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Review of Graphite Oxidation Research and Development Needs and Tests

Author(s): **K. Kühn (FZJ), H.-K. Hinssen (FZJ), R. Moormann (FZJ)**
D E Buckthorpe (NNC), M W Davies (NNC)

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RAPHAEL ***(ReActor for Process heat, Hydrogen And ELectricity generation)***

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Abstract

Within the RAPHAEL-IP framework, oxidation experiments on graphite are being performed on the graphites selected for the irradiation tests in the High Flux Reactor (HFR) in Petten. This report reviews the oxidation testing carried out to date, the requirements with respect to oxidation testing, and the planned tests to be performed within Raphael.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
01	14/04/2006	First issue	K Kuhn FZJ	Derek Buckthorpe NNC	Derek Buckthorpe NNC	Edgar Bogusch, ANP

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1 Introduction

The need for reliable graphite data is a crucial issue for existing and new HTR and VHTR projects. The performance of the graphite in the reactor has important safety implications because of structural and other property changes that occur when it is irradiated. Its selection also has significant consequences in terms of lifetime degradation and for future decommissioning activities. Oxidation resistance of graphites at high temperature requires special attention due to its relevance during normal operation and for licensing and safety analyses of air and water ingress accidents.

Most graphites that have been used in previous core designs are no longer manufactured commercially, and currently available grades are limited to a few specific sources of raw materials. Few graphites may turn out to be suitable or desirable for a modular VHTR and therefore the need for information for design and feasibility assessment is vital. With this in mind, cooperation with graphite manufacturers has been an important part of the selection strategy (identified in HTR-M/M1 projects). This is vital if there is a need to develop an improved graphite in the longer term. An important aspect within the selection strategy is the graphite's resistance to oxidation both under normal operation and accident conditions (Air Ingress). This report reviews the research and development needs of such graphites with respect to oxidation resistance, the testing carried out to date, and the planned experiments within Raphael SP ML.

2 Selected Graphite Grades within the Irradiation experiments

The graphite irradiation experiments within Raphael-IP (750^{o}C phase II plus 950^{o}C phase I and II) – see Figure 2-1) involve a number of major and minor graphite grades. These were selected at specialist (HTR-M1 and Raphael) graphite meetings. The graphites selected cover the two main coke sources (pitch and petroleum) and the three main manufacturing methods (extrusion, iso-moulding and vibro-moulding). The aim was to maximise the benefit and the information on the irradiation behaviour of different graphites that could be obtained from the forthcoming Raphael tests. The major and minor graphites within the higher temperature irradiation experiments [Ref 5.1] are listed in Tables 2-1 and 2-2.

