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Graphite Problems in Air-Cooled Reactors*

by

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OXIDATION, RADIATION INDUCED DIMENSIONAL EXPANSIONS, AND ACCUMULATION OF STORED ENERGY, ARE THREE MAJOR PROBLEMS AFFECTING LONG TERM USE OF GRAPHITE IN AIR-COOLED REACTORS. FREQUENT LOW TEMPERATURE ANNEALING ELIMINATES THESE PROBLEMS AND MAY EXTEND THE LIFETIME OF THE GRAPHITE INDEFINITELY.

In a chain reaction of the type occurring in nuclear reactors, uranium nuclei undergo fission liberating fast neutrons. These neutrons must be slowed down by a moderator so that they can be reabsorbed by the uranium in order that the fission process be sustained. Moderators therefore, must have the select properties of slowing down fast neutrons without absorbing too many of them. If a moderator is to be useful in low temperature research reactors as well as in advanced high temperature

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reactor concepts, graphite stands in a class by itself due to its small absorption cross section and because it is one of the few structural materials that can be used to temperatures as high as 2000°C. Early recognition of these advantages prompted extensive studies of radiation reactions in graphite.

In graphites irradiated below 250°C, displaced carbon atoms produced by collisions with energetic neutrons are retained by the lattice in interstitial positions. These displaced atoms (interstitials) increase the energy content of the graphite and cause the graphite to expand. The "stored energy" represents a potential operating hazard since much of it can be released rapidly at low temperatures resulting in local temperature excursions. Dimensional increases in the graphite lead to structural movements in the reactor which often alter critical design specifications. In practice, stored energy is removed and dimensional increases are reduced by thermal annealing of the reactor.

Normal operation of low temperature graphite moderated reactors uses forced convection of air through graphite channels to remove the heat generated by fission. When such reactors are annealed to remove dimensional damage and stored energy, temperatures are in-

creased by lowering the air flow. In addition to fission heat and stored energy releases, heat may be evolved from chemical reactions between carbon and oxygen. The large temperature coefficient and the highly exothermic nature of the carbon-oxygen reactions make it possible for the heat generated by the chemical reactions to exceed the heat that can be removed by the air stream. As a consequence, the graphite temperatures may increase to a value for which the chemical heat release is greater than the maximum installed cooling capacity of the reactor, and the system will "run away" or begin burning. This type of thermal instability and the conditions under which it occurs have been studied^(1,2,3,4,5) and are affected by many variables. The behavior of such systems can be described conveniently by considering the three general processes which may occur simultaneously at different positions when air is passed through a heated graphite channel. A section of channel can cool with time ("stable" section); a position can exist at which the graphite and air temperatures do not change from their initial values ("equilibrium" position); and a section of channel is sometimes observed to increase

in temperature with time ("unstable" section).

At any point in a stable section, the rate at which heat is removed by the air stream exceeds the rate at which heat is introduced into the system by oxidation.

At some point in the channel, both the initial graphite temperature and the air temperature may remain constant ("equilibrium" position) and the rate of heat removal by the air stream just equals the rate of heat generated by oxidation.

In an "unstable" section the rate of heat generation by oxidation exceeds the rate of heat removal by the air stream. Temperature changes of a channel in which all three processes occur are shown in Fig. 1.

Cooling occurs in a section of channel when the product of the heat transfer coefficient (h) and the initial temperature difference between the graphite surface and the air stream ($T_g - T_a$) exceeds the rate of heat generated by oxidation.

Since the oxidation rate is known to decrease exponentially with decreasing temperature, and the cooling rate, $h(T_g - T_a)$, is expected to decrease linearly with

decreasing graphite temperature (T_g) the graphite temperatures should continue to decrease with time. In practice, it is found that the rate of heat generated by oxidation does decrease exponentially with graphite temperature but the rate of heat removal by the air stream remains constant for very long periods of time. The latter effect is the result of the time independent constant difference in graphite and air temperatures at each point in the stable section of channel. A plot of the temperature differences for the stable section of the channel described in Fig. 1 is shown in Fig. 2. It can be seen that the constant difference is retained in time in spite of large changes in the absolute values of both the graphite temperatures and the air temperatures.

