RADIOLYTIC GRAPHITE OXIDATION REVISITED

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Abstract

The importance of radiolytic oxidation in graphite-moderated CO_2-cooled reactors has long been recognised, especially in the Advanced Gas-Cooled Reactors where potential rates are higher because of the higher gas pressure and ratings than the earlier Magnox designs. In all such reactors, the rate of oxidation is partly inhibited by the CO produced in the reaction and, in the AGR, further reduced by the deliberate addition of CH_4. Significant roles are also played by H_2 and H_2O.

This paper reviews briefly the mechanisms of these processes and the data on which they are based. However, operational experience has demonstrated that these basic principles are unsatisfactory in a number of respects. Gilsocarbon graphites produced by different manufacturers have demonstrated a significant difference in oxidation rate despite a similar specification and apparent equivalence in their pore size and distribution, considered to be the dominant influence on oxidation rate for a given coolant-gas composition. Separately, the inhibiting influence of CH_4, which for many years had been considered to arise from the formation of a sacrificial deposit on the pore walls, cannot adequately be explained by the actual quantities of such deposits found in monitoring samples which frequently contain far less deposited carbon than do samples from Magnox reactors where the only source of such deposits is the CO.

The rates of radiolytic oxidation have been shown to be independent of impurity content within the graphite, and the ability of the graphite to influence the classical water gas shift reaction, and thereby perturb the gas chemistry within the pores, has been shown to depend on the internal surface area of the material.

Significant differences have been found between the two gilsocarbon moderator graphites in their internal surface area and in their shrinkage behaviour under combined neutron and gamma irradiation. These are discussed in the context of the oxidation mechanism. The mechanism of inhibition of the oxidation reaction, and how this could be affected by changes in the surface potential energy of the graphite are also discussed.

The paper also describes the current status of moderator weight-loss predictions for Magnox and AGR Moderators and the validation of the POGO and DIFFUSE6 codes respectively.

1. INTRODUCTION

All of the electricity producing nuclear stations in the UK are, with the exception of the recently commissioned Sizewell B station, graphite moderated, carbon dioxide cooled reactors. The UK generating companies operate eighteen 'Magnox' type reactors (six reactors have been shut and are now being decommissioned) and fourteen Advanced Gas Cooled Reactors (AGRs). Throughout the course of the building programme, successive Magnox reactors were designed to operate at increasingly higher thermal powers, with consequent increases in the radiolytic oxidation of the core. The second generation AGRs were designed to operate at significantly higher coolant pressures and reactor powers, to increase markedly the thermal efficiency.

In addition to moderating the nuclear reaction the graphite core provides a significant structural function, and it is thus essential to the continuing safe operation of these stations that the continuing integrity of the core can be assured as radiolytic oxidation and thus loss of

graphite strength proceeds through life. In view of this the radiolytic oxidation of graphite in carbon dioxide and the inhibition of the reaction by the addition of simple gaseous species to the coolant has received considerable study, directed both to the fundamental mechanisms of the process and towards the development of methods to predict the evolution of graphite weight-loss profiles within both individual components and the core as a whole.

This paper outlines the current views on the mechanism of radiolytic oxidation in carbon dioxide based coolants, and indicates areas where, even after the extensive study of over four decades, in-reactor observations can confound predictions. The methods used to predict core weight loss in the UKs Magnox and AGRs are discussed, together with their validation. Finally, recent results are described in which in-reactor observations diverge markedly from prediction: experimental work to resolve the conflict is described.

2. MECHANISMS OF RADIOLYTIC OXIDATION

The rate of radiolytic graphite oxidation is strongly influenced by the reactor gas chemistry and by the pore structure of the graphite. The subject was last comprehensively reviewed in 1985 [1] and the purpose of the present paper is to take forward the position in the light of current thinking.

It is still firmly believed that the principal chemical species formed from irradiated carbon dioxide which is capable of chemical attack on carbon species is the negatively-charged ion CO_3^-. There have been a number of experiments using ion chambers with radioactively-labelled carbon electrodes which have been used in attempts to identify the charge on the oxidising species, but results must fairly be described as ambiguous. It is also known that photolytic attack (in the absence of charged species) is possible. However, the definitive test was to consider the reaction rate of candidate species with the inhibitor carbon monoxide (the product of the graphite oxidation), to identify the species which exhibited the appropriate kinetic characteristics, and then to test its behaviour in a suitable mass-spectrometer. This was followed by the replacement of the ion source in the spectrometer with a radioactive emitter, which was demonstrated to generate the same ionic species. In the reactor environment, parallel reaction from excited species which have insufficient energy to ionise will also occur, as in the pure photolysis tests.

