



# CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste Grant Agreement Number: FP7-211333



# **Deliverable D-2.4.3**

# Homogeneous Oxidation of Graphitic HTR Fuel Element Matrices

Authors: W. von Lensa, H.-K. Hinssen, B. Schloegl; Forschungszentrum Juelich

Date of issue of this report : 28/09/2009

Start date of project : 01/04/2008

Duration : 48 Months

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities				
Dissemination Level				
PU	Public			
RE Restricted to the partners of the CARBOWASTE project		X		
CO	Confidential, only for specific distribution list defined on this document			





# **Distribution list**

Person and organisation name	Comments
and/or group	
WP 2 partners	
Executive Board	





CARBOWASTE					
Work package: 2 Task: : 2.4	CARBOWASTE document no: CARBOWASTE-0909-D-2.4.3	Document type: D=Deliverable			
Issued by: Forschungszentrum Juelich, DE Document status: Internal no.: CW0908-WP2-Graphite Disintegration-d Review					

**Document title** 

# **Homogeneous Oxidation of Graphitic HTR Fuel Element Matrices**

#### **Executive summary**

This report summarizes the results of some previous experiments (see reference 21) at FZJ in which reactor graphites and matrix materials for HTR fuel elements were corroded in air at 673 K. Significant differences were found in the chemical reactivity of the various materials. The reactivity of the matrix graphites passes through a particularly pronounced maximum for burn-ups of less than 6 wt %.

The experiments were extended to include matrix spheres in a temperature range from 623 to 653 K. In individual cases, the catalytic effectiveness of metals precipitated from saline solutions was also incorporated. In this respect, caesium nitrate proved to be especially effective.

On the basis of the findings from the above-mentioned experiments, tests are described, which were performed with the aim of utilizing the observed losses in strength of matrix spheres during corrosion to disintegration in air at low temperatures for the reprocessing of fuel elements. It was attempted to disintegrate the elements with the least possible chemical burn-up in such a way that the coated particles were separated without being damaged and the remaining graphite dust could be processed into a weak- or medium-active product suitable for final disposal. This could lead to a considerable simplification of the approach for the head end processes to separate coated particles from the graphite matrix.

Results show that it is possible to disintegrate matrix spheres with a burn-up below 30 % in less than three days. In fact, it seems possible to achieve burn-ups of less than 20 % with optimized procedures. By using caesium nitrate as the catalyst the reaction temperatures can be limited to 670 K and to 870 K if the spheres are disintegrated without the addition of a catalyst.

A literature compilation is presented in the chapter 3.1.3 and in the 'References', at the end of the report.

	Revisions						
Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader	
00	dd/mm/yyyy	Issue	Name, Organisation	Name, Organisation <i>Signature</i>	Name, Organisation <i>Signature</i>	Name, Organisation <i>Signature</i>	
01	28/08/2009	First issue	von Lensa FZJ	K.H. Hinssen FZJ			
02	30/03/2010	2 <sup>nd</sup> Issue	von Lensa FZJ	B. Schloegl RWTH-Aachen			





## <u>CONTENTS</u>

E	XECU	JTIVE SUMMARY	3	
1	INT	TRODUCTION	5	
2	EX	XPERIMENTAL SET-UP AND METHOD	7	
	2.1	Corrosion experiments	7	
	2.2	Impregnation method		
3	EX	XPERIMENTAL RESULTS	10	
	3.1	Corrosion experiments without catalyst	10	
	3.1.	1.1 Specimen temperature 673° K	10	
	3.1.	1.2 Specimen temperature 623 to 793° K		
	3.1.	1.3 Comparison with results from external organisations		
	3.2	Influence of catalysts on corrosion in air		
	3.2.	2.1 Experiments on doped matrix spheres		
	3.2.	2.2 Data from the literature	21	
4	DIS	SINTEGRATION OF MATRIX SPHERES		
	4.1	Disintegration experiments		
5	CO	DNCLUSIONS		
6	References			



# **1** INTRODUCTION

Chemical reactions, which take place in only one phase, are called 'homogeneous'. In 'heterogeneous' reactions more phases are contributing to a chemical reaction. Heterogeneous reactions are much more influenced by transport phenomena than homogeneous ones. The main corrosion reactions for graphite are listed in Table 1.

