Comparison of the oxidation behaviour of 8 HTR-Graphites

1 Introduction

Based on the graphite work in the HTR-M Project, further corrosion tests were performed on those eight graphites which were chosen for the irradiation tests of European HTR-material program (HTR-M/M1, VHTR; irradiation start: 02/2004). The application of graphite materials in HTRs demanded the acknowledgement of the limited oxidation resistance of these materials at high temperatures, caused by contact with oxidising gases (oxygen/air and steam). This limited oxidation resistance in case of high temperature accidents has to be considered in safety analyses [1]. Oxidation occurring during these events may increase fission product release, may weaken the strength of components and even may destroy protecting structures by explosion of flammable mixtures. The frequencies of severe air ingress are nearly negligibly small, but the extended safety concept of modern HTRs requires answers on the safety behaviour until deep into the "hypothetical" range [1]. Safety analyses on graphite interactions with oxidising gases requires a detailed knowledge of the respective oxidation kinetics [1].

Further on, to some extent, graphite oxidation takes place in the normal operation reactor, too. This is due to the impurities of the cooling gas. In general, selection of graphite materials has to take into account their oxidation resistance, because graphite oxidation is to a large extent not only safety-relevant problem but also a general material one.

This report consists of:

- Oxidation measurements (oxygen/air) of eight chosen structural graphites in the chemical reaction controlled regime [2, 3, 4] in order to point out the differences in oxidation behaviour of the developed materials and to give a selection criteria for the application of the investigated materials. The discussion of the oxidation behaviour is besides irradiation / strength characteristics necessary in view of future development and application.

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Comparison of the oxidation behaviour of 8 HTR-Graphites

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2 Experiments

Experimental investigations of the eight chosen structural graphites (see Tab. 1) were done in oxygen and in air each at temperatures of 650 °C and 700 °C. Additional experiments of additive samples of NBG-20 were performed for comparison at 650 °C in oxygen.

Table 1: Investigated Materials

Manufacturer	Graphite	Apparent Density [g/cm^3]
UCAR	PCEA	1,82
	PCIB	1,85
	PPEA	1,84
SGL	NBG-10	1,81
	NBG-20	1,78
	NBG-25	1,81
TOYO TANSO	IG 110	1,77
	IG 430	1,82

All experiments were performed in the THERA facility, which is an simultaneous thermal analyser with a coupling of oxidation unit and weighing system [1, 5]. The gas supply system of this facility allows to switch over from inert gas to oxidation gas in the oxidation unit, when the experimental temperature is reached. All experiments were performed in the chemical reaction controlled regime [2, 3, 4] under isothermal and isobaric condition at the above mentioned temperatures and at pressure of 1 bar. In the chemical reaction controlled regime, the chemical reaction itself is the rate limiting step and the material is oxidised homogenously within the open pore system. The samples used in the THERA facility are small pieces of maximum weight of 250 mg. Measurements were done up to a final weight loss of ~ 70 -100 %, which means in case of 100 %, that the sample vanished because of complete oxidation. The run times diversified between ~ 12 min up to 20 h.

In case of the NBG-20 graphite additive samples were investigated under the same conditions at 650 °C in oxygen like all other. Therefore for NBG-20 three different qualities have to be distinguished (1), (2), (3p): **(1)** is the first allocated sample [NBG-20 (1)]; **(2)** is a second larger crude block of the same graphite, where three samples was extracted from the top [NBG-20 (2)T], the middle section [NBG-20 (2)M] and the bottom [NBG -20 (2)B]. **(3)p** is another larger block of this graphite, but with an additional purification.

3 Results

The experimental investigations show that the most materials have a comparable reactivity. It becomes obvious from the experimental results, that most of the new materials are of the same reactivity (IG 110) or even better than V483T, a well known standard nuclear graphite from a former HTR programme [4]. One exception of these continuous acceptable results is the NBG-20 with an essential higher reactivity (see Fig. 1 – 8).

3.1 Burn off versus time curves

For oxidation in air at 700 °C the PPEA graphite shows the lowest reactivity and needs 11 h to reach 50 % burn off. The IG 110 needs for the same burn off (50 %) ~3,5 h whereas the NBG -20 reaches 50 % burn off already after 2 h (Fig.1).

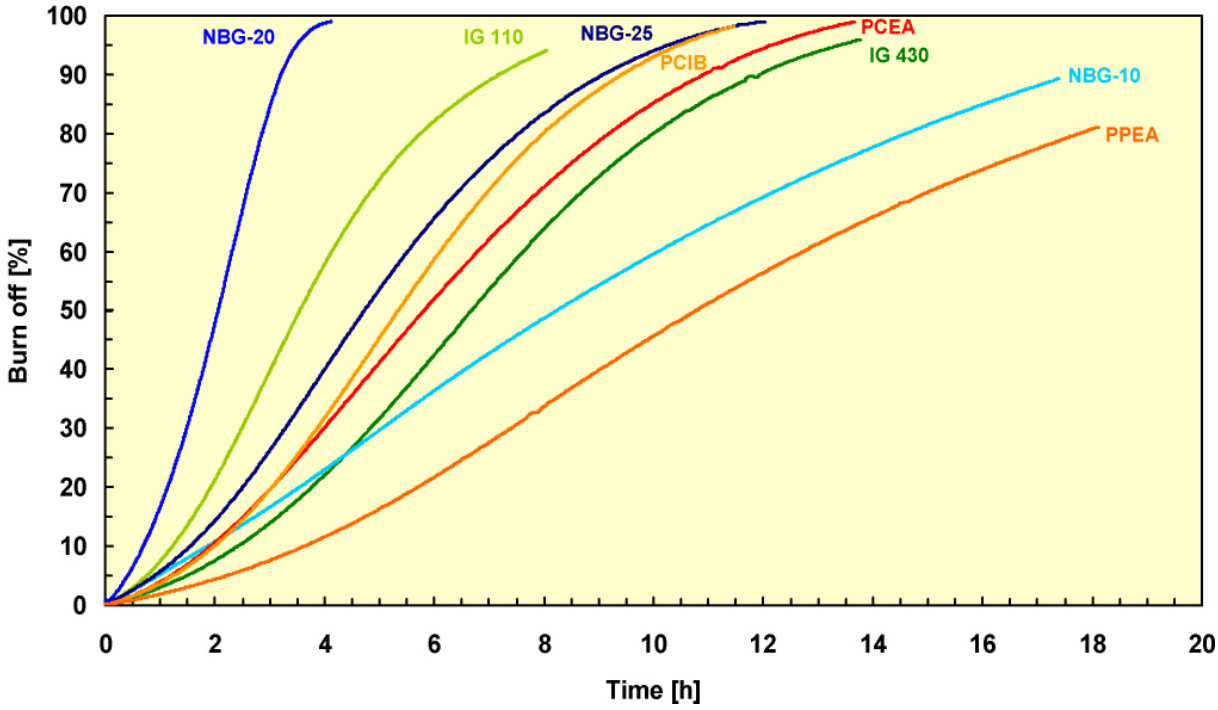

Fig. 1: Burn off versus time curves for oxidation in air at 700 °C

At oxidation in O_2 at 700 °C a similar behaviour can be observed. As is found in general, the oxidation process runs here faster because of the higher temperatures. The PPEA show again the lowest reactivity and need ~ 4 h to reach 50 % burn off, the IG 110 about 1h and the NBG –20 just 12 min., which is a higher reactivity of a factor of 5 compared with the IG 110 (see Fig. 2).