The reaction rate is proportional to the rate of energy absorption in the gas and hence, approximately, to reactor coolant pressure. The reaction product CO provides sufficient control of the oxidation process in the Magnox reactors (by gas-phase removal of the oxidation species) that no other deliberate additions of inhibitor are generally made, except in the Oldbury reactors, as discussed below. In the AGRs, operating at higher pressures, further inhibition is essential.

Since the oxidation process involves a surface reaction in competition with the gas-phase inhibition process, geometric considerations in pores accessible to the gas are important. The smaller the pore (or the greater the surface-area-to-volume ratio) then the more successful will the surface graphite be in competing with the inhibitor CO for the oxidising species, and so the net oxidation rate per unit of radiation energy absorbed locally in the gas will be higher. Thus, the differing pore-size/shape distributions in different graphites lead to differing oxidation rates under identical conditions, and the developing pore structure needs to be modelled when following the progressive oxidation through the life of a reactor.

The most significant developments in our understanding of radiolytic oxidation relate to the detailed chemical processes which take place on the surface. It has long been known that the oxidising species is mobile on the surface (or creates a 'mobile surface oxide'), since it is observed that oxidation is greatly favoured (by several orders of magnitude) at 'edge' sites on the individual crystallites. It is in this process that hydrogenous impurities, such as vpm quantities of water and hydrogen which are present in the Magnox-reactor coolants, are thought to be involved. The deliberately-added methane in AGR coolants results in similar interactions, but in this case a preceding gas-phase reaction is important, for the methane is attacked by the same oxidising species CO_3^- and other ionic and radical species to begin a decomposition process which ultimately leads to soot formation. In this sense, therefore, methane is another gas-phase inhibitor of the graphite oxidation process since it competes for the oxidising species, but as it is present only at very low concentration (approximately 230 vpm compared with 10,000-12,000 vpm CO), this role is unimportant. We shall now consider the roles of the hydrogenous additives in more detail.

Under all normal circumstances, the 'free' chemical bonds available at edge sites on the carbon (graphite) crystallites will be occupied by hydrogen atoms, and literature reports of radiolytic oxidation rates[1] imply measurements made under this condition, although the significance has not previously been discussed. However, it is noted that after long periods of 'dry' Magnox-reactor operation, with no ingress of either boiler steam or gas-circulator oil into the coolant circuit, values of G(-C) tend to rise significantly. Conversely, after significant steam leaks (or, indeed, after maintenance outages when the reactor has been exposed to atmospheric air at much greater moisture concentration than in normal operation), lower oxidation rates apply.

The surface role of the decomposed methane inhibitor is also deserving of further consideration. It has been the convention to describe the carbon deposit as a sacrificial inhibitor, literally covering the graphite-carbon atoms with a layer of non-graphitic carbon which is oxidised instead. If this were the correct mechanism, then one would expect to see much greater quantities of carbon deposited onto the surface of graphite in AGRs, where CH_4 is deliberately added and the graphite oxidation rates are much lower, than in the Magnox reactors where the methane is usually at very low concentration (<10 vpm). A Magnox graphite moderator, however, contains significantly larger amounts of non-graphitic carbon (locally up to 3% by weight in regions of one reactor compared with a typical 0.4% in an AGR core) which is derived from radiolytic polymerisation of the carbon monoxide, and yet the relative graphite oxidation rate remains much higher. Explanation of the effect of the added methane as a purely sacrificial process is therefore not adequate, although it may play some role.

3. THE PREDICTION OF GRAPHITE WEIGHT LOSS

In order to provide advice on how the Magnox reactors and AGRs should be operated in order to minimise graphite weight loss and to predict the evolution of weight loss throughout the reactor lifetime, it is necessary to incorporate the mehanistic observations of the previous section into a reliable model of graphite oxidation. Such a model is required to account for variations in coolant history and irradiation, as well as being able to calculate weight loss profiles within graphite components of complex and irregular shape. Differences in brick shape between the

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[1] Defined as G(-C), the number of carbon atoms oxidised per 100eV of radiation energy absorbed in the gas.