Nr.	Reaction	$\Delta H_R (kJ/mol)$
(1a)	$2C + O_2 \rightarrow 2CO$	-221.04
(1b)	$C + O_2 \rightarrow CO_2$	-393.51
(2)	$C + CO_2 \leftrightarrow 2CO$	+172.47
(3)	$C + H_2O \leftrightarrow CO + H_2$	+130.29
(4)	$C + 2 H_2 \leftrightarrow CH_4$	-74.77
(5)	$2CO + O_2 \rightarrow 2CO_2$	-565.98
(6)	$CO + H_2O \leftrightarrow CO_2 + H_2$	-40.38

#### Tab. 1: Reactions during Oxidation of Carbon in Air and steam

Chemical reactions are generally much more dependent on temperatures as transport of media by diffusion. This means that chemical reactions are dominating at low temperatures whereas transport mechanisms dominate at higher temperatures. Therefore, three corrosion regimes are differentiated with respect to the temperatures as shown in Fig. 1.



Fig. 1: Reaction regimes of graphite oxidations (heterogene reactions)

At low temperatures, the slowest step is the chemical reaction itself. This temperature range is called 'Regime I or 'Chemical Regime'. The chemical reaction is so slow that there is



practically no concentration profile of the reacting gases. Therefore, the corrosion is nearly *homogeneous* in the whole solid graphite material as is expressed in the title of this report.

In the next temperature range, diffusion of gas within the pore structure and the chemical reactions are influencing each other. This creates a characteristic concentration and corrosion profile, which is typical for the 'Regime II' or 'Pore Diffusion Regime'.

At higher temperatures, all chemical reactions mainly occur at the surface of the material. Thus, reactive gases cannot penetrate into the solid material, in 'Regime III'.

The temperature ranges depend on the corrosive media, from the porosity of the graphite, flow speed and presence of catalysts.

Experiments on graphite corrosion due to oxygen with respect to the investigation of air ingress accidents for the HTR have mainly concentrated on a temperature range from approx. 870 to 1220 K. In this range the reaction rate is characterized by diffusion processes in the pore structure of the graphite. The higher temperature ranges, in which the graphite only experiences burn-up on the surface and thus where the analogy between heat and mass transfer is valid, are particularly interesting for accident analysis and for reprocessing head ends due to the relatively fast reactions.

In the lower temperature range, the reactions proceed so slowly that they can only have a perceptible influence on the accident sequence if the oxygen supply is maintained for a considerable time. In order to provide information on this temperature range, particularly on the time available before mitigating measures are introduced in the case of accidents lasting a considerable time with the addition of air, simple experimental set-ups were used to perform initial exploratory corrosion experiments on various reactor graphites between 623 and 853 K, the results of which will be presented in the following as they are also relevant for the (pre-) treatment of graphite in a reprocessing head end.

It will be shown that the strength of the graphite can be significantly reduced by homogeneous oxidation. This may allow to separate coated particles form the graphite matrix much easier in combination with other separation techniques.



# 2 EXPERIMENTAL SET-UP AND METHOD

#### 2.1 Corrosion experiments

Four "annealing boxes" and a convection furnace were available for the experiments. The annealing boxes were small W 10/10 type muffle furnaces from Heraeus with a useful volume of approx. 0.8 l, which could be employed in a temperature range of up to  $1270^{\circ}$  K.

The convection furnace (Heraeus, type RL 320) had a useful volume of approx. 11.5 litres. It was designed for a temperature range of up to  $970^{\circ}$  K.

In the annealing boxes, corrosion experiments were performed exclusively on matrix spheres or fuel spheres with natural uranium cores, preferably at  $623^{\circ}$  K. In the first experiments, the sphere temperature was not measured directly, but rather a thermocouple was placed in a graphite tube (borehole diameter 6 mm, wall thickness 4 mm, length 50 mm) positioned in the furnace directly adjacent to the sphere. In preliminary experiments at a working temperature of  $623^{\circ}$  K, measurements were made with this thermocouple to ensure that, on the one hand, the time-dependent fluctuations did not exceed  $\pm 2$  K, and, on the other hand, that the deviations from a thermocouple located in a borehole through a matrix sphere remained below  $\pm 3^{\circ}$  K. Nevertheless, in later experiments, especially in the case of those with impregnated spheres, a thermocouple with its measuring point was placed directly at the centre of the sphere through a borehole.

The convection furnace was operated exclusively at  $673^{\circ}$  K. Both matrix spheres and also tubular specimens of different varieties of graphite (of the dimensions described above) were corroded in this furnace. The spatial and time-dependent temperature fluctuations measured at  $673^{\circ}$  K remained below  $\pm 5^{\circ}$  K.