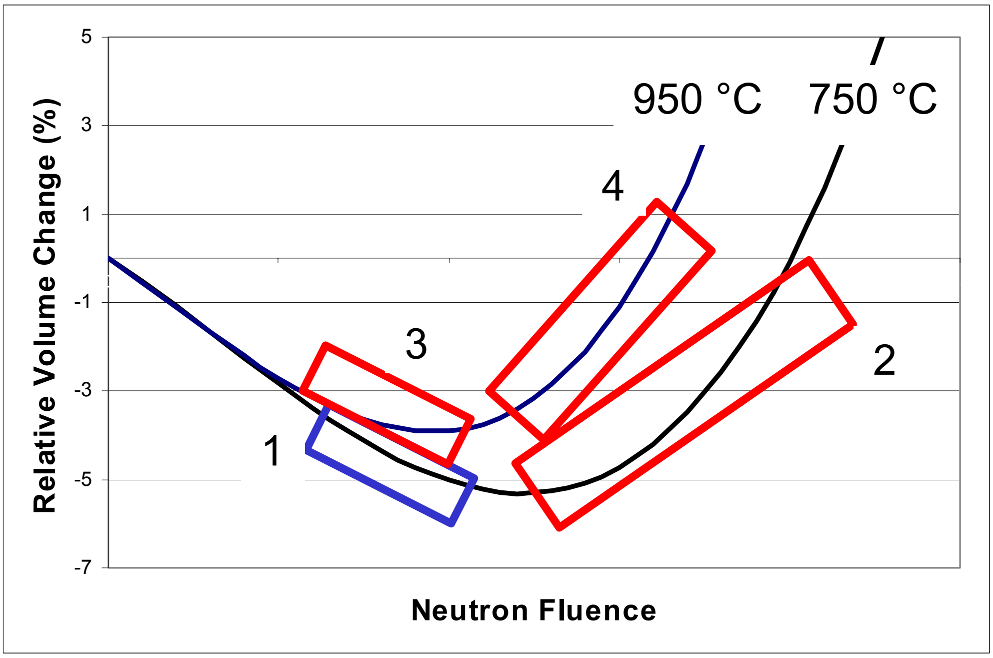

Figure 2-1 Schematic overview of the different irradiation experiments within HTR-M1 and Raphael-IP

Grade	Manufacturer	Coke	Process
PCEA	GrafTech	Petroleum	Extrusion
PPEA	GrafTech	Pitch	Extrusion
NGB-10	SGL	Pitch	Extrusion
NBG-18	SGL	Pitch	Vibro-moulding

Table 2-1 Selected graphite grades: major grades

Grade	Manufacturer	Coke	Process
PCIB-SFG	GrafTech	Petroleum	Iso-moulding
BAN	GrafTech	Needle	Extrusion
NBG-25	SGL	Petroleum	Iso-moulding
NBG-17	SGL	Pitch	Vibro-moulding
IG-110	Toyo Tanso	Petroleum	Iso-moulding
IG-430	Toyo Tanso	Pitch	Iso-Moulding

Table 2-2 Selected graphite grades: minor grades

Most if not all of these graphites will need examination and prioritisation in terms of their suitability and oxidation resistance for VHTR application.

3 Review of oxidation needs and testing to date

3.1 Identification of requirements for tests on oxidation under accident and normal operation conditions:

Based on the results of oxidation tests performed in the former FP 5: HTR M / M1 programs [Ref 5.2 & 5.3] further investigations on current and newly developed graphites are necessary for accident and normal operation conditions. The limited oxidation resistance of porous C-based materials causes potential problems when in contact with oxidising atmospheres. During accident conditions this can for example lead to a localised reduction in strength at exposed surfaces and an increase of fission product release. The necessary safety analyses on graphite oxidation therefore require a detailed knowledge of the oxidation kinetics.

High oxidation rates of the graphite materials are also a general material problem which should be addressed by a careful selection. During normal operation graphite oxidation takes place due to impurities in the cooling gases; here, catalysis plays a major role. However the level of impurities within the gas under normal operation is not well known.

The oxidation data derived from the HTR-M/M1 programme showed a good comparable reactivity for most of the investigated graphites, with the pitch coke graphites having a lower reactivity than the petroleum coke graphites. There was, however, one clear exception (NBG-20), which had a much higher reactivity (see Figure 3-1). The reason for this is not well understood. Initially it was thought that either higher impurities or different heat treatment temperatures during fabrication could be the cause. However investigations within HTR-M1 showed that neither of these could satisfactorily explain the much lower oxidation resistance of the NBG-20 material.

A further consideration was the production process. In comparison to NBG-10, which is formed using an extrusion process, the NBG-20 is formed by extrusion but on a laboratory scale and produced (contrary to NBG-10 with pitch coke) from petroleum coke which has a high V and Ni basic impurity value.