Magnox and AGR systems, as well as the simpler coolant composition in the former reactors, has led to the use of two models for estimating weight loss: POGO12 for Magnox and DIFFUSE6 for AGRs.

3.1 POGO12

In POGO12 the pore structure of the graphite is represented by a finite number of pore -size groups, each having a characteristic dimension and shape and a fraction of the total open pore volume. $G_i(-C)$ for each pore group is defined by the relationship

$$G_i(-C) = F_i \cdot P \cdot G(+Ox)$$

where $G(+Ox)$ is defined as the number of oxidising species generated per 100eV of radiation energy absorbed; the recommended value in dry gas is 3.0, which is the experimentally measured ion yield from CO_2. P is the probability of carbon gasification resulting from the oxidised species reaching the pore surface, and can be considered as the probability that the active species is scavenged on the surface. The value of P is determined empirically from experimental data obtained in irradiation facilities. F_i is the efficiency of oxidation for the ith pore group, and is the proportion of the oxidising species that reach the pore surface. It is calculated for each pore group by solving the diffusion equation for the oxidising species of concentration c

$$D \nabla^2 c + \beta - Kc = 0$$

where D is the diffusion coefficient of the oxidising species, β is the rate of production of the oxidising species per unit volume and K is the rate of removal of the oxidising species by carbon monoxide and methane. The characteristic dimensions of the pore groups can be obtained by either mercury porosimetry or, preferably, image analysis.

In practice, the value of $G(Ox)$ calculated from observed $G(-C)$ data is less than 3.0 for samples retrieved from Magnox reactors. The shortfall arises from hydrogenous material from the coolant deposited on the graphite surface, acting as a sacrificial species and effectively supplementing the value of P. With this correction, the model gives a good account of the measured weight loss of samples trepanned from the bores of both fuel and interstitial channels of Magnox reactors (see Figure 1).

3.2 DIFFUSE6

DIFFUSE6 is a three-dimensional finite element program which solves the coupled equations for mass transfer and graphite oxidation to produce a composition profile of methane, carbon monoxide and water and the distribution of graphite weight loss within a graphite component. The graphite oxidation within the program is calculated from the Reactive Pore Volume (RPV) model developed by the UK Atomic Energy Authority. The RPV model is based on the experimental observation that only pores below a certain size are actively involved in graphite oxidation; this porosity is known as the reactive pore volume and is used instead of the open pore volume.