Each furnace was connected to a potentiometric recorder that was used to continuously record the temperature of the useful volume. At predefined time intervals, the specimens were removed from the furnace, cooled to room temperature, weighed and, as a rule, replaced in the furnace. In individual cases, it was also possible to continuously record the weight loss from the spheres by placing an annealing box directly on a balance (Sartorius, type 3802 MP 6, reproducibility: < 0.05 g). Fig. 2 shows a set-up of this type.





Fig. 2: Automated sphere corrosion experiment

The furnace doors were opened slightly in order to ensure sufficient gas exchange between the furnace and the environment. In preliminary experiments, a mass spectrometer was used to determine that the oxygen content in the furnace differed from that of the ambient air by no more than 1 %. The air remained unfiltered. Fluctuations in air pressure and moisture were not taken into consideration.

### 2.2 Impregnation method

In order to verify the catalytic efficiency of some characteristic metals, individual spheres were doped with CsNO<sub>3</sub>, SrCl<sub>2</sub>, AgNo<sub>3</sub> and Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O. This was done by the following method. A sphere was boiled in an aqueous saline solution in a reaction flask for 2 to 3 hours, in the course of which the liquid was degassed and at the same time part of the gas contained in the pore structure of the sphere was expelled. The vessel was then closed and cooled to room temperature. The pressure was thus reduced to approx. 25 mbar, which led to a further release of gas from the pore structure of the sphere. After a retention time of a few hours, the reaction flask was once again opened to the atmosphere while the sphere remained completely immersed in the solution so that the solution was forced into the pore structure. The sphere was removed after about 12 hours.





Using this method, the weight of the sphere increased by 5 % on average. The sphere was then dried at temperatures of up to  $393^{\circ}$  K.

The distribution of the salt in the graphite matrix was measured in individual experiments with spheres doped with  $CsNO_3$  and  $SrCl_2$ . To this end, the spheres were sawn apart after drying. Specimens of various radii from the cut surface were then turned on a lathe. The powder arising during cutting was mixed with distilled water in a ratio of 1 : 10. After a boiling and filtration step, the saline concentration in the solution was determined by an atomic absorption spectral photometer. The measurements from three experiments converted to fractions of salt / quantity of graphite are shown in Figures 3 and 4. The analyses show that the method described above can achieve a sufficiently uniform distribution of the catalyst in the graphite. Only in the top layer close to the surface does the salt concentration rise steeply. However, no measures to further smooth the concentration profile were taken in the experiments described.



Fig. 3: Concentration profile of the CsNO<sub>3</sub> precipitated from the aqueous solution





Fig. 4: Concentration profile of the SrCl<sub>2</sub> precipitated from the aqueous solution in A3-3 matrix spheres

# **3 EXPERIMENTAL RESULTS**

#### 3.1 Corrosion experiments without catalyst

### 3.1.1 Specimen temperature 673° K

The experiments at a specimen temperature of 673 K were performed in a convection furnace and were intended to provide information about differences in the corrosion behaviour of various materials. Use was made of 5 spheres each ( $\emptyset$  60) of the matrix materials A3-3 and A3-27 as well as 5 tubular specimens each ( $d_a = 14$ ,  $d_i = 6$ , 1 = 40-50 mm) of A3-3, A3-27, V483T, ATR-2E, ASR-1RS and ASR-1RG.

The A3-3 spheres were taken from a batch fabricated in December 1979 (P.70.386) and the A3-27 spheres from an experimental batch (P.2319).

The A-3-3 and A3-27 tubes were taken from a batch delivered in February 1980. They were turned from matrix spheres and then annealed once again at 2223 K to reduce any impurity gradients.

The remaining graphite specimens were mainly taken from cylindrical blocks – as a rule from various cross-sectional zones, as shown in Tab. 2.





Material	Block no.	Removal zone	
		(dimensions in mm)	
V483T	125 (batch VI)	"core": d = 90 ø	
		"edge": 90 < d < 180 ø	
ATR-2E	46,660 (batch V)	"core": d = 130 ø	
		"centre": 130 < d < 270 ø	
		"edge": 270 < d < 400 ø	
ASR-1RS	8/79	"core": 200 x 200	
		"edge": 370 x 370	
ASR-1RG	121/78	close to centre	
		(block ø 1200, h = 700)	

Tab. 2: Removal zones for graphite samples from large blocks



Fig.5: Time-dependent burn-up at 673 K



In Fig. 5, the burn-up of the various materials is plotted as a function of time for a period of 185 days. The curves are arithmetic means of the burn-ups of 5 specimens. However, individual spheres were removed before this point in time for follow-up examinations. This is indicated by the dotted curves.