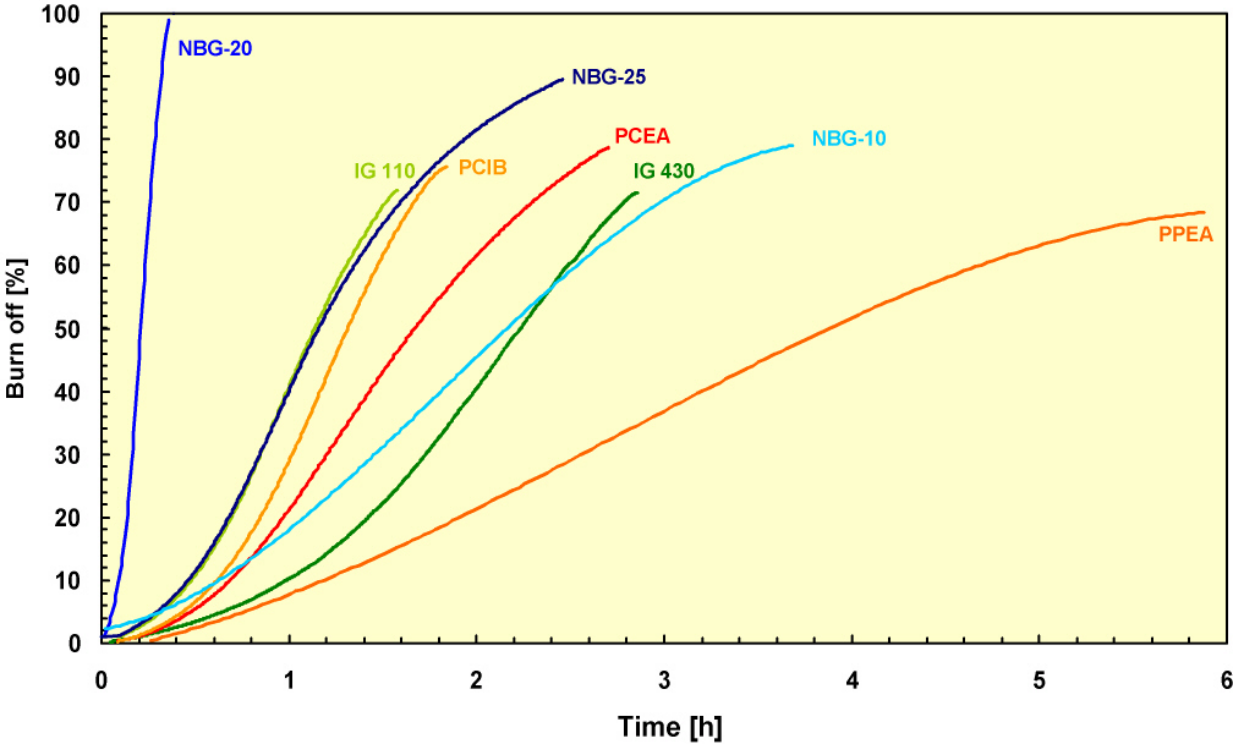

Fig. 2: Burn off versus time curves for oxidation in O_2 at 700 °C

Experiments at lower temperatures in air show again similar results. At 650 °C and 50 % burn off the PPEA reveals the lowest reactivity, but it is very close to the IG 430 and the NBG-10. Also the PCEA, IG 110, NBG-25 and the PCIB are very close together. A clear exception is once again the NBG-20 with a higher reactivity of a factor of 4 (Fig. 3).

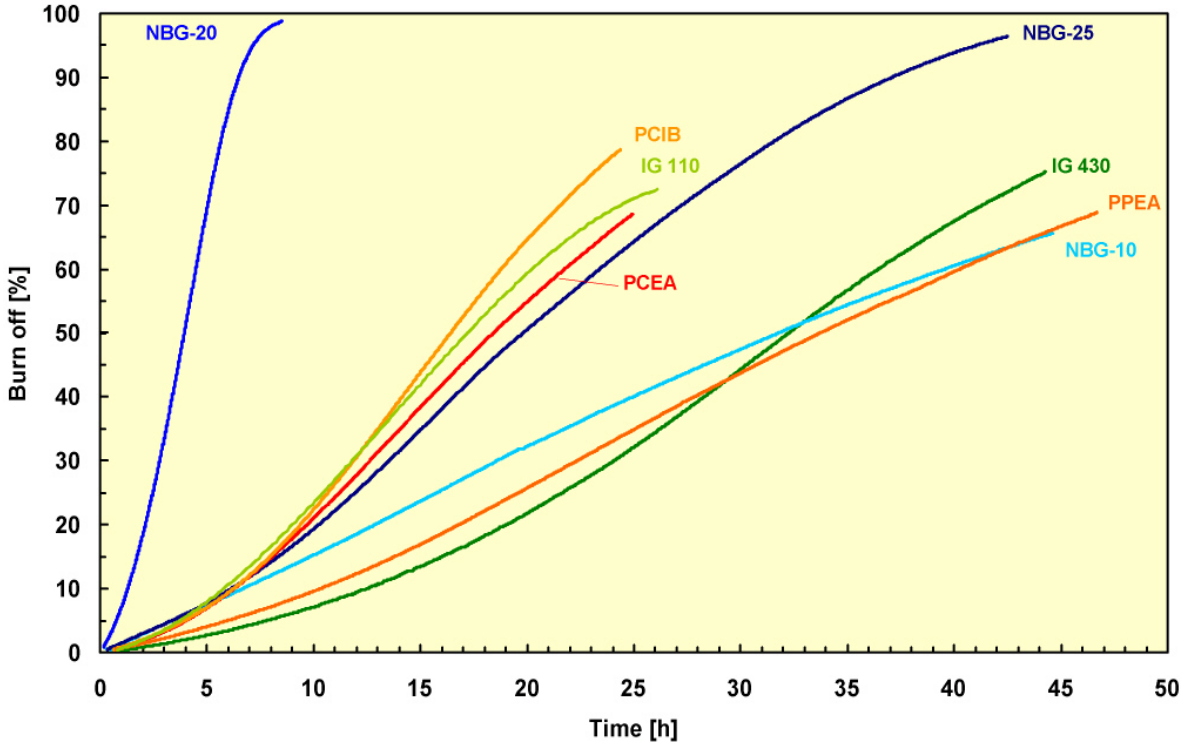

Fig. 3: Burn off versus time curves for oxidation in air at 650 °C

In Fig. 4 the reactivities of oxidation in O_2 at 650 °C are diagrammed. The results barely differ from the results presented before. In this figure the experiments with additional NBG -20 samples are plotted.