The RPV model requires values for the attack rate (initial oxidation rate); in the endorsed model this is obtained by interpolation into a look-up table of initial oxidation rates as a function
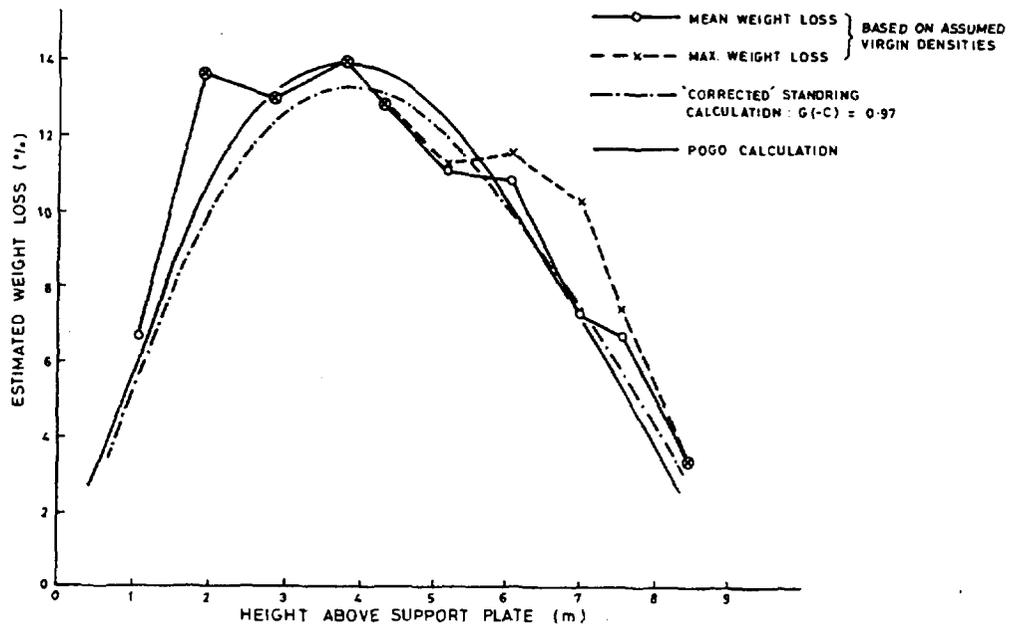
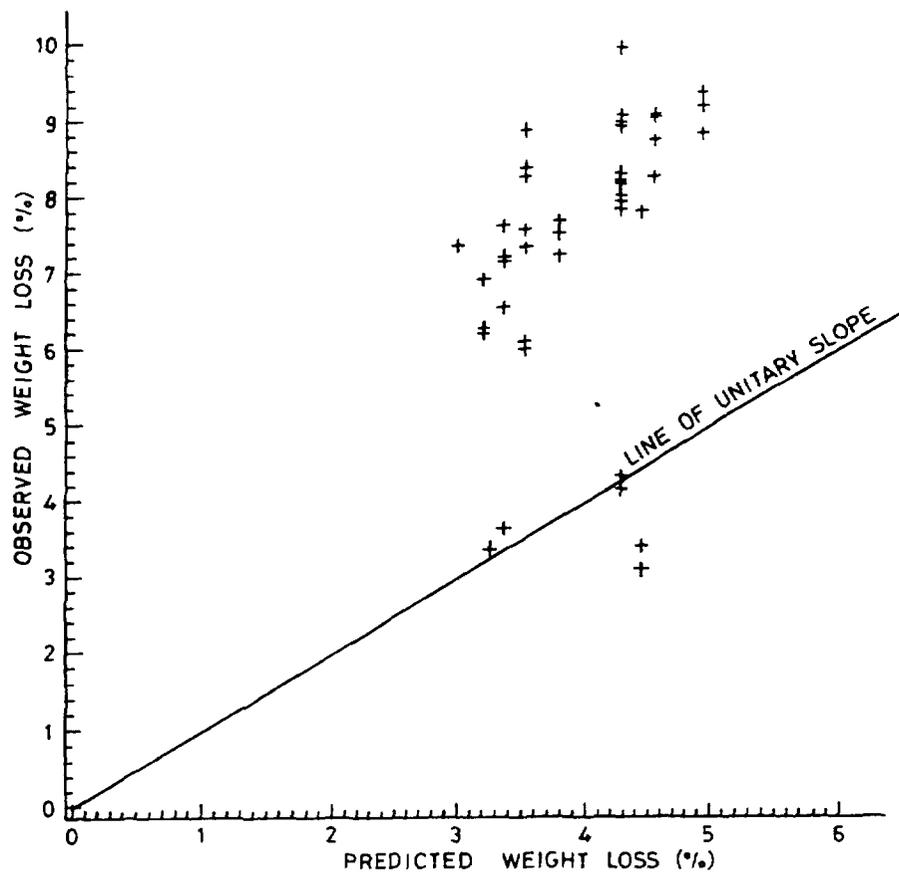**Figure 1** Comparison of Observed Weight Losses With Predictions of POGO12 Oldbury Interstitial Channel

Figure 2 Comparison of Observed Weight Loss of BAEL Graphite From Hinkley Point B R3 With Prediction By DIFFUSE6.

of CO and CH_4 concentrations. The look-up table has been derived by fitting a database of measured initial oxidation rates for a wide range of coolant conditions. The database includes measurements from AGL, BAEL and Union Carbide graphite; in principle, it should give best-estimate predictions of the mean weight loss in a reactor.

The initial attack rates were validated against results from accelerated oxidation tests in the BFB reactors: the program gives a good account of the measured weight loss of samples trepanned from the fuel channels of Hinkley Point 'B', the longest running AGR for which such samples are available.