It should also be noted that differences in oxidation rates do occur depending on the location in a graphite block where the sample was extracted. Similar observations but at lower reactivities were made during new tests with NBG-10 samples extracted from different parts of a 55 kg block. (Figure 3-2 to 3-4)

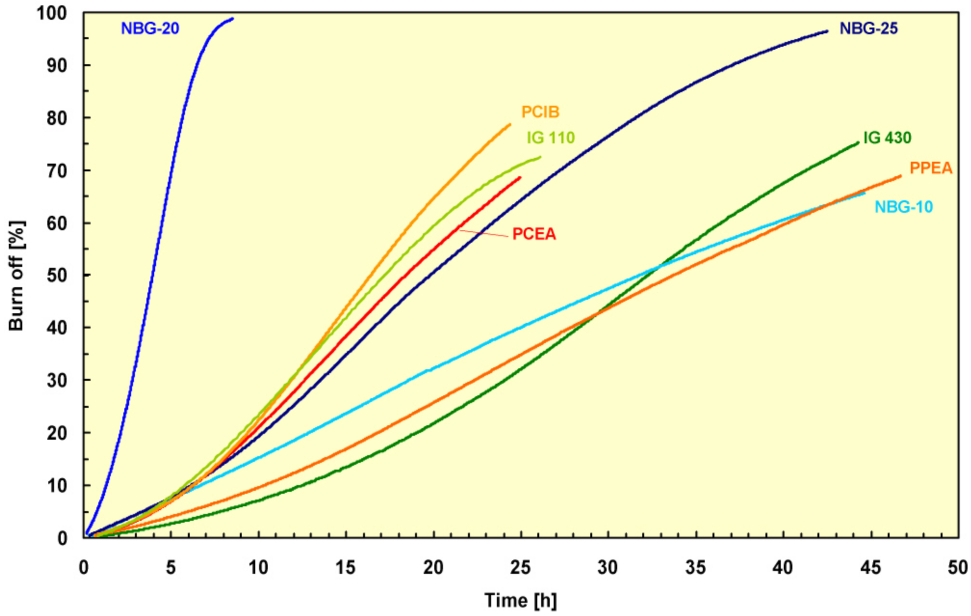

Figure 3-1 Exemplary graph from FP5 for high oxidation rates of the selected graphites at 650 °C in air