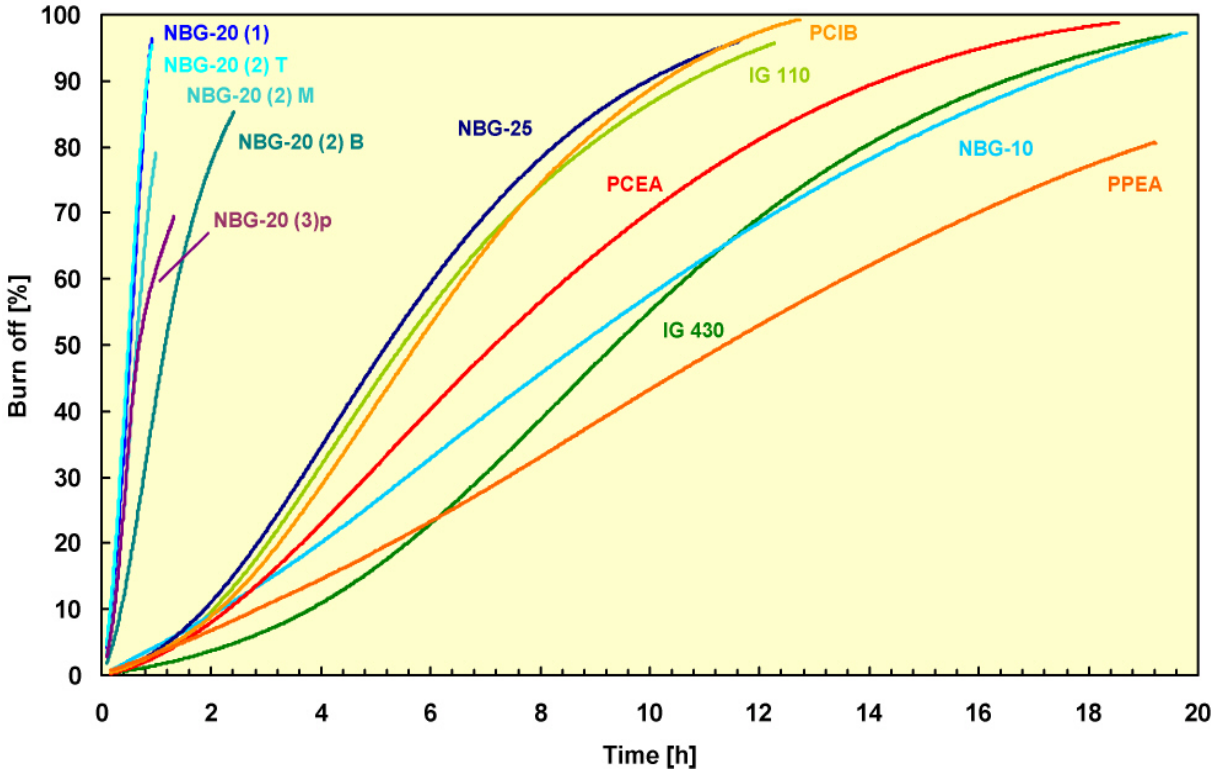

Fig. 4: Burn off versus time curves for oxidation in O_2 at 650 °C. The samples are extracted from: **(1)** first graphite sample block [NBG -20 (1)]; **(2)** second block [NBG-20 (2)]: T = Top, M= Middle, B = Bottom; **(3)p** = third block / purified sample.

It becomes obvious from this figure, that the oxidation rate of all three NBG-20 samples is at least by a factor of 5 larger compared to the NBG-25, which shows here the highest reactivity of all remaining samples. Even the purified sample has the same "bad" reactivity like the other NBG-20 samples. The differences between these samples are relatively small, anyhow this might be an indication, that the position of a sample in a production charge can have an effect to the properties, and that there may be differences caused by production.

3.2 Rate versus burn off curves

All graphites show rate increases with increasing burn off, up to rate maxima between ~ 30 - 60 % burn off, followed by a nearly linear decrease. This formation of rate maxima can be explained by the kinetics of carbon oxidation [1], or even porous solids, forming only gaseous products in general.

For oxidation in air at 700 °C the results are given in Fig. 5. The NBG-20 shows - as expected from burn off vs. time curves – also in this kind of presentation the highest reactivity: The maximum rate is 1.05E-02 [%/s] at 55 % burn off.