4. THE ANOMALOUS WEIGHT-LOSS RATE OF BAEL GRAPHITE

Although the moderators in the AGRs are all gilsocarbon graphite, graphite for Dungeness 'B', Hunterston 'B' and Hinkley Point 'B' was manufactured by Anglo Great Lakes whilst that in the later reactors was provided by British Acheson Electrodes Ltd. (BAEL). {The graphite sources are referred to by the manufacturers initials.} Both graphites were made from the same coke (derived from natural Gilsonite pitch from the American mid-west) and binder (also natural Gilsonite pitch) to the same specification of average density and open pore volume. Image analysis and mercury porosimetry had shown that the two graphite sources had the same range of pore-size distribution and thus, given that the radiolytic oxidation rate for a given coolant composition and dose rate is a function of the pore structure only, the two sources were expected to oxidise at the same rate. This assumption was borne out by an extensive programme of tests in Materials Testing Reactors as well as some limited investigations at the Gamma Irradiation Facility at Berkeley Nuclear Laboratories.

As part of the graphite monitoring schemes for the AGRs, one interstitial channel in Hinkley Point 'B' Reactor 3, was loaded with sample carriers that contained, amongst other types of graphite, a large number of samples of both AGL and BAEL graphite. Both sources were represented by about eight separate graphite heats. (A heat is the batch of raw bricks that are graphitised together in a production run) A total of four sample carriers containing specimens from both sources have now been removed from Hinkley Point B. Whilst the weight losses of the AGL specimens agreed well with prediction, it is clear from a comparison of the observed weight losses for the BAEL specimens (Figure 2) with prediction that the BAEL source is corroding at a rate approximately 1.9 times faster than the AGL graphite. As these graphites have been exposed to identical dose and gas conditions, and as samples of each type of graphite were in close proximity to each other in the sample carriers and have not therefore been subjected to differences in environment, the discrepancy in oxidation rates can only arise from a divergence in the attack rates of the two graphites. It is worthy of note that the observed attack rates of both graphites show considerable variance, although the data falls into two well-separated groups with the exception of samples from one heat of the BAEL graphite, which shows attack rates equivalent to the mean rate of the AGL source. The experimental observation of this variation has been subsequently confirmed by comparing the weight loss of samples trepanned from both reactors at Hartlepool and Heysham A with those taken from several separate trepanning campaigns at Hinkley Point 'B'.

The question arises as to why the MTR programme had not uncovered such a large difference between the two sources of graphite. A reexamination of the BFB test data demonstrated that samples were used from only three AGL and three BAEL bricks. Of these, two

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AGL bricks showed high oxidation rates, whereas one was less reactive. Similarly, two BAEL bricks showed a high oxidation rate whilst the third showed a low rate. The spread and overlap of the two sets of data therefore suggested at the time that the two sets of oxidation rates were equivalent, a conclusion that was expected as the mean properties that were held to determine oxidation rate were the same for the two graphite sources. With hindsight it is clear that the sample size was statistically unrepresentative of the whole populations of bricks.

The results for the samples withdrawn from Hinkley Point B were similar to those examined previously in that there was no apparent difference in the two graphite sources to which the divergence in weight loss could be attributed. The only apparent observable difference was that the irradiated BAEL graphite appeared to be more radioactive than the AGL source. There had also been a reference in early UKAEA work to BAEL graphite catalysing the thermal Water Gas Shift reaction whilst AGL graphite showed no activity. This suggested that the origin of the variation might lie in the presence of catalytic material in the BAEL graphite, which may either interfere with the surface component of the oxidation reaction (although not the radiation-mediated reactions), perhaps by changing the mobility of species on the graphite basal plane, or by perturbing the H_2/H_2O ratio within the graphite pore. Both of these processes might be expected to be thermally activated. The known role of hydrogen as an inhibitor of the oxidation reaction seemed particularly suggestive in this context. To test these ideas a number of investigations were carried out using both the irradiated samples taken from the carriers and
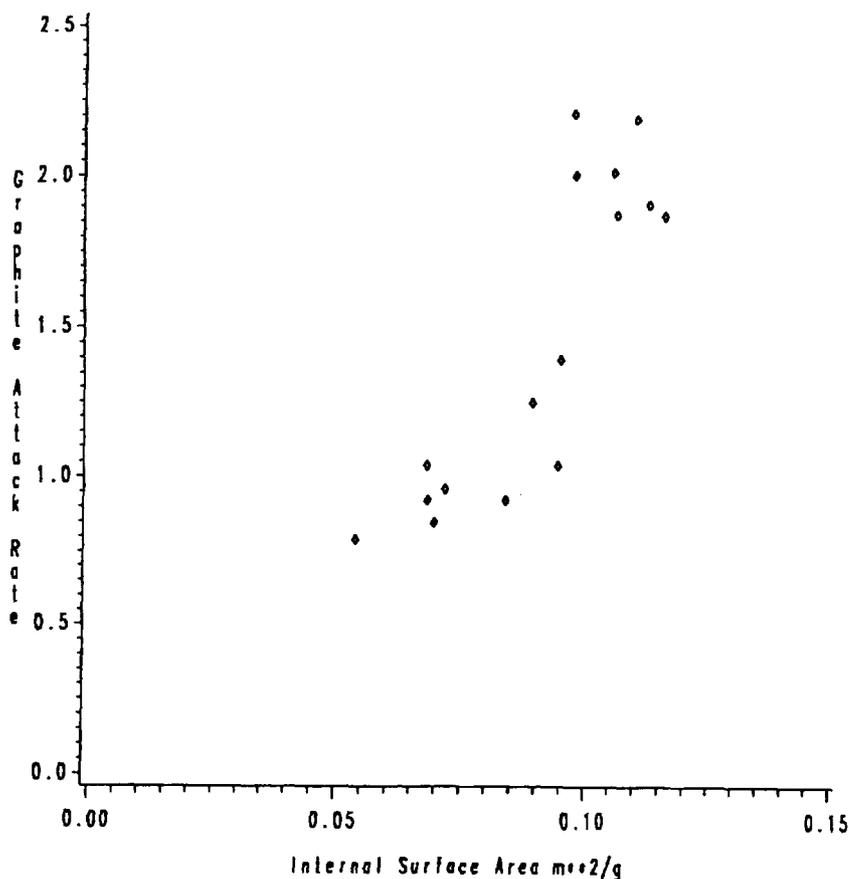

