemical carriers like $Cd\,(PO_3)_2$ glass [41].

Helium-3

The isotope He^3 shows a large (5400 b) absorption cross-section, and has been suggested as a control material [42]. One method of so employing this substance is by allowing it to permeate the pore volume of all or a part of the graphite moderator. A mechanism of rapid removal of He^3 from such a volume without prohibitively large changes in pressure remains to be devised. Also to be explored is the possibly undesirable consequence of the energetic recoil of protons and tritons from the (n, p) reaction on He^3.

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