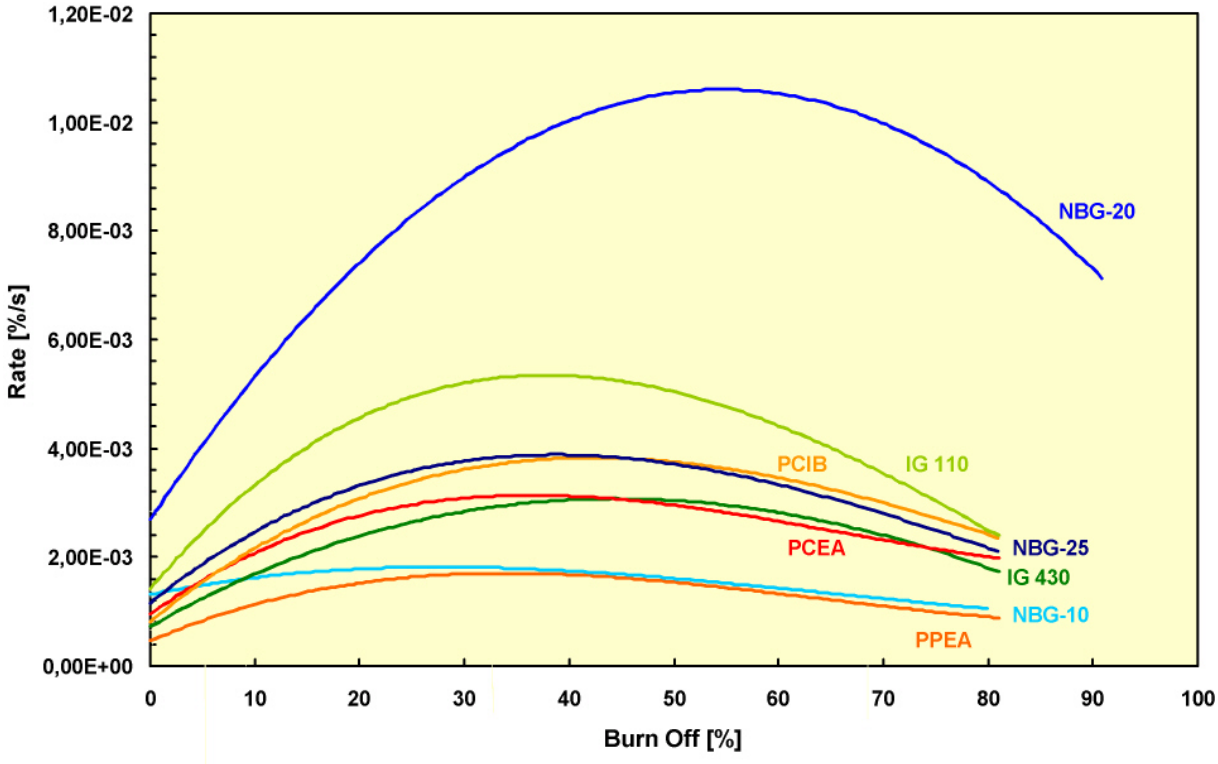

Fig. 5: Rate versus burn off curves for oxidation in air at 700 °C

This behaviour is even more pronounced for oxidation in O_2 at 700 °C (Fig. 6a, b). In Fig 6a the rate versus burn off curves is shown for all samples, in Fig. 6b a section of Fig. 6a is given to point out the differences between the graphite materials other than NBG-20. During oxidation in O_2 at 700 °C again the NBG-20 is the material with the highest oxidation rates. It shows a reactivity of at least a factor of 6 higher than all the other investigated materials. The rate maximum of the NBG-20 is 1.25E-01 [%/s] at 45 % burn off.

In Fig. 6b all materials show more or less distinct rate maxima (~ 30 to 50 % burn off). IG 110- and PCIB-materials reveal the highest reactivities and the NBG-10- and PPEA-materials the lowest rates.