Figure 3 Variation of Graphite Attack Rate With Internal Surface Area

archived material derived from the same graphite bricks used to generate the samples for the carriers. It was thus possible to relate observed properties of the unirradiated graphite samples to the measured radiolytic oxidation rates.

4.1 Experimental Observations

4.1.1 γ-Spectroscopy and Neutron Activation Analysis

A selection of samples were removed from the hot cells and γ-spectra obtained. In parallel, a number of the archive specimens of BAEL graphite were analysed using neutron activation analysis. Although considerable variation was found in the extent of metal contamination, particularly of cobalt, there was no correlation with the attack rate ratio.
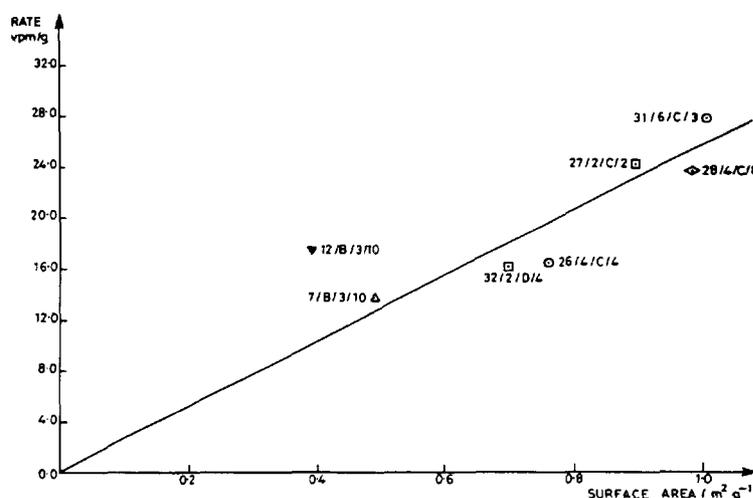

Figure 4 Variation of Hydrogen Conversion With Graphite Internal Surface Area

4.1.2 Properties of Archive Samples

Before the graphite samples were installed in the carriers a number of characterisation tests were carried out. These included the determination of bulk density, open pore volume and total (BET) surface area. It was found that the correlation between bulk density and open pore volume with attack rate was barely significant at the 95% level but, in contrast, there was a very strong correlation between BET surface area and attack rate (Figure 3).

4.1.4 Water Gas Shift Reaction

The rate of conversion of hydrogen to water in carbon dioxide containing 1% carbon monoxide flowing over graphite was investigated at 400°C and 0.101MPa gas pressure (1 atm.). No correlation was found with impurity concentrations, but a strong correlation was found with BET surface area (see Figure 4 in which the sample numbers beginning 7 and 12 are AGL grpahite and the remainder are BAEL).