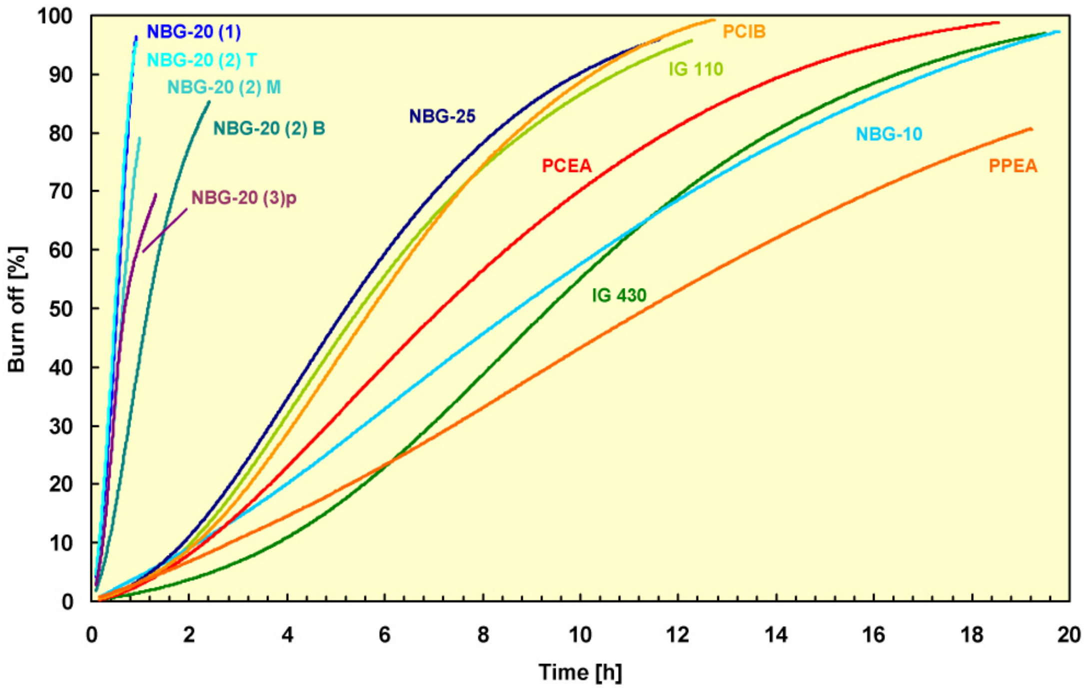

Figure 3-2 Exemplary graph from FP5 for high oxidation rates of the selected graphites at 650 °C in O_2

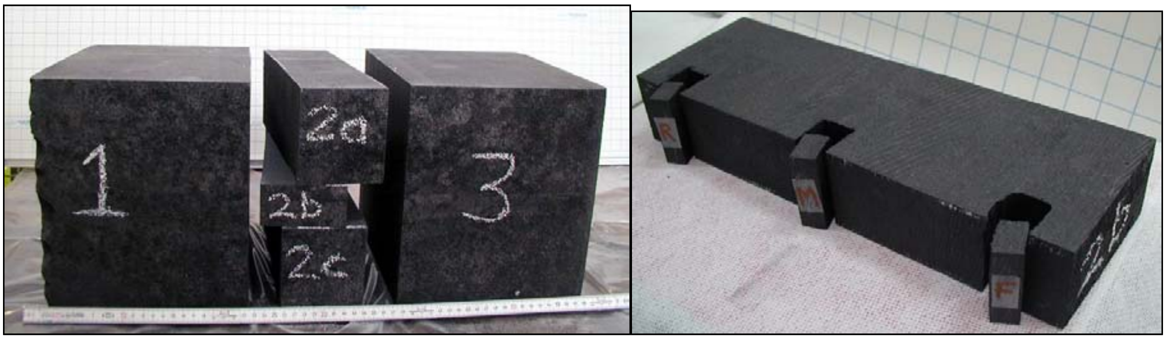

Figure 3-3 NBG-10 Block with parts of extracted samples (R, M, F)

The oxidation behaviour of NBG-20 shows that this graphite is the least satisfactory out of the graphites tested for VHTR application. It is important to understand the reasons for its higher oxidation rate and so further investigation is required.