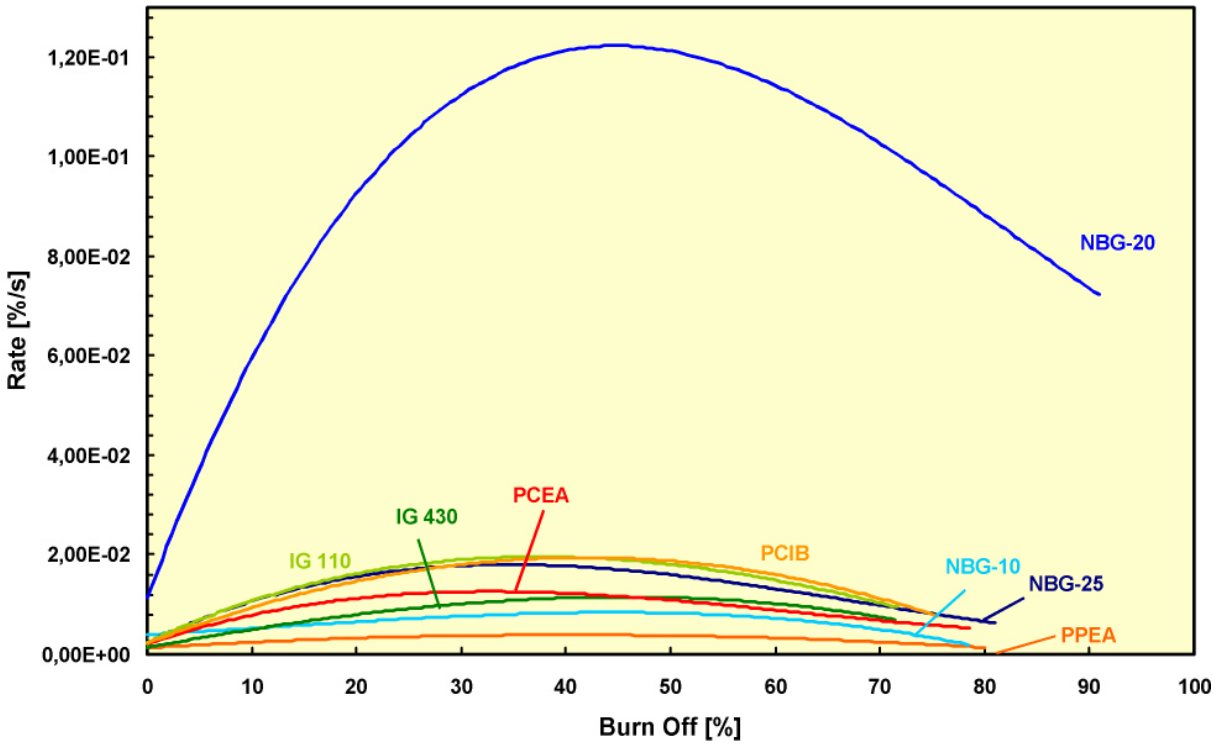

Fig. 6a: Rate versus burn off curves for oxidation in O_2 at 700 °C

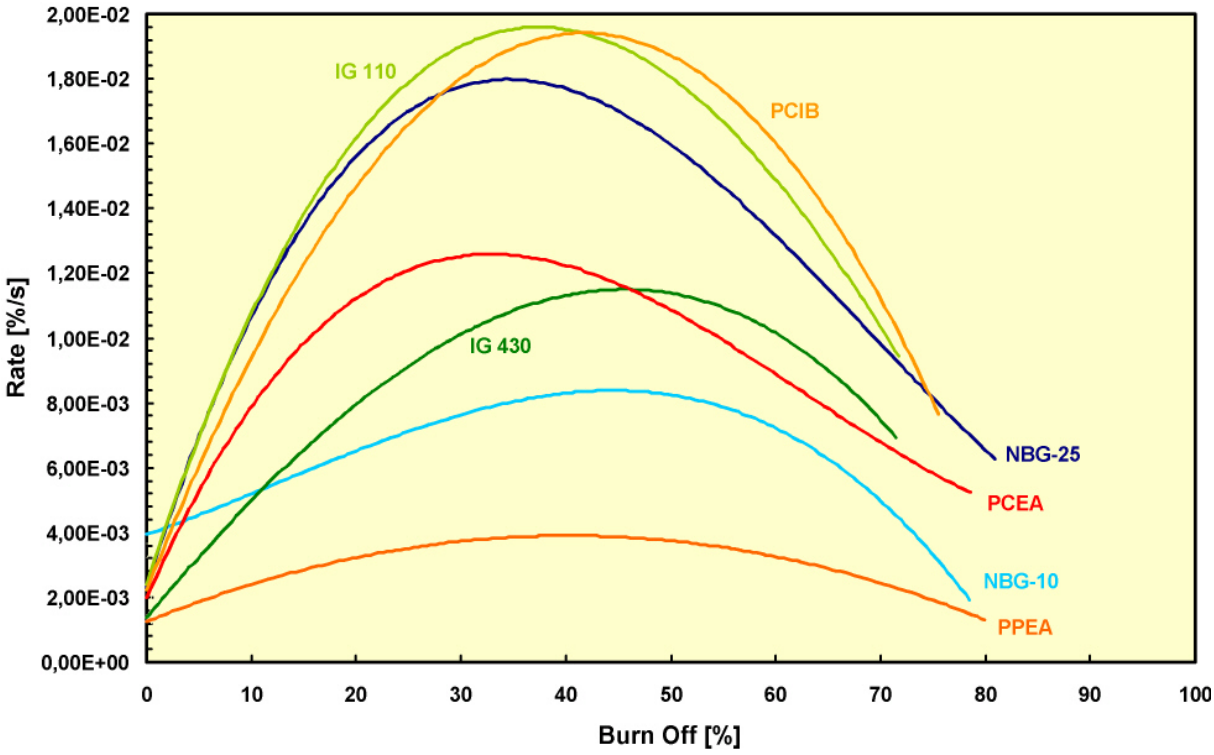

Fig. 6b: Section of rate versus burn off curves of Fig. 6a for oxidation in O_2 at 700 °C

In Fig. 7a and 7b the results for oxidation in air at 650 °C are diagrammed. In this figures the results are similar to the results in air at 700 °C (see Fig. 5) but in relation to the lower oxidation temperature at lower rates.