Cooling at any point in a stable section of graphite channel is then determined by the thermal conductivity of the channel wall and the radial temperature gradient in the wall. Consequently, once cooling begins in a portion of graphite channel, the thermal reactions in this section become similar to those in an inert channel and the chemical reactions can be neglected. A typical illustration of cooling a ten foot graphite channel is shown in Fig. 3.

The stability of the equilibrium position and the time independent nature of the cooling offer a convenient means of defining potentially dangerous oxidation conditions in air-cooled reactors. When the equilibrium distance is described as a function of the pertinent parameters, all channel lengths shorter than this distance are under stable conditions. The variables affecting the equilibrium position are the heat transfer coefficient, the graphite and air temperatures, and the chemical reactivity of the graphite. At a given temperature and for a given reactivity of graphite, the equilibrium position is determined solely by the heat transfer coefficient. Fig. 4 shows how the equilibrium position (length of channel cooled) varies with flow rate in a 1" diameter channel. Such data can be used to calculate the flow rates necessary to obtain the same equilibrium distances in channels of different diameters by obtaining corresponding values of flows and diameters that give the same turbulent heat transfer coefficient. Experimentally determined values are shown with calculated values for a 2" channel in Fig. 5.

The length of a channel that can be cooled as a function of the original channel temperature is shown in

Fig. 6 for channels of different diameters and reactivities. The results are significant in that they can be used to show that the maximum temperature at which thermal equilibrium occurs in a channel can be predicted from the heat transfer coefficient, the activation energy for graphite oxidation, and a single value of the graphite reactivity at any temperature.⁽⁴⁾ Above this maximum temperature the total length of channel is thermally unstable.

Oxidation and heat transfer studies in graphite channels indicate that the temperatures necessary to cause "runaway" are higher than the melting temperatures of fuel elements used in air-cooled reactors. In such reactors "runaway" would occur after a fuel meltdown and rapid graphite oxidation becomes a problem of secondary importance. The primary problem associated with graphite oxidation is, then, long term carbon removal resulting from low temperature oxidation.

Continuous oxidation of graphite can lower the density of the moderator, decrease its mechanical strength, and change the neutron diffusion length. Fortunately, long term oxidation effects are very sensitive to temperature due to the high activation energy for oxidation (about

50-65 KCal/g-atom). Thus at 400°C, the oxidation rate of the graphite in the Brookhaven Reactor (BGRR) is about 0.06% per day while at 300°C it is only 0.0005% per day, and at 250°C it is of the order of 0.0001% per day. In principle, then, an air-cooled reactor such as the Brookhaven reactor, where the maximum operating graphite temperature is 250°C, could function for more than 25 years without losing 1% of the graphite.

The benefits of low temperature operation are however, partially negated by the large amounts of stored energy and dimensional expansion that result from irradiations at temperatures below 250°C.

Existing literature on dimensional and stored energy recoveries show that only a small fraction of accumulated radiation damage can be removed by annealing at low temperatures. Since material stresses and safety requirements make the annealing of a reactor structure a difficult and complicated process, high temperature anneals are impractical and are often impossible. In an effort to improve annealing recoveries, the effects of frequent low temperature anneals on graphite were studied at Brookhaven. The property changes in graphites

treated in this manner are strikingly different from the changes after the first irradiation and anneal. Data obtained from periodically irradiated and annealed graphites⁽⁶⁾ show that initial irradiations of graphite below 250°C produces only trapped (immobile) single interstitials, immobile C₂ molecules, and a small steady state concentration of mobile single interstitials. During subsequent reirradiations interstitial clusters (formed at higher temperatures during the first thermal anneal) interact through consecutive chains via the mobile single interstitials.⁽⁷⁾ In marked contrast to the effects observed after the first irradiation and anneal, the consecutive reactions lead to steady state concentrations of interstitial species that do not increase with irradiation interval as they do after annealing continuously irradiated graphite. When new damage is formed during reirradiations it arises from large interstitial complexes formed at the end of a reacting chain. The reactions can be described by the simplified mechanism

- 1) radiation + graphite → C₁ (mobile single interstitial)
+ vacancy
- 2) C₁ + Trap → C₁ T (annealing reaction)

where ϕ represents one type of radiation decomposition in which a single carbon atom is removed from a cluster by direct or indirect effects of energetic neutron collisions.