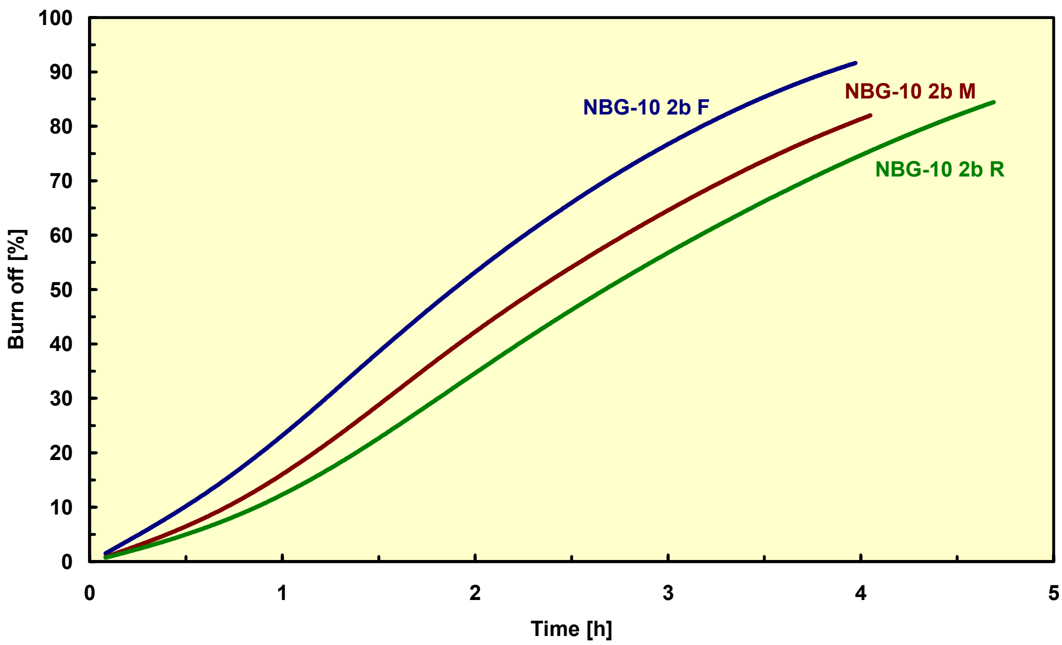

Figure 3-4 Burn off vs. time of NBG-10 samples extracted from different locations. Oxidation in air at 750 °C.

During the initiation of an additional, new constructed facility (THERA II) for oxidation experiments some first tests using V483T5 and NBG-20 material at 700 °C have been carried out in air and these also showed the same tendency of oxidation behaviour with a higher reactivity for the NBG-20 material. Further tests within the THERA II are necessary to confirm the results. The THERA II facility will allow a mass spectrometric analysis of the product gas composition to be carried out and also it has the capability of accommodating a larger sample size up to 400 mg, which is part of the future test programme.

3.2 Specification of tests / sample requirements for tests under accident (air ingress) conditions

The main aims of the graphite oxidation work should be to characterise the oxidation behaviour of the graphite materials selected for the current and future irradiation experiments and the generation of kinetic data for the Boudouard reaction (C/CO_2) on fuel element graphites.

3.2.1 Graphite characterisation concerning oxidation:

The characterisation of current and newly developed nuclear graphites should continue. For direct cycle HTRs the oxidation behaviour in oxygen / air is more relevant than in steam.

The methods of characterisation for behaviour under air ingress conditions should be performed in the chemical reaction controlled regime (Regime I), and additionally in the in-pore diffusion controlled regime (Regime II).

In Regime I predominantly volume oxidation takes place. Here the advantages are large sensibilities against catalytic impurities, incomplete graphitisation and a specific reactive surface. For this kind of investigation small samples are required (250 mg) and the temperature limit is about 750 °C (if V sample > 100 * Vmax. grain). The samples used are small blocks of ~5*5*5 mm or cylindrical samples with a diameter of 8 mm and ~3mm height (dependent on density). It has to be noted in this context, that there are some doubts about an independence of the volume related reaction rate on the specimen size in Regime I, as a consequence of respective experiments in other laboratories. Also since the definition of Regime I is strictly related to a homogeneous pore model, which is not found in reality, these doubts have to be taken seriously: Experimental and theoretical examinations of the nature and limits of Regime I oxidation remain to be performed. Long-term experiments at low temperatures and with different specimen size are planned for clarification of this problem. Nevertheless, one should bear in mind, that only (real) Regime I oxidation gives sufficient information about chemical behaviour in oxidation.

On the other hand it has to be recognised that oxidation in reactor conditions occurs mainly in Regime II. In Regime II the rates are controlled by in-pore diffusion, and by chemistry. A gradient in oxidation occurs that changes in a complicated manner with increasing burn-off. A complete analytical description of Regime II (as performed in several oxidation codes) is far more complicated than that of Regime I and requires at least burn-off dependent Regime I rates and effective diffusion coefficients, plus the assumption of a homogeneous graphite (with respect to pore size distribution etc.) is required. In Regime II the test conditions are closer to reactor conditions, but the sensibility against specific graphite parameters decreases. High temperatures up to 950 °C in air can be tested when high flow rates are applied. Here larger samples are required (where a near surface oxidation takes place). The shape of the samples is fixed for the INDEX facility. Here tube shaped samples with an outer diameter of 20 mm an inner diameter of 10 mm and a total length of 40 mm were used..