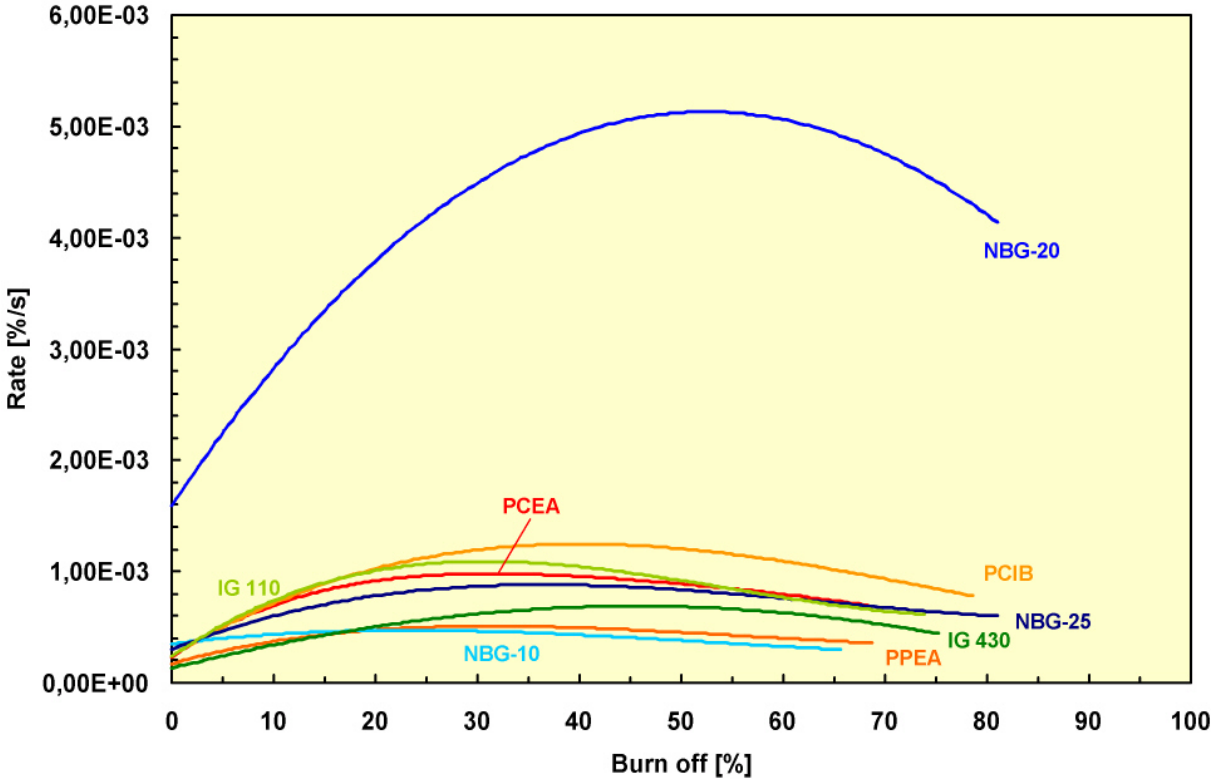

Fig. 7a: Rate versus burn off curves for oxidation in air at 650 °C

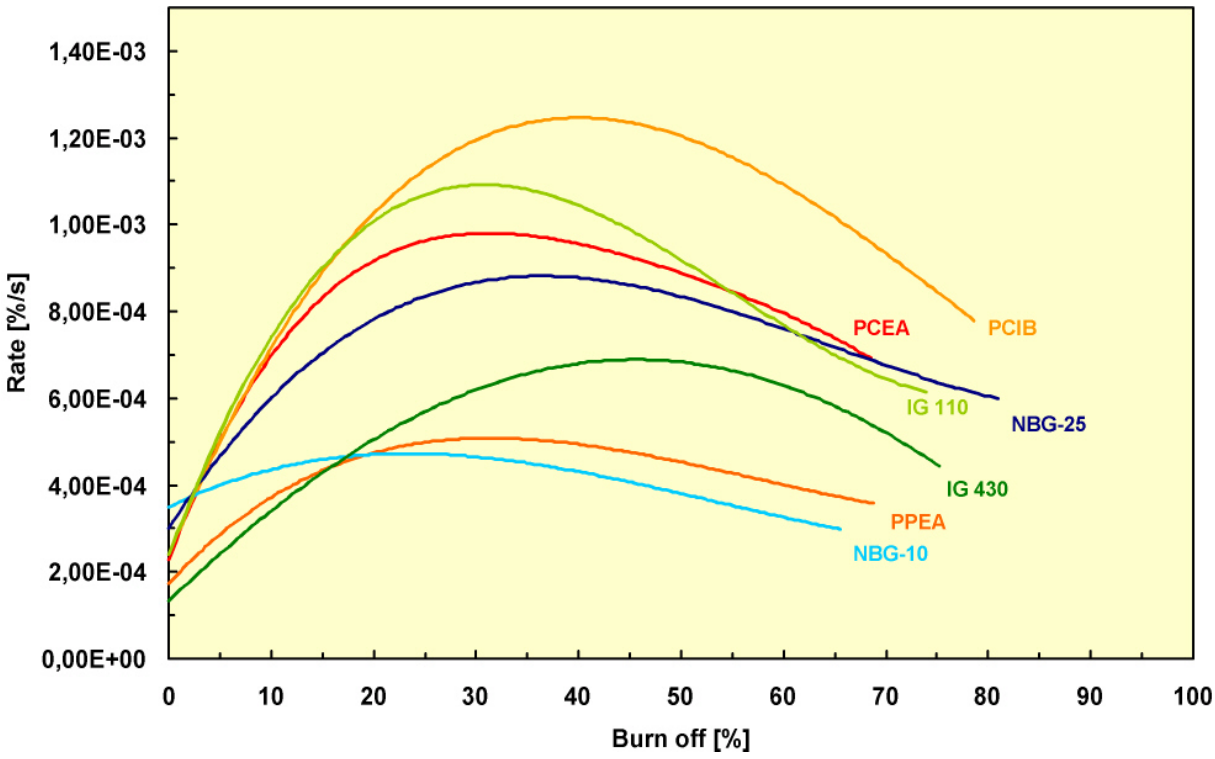

Fig. 7b: Section of rate versus burn off curves of Fig. 7a for oxidation in air at 650 °C

In Fig. 8a and 8b the results for oxidation in O_2 at 650 °C are given. In Fig. 8a the additional samples of the NBG-20 material are shown. Fig. 8b presents the graphite materials other than NBG-20 only for a more detailed view.

It arises clearly from Fig. 8a, that all investigated samples of the NBG-20 material have significantly higher reactivities than all other graphite materials. Within of the NBG-20 qualities there are obvious differences, but the rates are at least a factor of 3 higher than the graphites other than NBG-20.

The consideration of the NBG-20 (2) samples show the differences related to the location, where the sample was extracted from the block. Here a clear sequence in rate decrease from the top, middle and bottom section of the sample block can be observed. The purified sample [NBG-20 (3)p] shows amazingly not the lowest reactivity of the NBG-20 samples. This sample reaches a rate maximum already at 25 % burn off and the subsequent rate decrease is up to ~ 60 % burn off faster than for other graphites. After reaching ~ 60 % burn off this curve flattenes to a very low rate decrease.

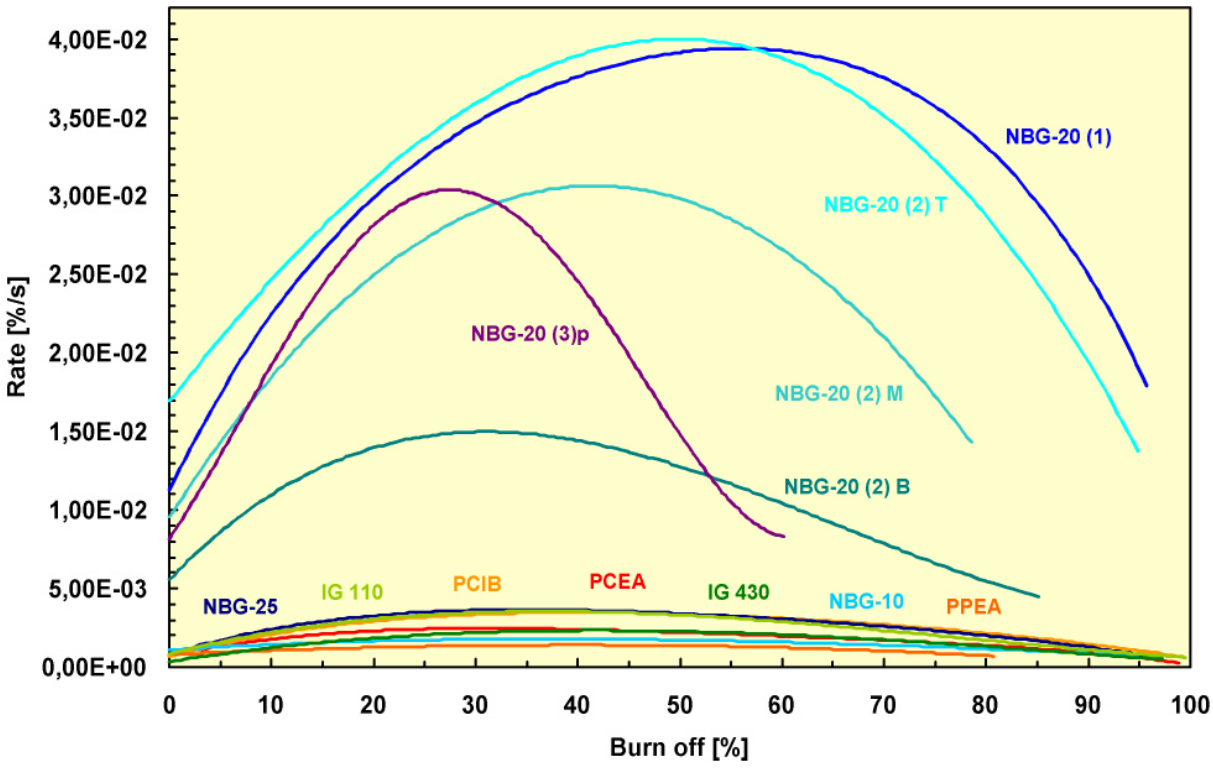

Fig. 8a: Rate versus burn off curves for oxidation in O_2 at 650 °C The samples are extracted from: **(1)** first graphite sample block [NBG -20 (1)]; **(2)** second block [NBG-20 (2)]: T = Top, M= Middle, B = Bottom; **(3)p** = third block / purified sample.