Both the forward and backward reactions in 3) occur only during reirradiations. When the graphite is removed from the neutron field, the immobile interstitial clusters are frozen in and reactions 1), 2) and 3) are quenched.

Kinetic calculations⁽⁷⁾ of such chain reactions show that if the low end of the chain is removed (i.e., by a thermal anneal), reirradiations can decompose large complexes to form smaller ones. The calculations indicate that periodic removal of the smaller complexes by low temperature anneals should result in the net removal of damage associated with the larger interstitials. A good deal of experimental evidence has been obtained that supports this model. One such experiment is shown in Fig. 7. The figure shows typical data of dimensional changes resulting from 350°C anneals after different reirradiation intervals. The linear portion of the curve from 0 to about 1000 MWD (in the BGRR 1 MWD (megawatt day per adjacent ton of uranium) = 7×10^{16} nvt

for neutrons with energies above 0.6 Mev) shows the expansion before the first anneal. The mid portion of the curve depicts changes after 350°C anneals when the annealing frequency was the same as that used to anneal the Brookhaven reactor. It can be seen that "high temperature" dimensional damage is continuously removed when low temperature annealing follows 15 MWD reirradiations. Thus, in heavily irradiated graphite, excess damage can actually be removed by combining low temperature anneals with the proper reirradiation intervals. Similar effects of consecutive reactions appear in graphites that are frequently irradiated and annealed from the onset. Under these conditions many types of damage effects that normally must be removed by high temperature anneals are prevented from forming. One important practical consequence of applying periodic annealing immediately, is the resultant dimensional stability obtained. All dimensional damage formed during irradiation can be removed by annealing at 150°C when the irradiation interval is 15 MWD. The dimensional changes for a group of samples annealed at 150°C after each 15 MWD irradiation (at 30°C) are shown in Fig. 8.

It can be seen that the samples retain their original sizes and do not show the expansions characteristic of continuously irradiated graphites. The effect is general in nature and 100% recovery can be obtained at different anneal temperatures after any repeated irradiation interval. Anneal temperatures for 100% recovery are plotted vs the appropriate reirradiation intervals in Fig. 9. The function $G/|R|$ represents the ratio of the absolute values of the dimensional expansion (G) occurring during the irradiation and the dimensional recovery ($|R|$) obtained after the anneal. When $G/|R|$ is equal to unity, the anneal removes all of the growth accumulated during the irradiation interval. (The 500°C anneal data was obtained from Woodruff.⁽⁸⁾)

The final problem of low temperature stored energy releases is also eliminated by the steady state concentrations resulting from consecutive interstitial reactions in periodically irradiated and annealed graphites. Again, in marked contrast to the effects observed after the first irradiation and anneal, the steady state reactions result in stored energy releases that do not increase with irradiation interval as they do in continuously irradiated graphites. The steady state value of the "200°C" stored

energy release is shown in Fig. 10. It is immediately obvious that in periodically irradiated graphites the "200°C" stored energy no longer increases with irradiation beyond the steady state interval.

The technique of frequently irradiating and annealing graphite yields a wealth of original information that sheds new light on the basic reactions occurring during the irradiation and annealing processes. Information obtained from such studies has important practical applications and shows that major problems interfering with extended use of graphite in low temperature reactors can be eliminated.

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TEMP CHANGES ALONG A 1" DIAM CHANNEL

FIGURE 1

15

FIGURE 2

TEMPERATURE CHANGES IN A 2" DIAMETER CHANNEL WITH TIME

FIGURE 3

FIGURE 4

EQUILIBRIUM POSITION AS A FUNCTION OF FLOW RATE (705°C)

FIGURE 5

EFFECT OF TEMPERATURE ON THE LENGTH OF CHANNEL COOLED

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

STORED ENERGY RELEASED AT 200°C

FIGURE 10