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4.2 Discussion

The lack of any dependency of the observed radiolytic oxidation rates with the concentration of impurities seems to rule out the possibility of catalysis as the origin of the difference in behaviour between AGL and BAEL graphite. This is consistent with our current understanding of the radiation induced oxidation of graphite, where the dependent parameters are the pore size and shape, and the local gas composition within the pores. It is possible to conceive of mechanisms whereby metallic impurities interfere with the mobility of the active intermediates on the graphite surface, and there is at least one report which implies that impurities in the graphite can affect the rate of radiolytic oxidation [2]. No evidence, however, has emerged from this study to support these speculative mechanisms and thus changes in metallic content can be held to have no observable influence. One explanation for the change in rates is related to an observed differences in neutron-induced shrinkage behaviour. Figure 5 compares the observed shrinkage of the cylindrical specimens withdrawn from Hinkley Point 'B' with those predicted from the data base of experimental values for gilsocarbon graphite and demonstrates a clear distinction in the shrinkage behaviour of the BAEL and AGL graphite. It is noteworthy that the sample of BAEL graphite from the unreactive heat exhibits shrinkage similar to that of the AGL samples. It is assumed that gilsocarbon graphite shrinks as a consequence of neutron irradiation because the expansion of crystallites in the c axis is taken up
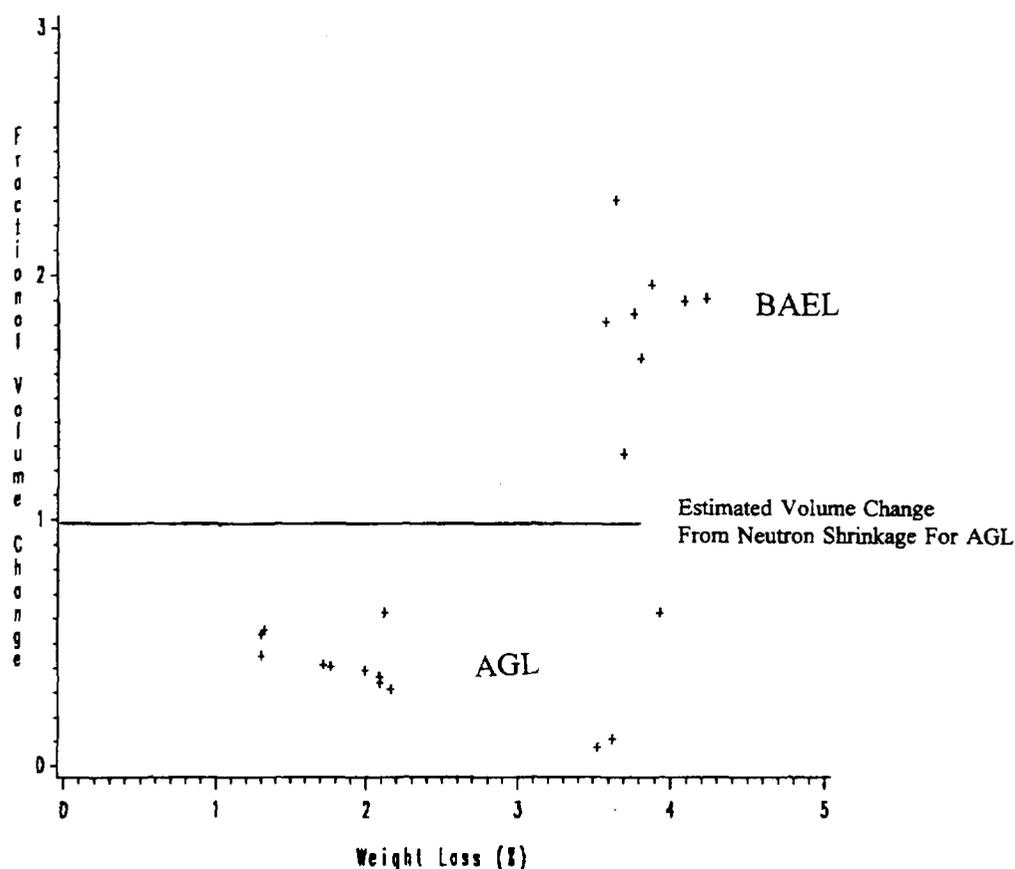