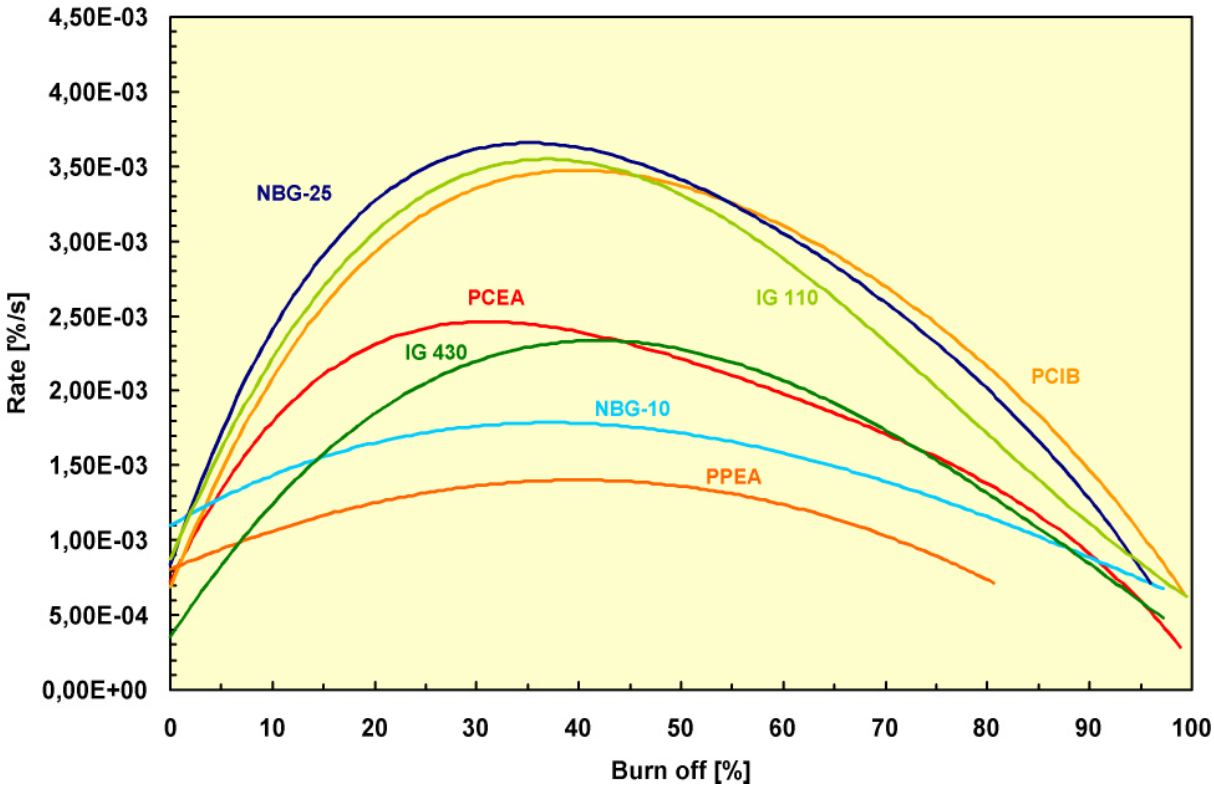

Fig. 8b: Section of rate versus burn off curves of Fig. 8a for oxidation in O_2 at 650 °C

3.2 Kinetics

For interpretation of the curves, a fitting parameter [A] was used *(A = [Δ ln RG / Δ 1/T]/R with R = gas constant [8,314J/mol/K], and RG=rate)*. This parameter A is more an absolute term to fit the data and to interpolate within of the measuring range: $RG=RG_0 * \exp(-A/T)$. It should not be interpreted to much in sense of a physical value like the activation energy ($E_A=A*R$], because two temperatures of 50 K difference, as available here, are not sufficient for a reliable determination of activation energies. For oxidation in air and in oxygen the parameters A valid for rate maxima and RG_0 are given in Tab. 2.

Table 2: Fitting parameter [A] for rate maximum and RG_0 [%/s].

Graphite	Oxidation in air		Oxidation in O_2	
Parameter	**A**	**RG_0 [%/s]**	**A**	**RG_0 [%/s]**
PCEA	20,89	3,38E+06	18,85	1,04E+06
PCIB	19,82	2,96E+06	30,85	1,15E+12
PPEA	20,88	6,58E+06	29,41	1,70E+11
NBG-10	22,73	2,42E+07	27,66	1,88E+10
NBG-20 (1)	12,62	4,52E+03	20,25	1,34E+08
NBG-25	26,40	2,36E+09	28,41	8,68E+10
IG 110	26,72	2,64E+09	29,06	1,09E+11
IG 430	28,57	3,08E+10	30,94	1,27E+12

Table 2 show that the parameter [A] is for most cases higher for oxidation in oxygen than for oxidation in air. This can be interpreted by the increase of the O_2 partial pressure, which is known to reduce the reaction order (= $dlnRG/dlnpO_2$), but at low temperatures more than at higher ones. Accordingly, the temperature dependence of rate in pure oxygen is more pronounced. The parameters A of the NBG-20 material show in both gases the lowest values, which means, that the NBG-20 has the lowest temperature dependence of rates of all materials examined and, as a first approximation, also the lowest activation energy of all materials in both gas compositions. This means also (however, bearing in mind the small reliability limit of extrapolations due to the small data basis), that the differences between NBG-20 and other graphites will become even more pronounced at lower temperatures, but will vanish with further temperature increase. For a more detailed evaluation of the kinetics more examinations are necessary, which was not possible as not part of this project. The same is necessary to give an estimation of the catalytic effect of ash contents. In general catalytic effects are higher at low temperatures and, accordingly, a higher ash content decreases the activation energy. However, besides catalysts, which decrease the activation energy (but with constant RG_0) some catalysts are known for graphite, which do not affect the activation energy by increase RG_0 (or probably the number of reactive sites). From the point of view of kinetics the unusual rate vs. burn-off behaviour of purified NBG-20 is difficult to interpret.

4 Discussion

It becomes obvious from the experimental results, that the investigated 8 HTR graphites show different behaviour in air and in oxygen. Except of the NBG-20 their reactivities are in the same range or even better in comparison to graphite materials, foreseen for the former German HTR-programme. Within the investigated graphites there are two materials (PPEA and NBG - 10) which show always the lowest rates. The others have higher rates, which are however still in an acceptable range. In contrast the NBG-20 material show in all investigated samples much higher oxidation rates up to a factor of 6 at 700 °C during oxidation in O_2 (see Fig. 1 – 8).

As a general rule one reason for a lower oxidation resistance of graphite materials can be a higher impurity. The ash content of the NBG-20 material is with 160 ppm only slightly higher than the ash content of the NBG-10 with 140 ppm, the latter being one of the materials with the lowest reaction rates.