For long-term experiments at lower temperatures (e.g. 450°C) different sample sizes can be used. Here a larger quantity of graphite is required for the production of samples (max 10*10*30 mm is needed). Respective furnace facilities (BRUNO-furnace) are available at FZJ for this work.

3.2.2 Kinetics of Boudouard reaction

These tests are relevant because for many air ingress scenarios the oxidation does not reach the fuel containing active core. The oxygen is consumed within the bottom reflector and CO_2 is formed there and then passes through the active core and oxidises the fuel elements. The kinetics of the Boudouard reaction are not well known, accordingly there is a comparatively large degree of uncertain scatter of fuel element oxidation.

These kinds of investigations can also be made in the THERA and INDEX facilities. The requirements for the samples are facility dependent as described above. The temperature range used is 900 – 1250 °C with a CO_2 partial pressure up to 20 vol-% and a CO partial pressure up to 40 vol-%.

3.3 Specification of tests / sample requirements for tests under normal operation conditions

Due to the impurities in the helium cooling gas, graphite oxidation takes place during normal operation. The reactive components of a HTR atmosphere (Helium + H_2O, H_2, CH_4, CO, CO_2, O_2) under normal operating conditions have to be considered in the oxidation process. As mentioned previously, the normal operation atmosphere of a VHTR is not well known, and some effort has to be spent as far as possible to define a reference atmosphere. Because of the absence of a steam generator it is assumed that steam plays a minor oxidation role compared with steam cycle applications.

For investigation of oxidation during normal operation a long-term oxidation test should be defined. Here it is necessary to define a suitable test arrangement and oxygen concentration that will give representative end-of-life oxidation levels over a manageable time period. The test arrangement should provide a relatively uniform and low burn–off rate throughout each specimen. Two temperatures should be used to exclude strongly deviating activation energies, if the problem of a large scatter from certain graphites is to be avoided.

The parameters for such a test, for example the oxygen concentration, the optimum sample, size, pressure drops and flow rates will have to be determined. Account should be taken of the experience obtained from tests carried out in support of other HTR program (e.g. Dragon and THTR-300).

4 Conclusion

4.1 From the above discussions it is considered that most of the characterisation work (for air ingress accident conditions) should be performed in Regime I, but some selected characterisation experiments should also be carried out under Regime II. For normal operation the presently available graphites and the later newly developed materials should be compared on the basis of an appropriate long-term test under Regime II.

4.2 The examinations on unusual oxidation behaviour of graphites requires post examinations including investigation of impurity concentrations, density profiles etc.. For the NBG-20 or material with similar oxidation behaviour, tests in steam at 900 °C should be done in order to find out, whether a similar high oxidation rate also occurs under steam oxidation.

4.3 Parallel oxidation tests should be performed in other laboratories.

4.4 The proposed Raphael graphite oxidation test program should include the following investigations:

- Initiation of the test facilities INDEX and THERA II and verification of these facilities.
- Test experiments at high temperatures (CO_2 / air / steam) :
- Further investigations of the oxidation resistance on available selected graphites from FP5 and FP6 (and later on for new materials).

- Measurements at different temperatures (e.g. 650 – 750 °C) and different oxidant partial pressures. Evaluation of kinetic data [EA]
- Definition of standard tests and a maximum acceptable oxidation rate during normal operation for application in HTR regions, where oxidation is a major concern (also for direct cycle pants).

4.4 Investigations of the oxidation resistance of fuel graphite material via Boudouard reaction (CO_2).

4.5 Test experiments should be performed at high temperatures and high flow rates on graphite used for pebble bed reactors (A3-matrix or similar) and later on for fuel element graphite of block type reactors.

5 References

5.1 Progress of graphite Irradiation tests at higher temperature
RAPHAEL 06/03 D ML3.2

5.2 HTR-M Final Report
HTR-M1 04/12 P 0 0 105

5.3 HTR-M1 Final Report
HTR-M1 05/12 P 0 0 46