Figure 5 Variation of Observed Fractional Volume Change With Weight Loss For AGL and BAEL Graphite Withdrawn From Hinkley Point 'B' R3.

by porosity and thus only the shrinkage along the a and b axes contribute to the overall dimensional change. Changes in pore geometry would therefore be expected to alter the shrinkage properties as is observed in these studies. Such a change in pore geometry could leave the open pore volume unchanged whilst the internal surface area alters and would have a significant effect on radiolytic oxidation by changing the mean distance by which the oxidising species has to diffuse to the graphite surface. With this explanation, therefore, the origin of the divergent behaviour is purely geometric and lies within the framework of our current model of graphite oxidation as exemplified in our predictive codes POGO and DIFFUSE6.

The studies described here have supported previous observations that BAEL and AGL graphite differ in their activity towards the thermal Water Gas Shift reaction. However, our data would suggest that the origin of the divergence lies in the differing surface area rather than in the catalytic properties of the impurity content. A speculative mechanism for the divergent behaviour of the two graphites lies in the different ability of the graphite surfaces to mediate hydrogen/water conversion reactions. Hydrogenous material has been shown to influence the process of radiolytic oxidation. Tests in the Oldbury reactors (with Pile Grade 'A' graphite) have demonstrated a beneficial effect in terms of reducing the overall graphite oxidation by elevating the net concentration of hydrogenous impurities by injecting methane. Further, there appears to be a 'memory' effect such that a six-month cycle of one month at 200 vpm H_2 (achieved through methane injection) followed by decay to a minimum of 50 vpm for the succeeding five months[1] provides an effectively *continuous* reduction in graphite-oxidation rate. The observation of such memory effects strongly implies that these inhibiting processes operate on the graphite surface. One such mechanism is some form of sacrificial interception of the oxidising intermediate, similar to that proposed for the oxidation-inhibiting role of methane. A perturbation of the dynamic equilibria between these processes as a consequence of surface energetics would thus account qualitatively for the observed behaviour of the two graphites. Against this, however, is the observation that these surface chemistry processes are essentially thermal processes and, as such, would be expected to show some dependencies on temperature. No such temperature dependencies have been observed in the observations of radiolytic oxidation of graphite, in accord with the presumption that the rates of radiation mediated processes are independent of temperature.

A sacrificial mechanism, however, is not the only process whereby radiolytic oxidation can be inhibited; it has already been mentioned (Section 2) that the observational evidence for the formation of sacrificial deposit from methane is not convincing. We can consider an alternative process in which the extent of inhibition is proportional to the lifetime of the oxidising intermediate on the graphite surface, between its arrival from the gas phase to its destruction by the gasification of a surface carbon atom at an edge or defect site. The longer the lifetime of the intermediate, the greater the probability that it will react, either with a surface species such as carbon monoxide (the surface analogue of the gas-phase inhibition) or directly with a gas-phase species by an Ely-Rideal mechanism. The lifetime of the intermediate will be governed by its mobility, which will in turn depend on the potential energy surface of the graphite basal plane. The role of the inhibiting species is therefore to modify this potential energy surface, impeding or even trapping the active intermediate. The observed difference between AGL and BAEL graphite thus derives from a change in the potential-energy surface of

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[1] Thereby avoiding excessive mild-steel oxidation in other reactor components.

the planes, arising from the subtle geometric differences between the two sources that have been discussed here.

Preliminary indications are that the effects of surface potential variation on radiolytic oxidation can be investigated by theoretical calculations using density functional theory. An initial study (M. Heggie, University of Exeter, Personal Communication) has examined how the proposed intermediate, CO_3^-, interacts with the graphite surface and has shown that it does indeed form a bound state. It is hoped to extend these calculations to study the interactions between species on the surfaces; to test these speculative mechanisms, as well as investigating how geometric changes in the graphite could alter the course of the oxidation reaction.

Although the foregoing has indicated that there are still areas in the field of radiolytic graphite oxidation where our understanding is incomplete, we are still able to use the predictive models described here to assess the current and future weight losses in our reactors. The monitoring results enable empirical graphite attack rates to be derived which are then incorporated into the models. The monitoring programmes therefore have a continuing role in both defining the graphite behaviour and validating the oxidation models so derived.

ACKNOWLEDGEMENTS

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