Looking not only on the total ash content, but on the detailed ash analyses of NBG-20 and NBG-10, data are given in Tab. 3. The ash content of NBG-20 is for some elements significantly higher than that of NBG-10. These elements are predominantly Si, Fe, V, Ti, Al and Zn. But the catalytic effect of some of these elements is as a matter of fact important for oxidation in steam, but not so much in oxygen/air. Elements, strongly catalysing the air/carbon reaction are e.g. Cs, Pb, Mn, Ag, which are not present in the ash, or to comparable concentrations (Mn, Pb). Also the fact, that the purified sample of the NBG-20 material did not show better oxidation resistance than the polluted samples, is an argument against higher reaction rates caused only by impurities.

Tab. 3: Ash analyses of NBG-20 and NBG-10 [ppm]

Element	NBG-20	NBG-10	Element	NBG-20	NBG-10
B	1	0,4	**Cd**	-	< 0,1
Si	3	45	**Cr**	0,3	< 0,1
Fe	9	3	**Cu**	< 0,1	< 0,1
Ca	8	5	**Li**	-	< 0,1
V	8	0,2	**Mg**		0,5
Ni	1	0,2	**Mn**	< 0,1	< 0,1
Ti	2	0,4	**Mo**	< 0,1	0,1
W		0,2	**Na**	-	0,2
Co	< 0,1	< 0,1	**P**	2	0,6
Al	10	< 0,1	**Pb**	< 0,1	< 0,1
Ba	0,7	0,3	**Sr**	0,4	< 0,1
Be	< 0,1	-	**Zn**	5	< 0,1

Another reason for higher oxidation rates could be a different heat treatment temperature during fabrication. With increasing annealing temperature of a graphite the degree of graphitization increases, too (up to about 2800°C). If the graphite contains some ungraphitized components, the low temperature reaction rates increase due to a smaller activation energy of the ungraphitized carbon.

To control the degree of graphitization of the NBG-20 (and for comparison of the NBG-10), an x-ray interference test at the 002 base plane was accomplished. Here with a higher

graphitization degree, a shifting of the basis reflex to a higher diffraction angle and a decrease of its halve width happens.

The results of this test are given in Fig. 9. Also given in Fig. 9 are the x-ray interferences results of an petroleum coke and a natural graphite at different temperature treatments and graphitization degrees.

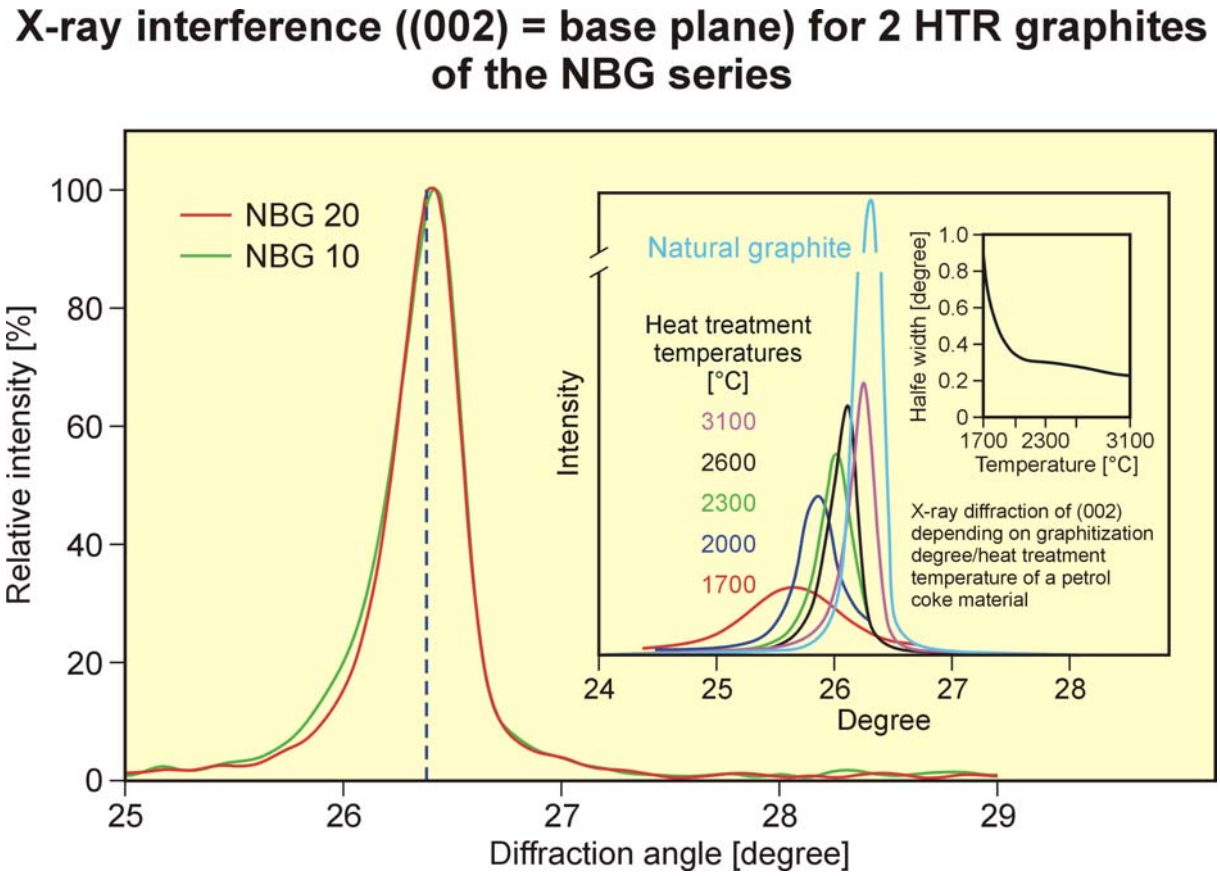

Fig. 9: X-ray interference of NBG-20 and NBG-10 in comparison with petrol coke and natural graphite.

It becomes obvious from this figure, that both graphites are completely graphitized and show an diffraction angle between 26 – 27 °, which point out a heat treatment temperature between 2600 and 3100 °C. So an insufficient graphitization can not be the reason for the high reaction rates of NBG-20.

There is a slightly higher open porosity in NBG-20 than in other graphites for virgin material. This however can only explain a slightly larger starting reactivity, but not the differences at intermediate and large burn-off values: The total porosity is the same for all NBG types (see densities in table 1) and the closed porosity is completely opened with increasing burn-off. Altogether, we are not yet able to explain the unusual large reactivity of NBG-20.

Comprising it has to be noted, that the reason of the insufficient oxidation resistance of the NBG-20 material can not be shown clearly by one obvious defect. But as a matter of facts the oxidation behaviour of this material as it is, is not yet suitable for application in HTR regions, were oxidation is a major concern. The other materials give a spectra of materials with feasible oxidation behaviour for application in HTRs.

Further observations in case of dust formation by collapsing samples, which was observed at the first test experiments, have not been carried out during this test series.

5 References

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