The diagram shows that the burn-ups of the graphites V483T, ATR-2E and ASR-1RS are located close together in a relatively narrow band. Of the well-graphitized materials, only ASR-1RG displays clear deviations, which can probably be attributed to the high ash content and thus to catalytically effective substances. There also seems to be a correlation between ash content and chemical reactivity for the other graphites.

The burn-up curves of the matrix materials differ greatly from those of the "pure" graphites, although there are only slight differences between the spheres. In the case of the tubes, however, a higher corrosion resistance is apparent for A3-27 in comparison to A3-3. It may be assumed that the reactivity of the ungraphitized binder contributes to the high reactivity of the matrix materials, as also described for corrosion with steam in /1/.



Fig. 6: Time-dependent burn-up at 673° K



Fig. 6 once again shows the burn-ups of the graphites on a different scale. In the case of materials ATR-2E and ASR-1RG, there is, as expected, an increase in reactivity towards the centre of the graphite block from which the tubes were taken (cf. Tab. 2). Only in the case of V483T was the tendency reversed, although the differences were in any case slight.

As already indicated in Fig. 5, the corrosion rate depends on burn-up. This was already made clear in Fig. 7, where the reaction rate is plotted as a function of burn-up. After a steep rise in the reaction rate, this rate passes through a maximum for the matrix materials at approx. 3 to 5 % burn-up, and then after a similarly relatively steep drop reaches an almost constant value at approx. 10 % burn-up. It should be noted that the ungraphitized binder fraction in the matrix amounts to 10 %.

For the tubular specimens, the maximum reaction rate was found to be at lower burn-up values than for the spheres. It has not yet been determined whether, contrary to expectations, differences in geometry may have an effect here. No results are yet available from porosity profile measurements on the corroded spheres which could be used to determine this effect.

Even in the case of well-graphitized materials, it can be seen that the reaction rate passes through a maximum at burn-ups of up to approx. 6 %, but with a much flatter curve. The sole exception is ASR-1RG, which only appears to display a maximum value after approx. 18 % burn-up after a flat rise.



*Fig. 7: Time dependence of the reaction rate at* 673° *K* 



In Fig. 8, the reaction rates are plotted as a function of time. This thus presents a clear connection to Fig. 5.



Fig. 8: Time-dependent reaction rates at 673° K

### 3.1.2 Specimen temperature 623 to 793° K

Individual corrosion experiments at temperatures other than 673° K were carried out exclusively on matrix material, mainly on spheres. Results from experiments on two A3-3 spheres corroded at 623 and 793 K and a tubular A3-3 specimen corroded at 623° K are summarized in Fig.

9 in comparison to the burn-up curve at 673° K already shown in Fig. 5. Fig. 10 shows the associated burn-up-related reaction rates.





Fig. 9: Time-dependent burn-up of A3-3 matrix at different temperatures



*Fig. 10: Burn-up dependence of the reaction rate of A3-3 at 623 and 673 K* 

If the activation energy of the C/O<sub>2</sub> reaction is to be determined from the reaction rates at 623 and  $673^{\circ}$  K under the given partial pressure conditions then it is necessary to define a reference point due to





the strong burn-up dependence. If the maximum value of the reaction rates is taken as the reference then an activation energy of  $E_A = 110$  kJ/mol is obtained for the A3-3 sphere and for the tubes  $E_A = 130$ kJ/mol. Both values are strikingly low. For example, in earlier experiments with smaller oxygen partial pressures in the temperature range from 1073 to  $1173^{\circ}$  K (i.e. in the pore diffusion range with a theoretical activation energy of only half that valid in the volume corrosion range) an activation energy of 117 kJ/mol was found /2/.

A few estimates were made in order to verify whether diffusion processes may play a rate-determining role. If at a maximum corrosion rate of A3-3 (30 w/o/100 d) at 673° K, a diffusion coefficient of 10<sup>-4</sup>m<sup>2</sup>/s is taken for O<sub>2</sub> in N<sub>2</sub> and a  $\lambda$  value (D<sub>eff</sub>/D<sub>free</sub>) of 0.01, then according to Aris /3/ a pore utilization degree of 0.7 – 0.8 is obtained in matrix spheres for an order of reaction of 1, i.e. only a slight influence of diffusion. However, this calculation does not consider burn-up-related structural changes in the matrix. If the formula taken from Churchill /4/ is used to estimate the degree of 0.79 is obtained. With an order of reaction of 0 (assuming the same overall reaction rate as with an order of reaction of 1), a pore utilization degree of 0.88 is obtained so that with this assumption a perceptible influence of diffusion cannot be expected either.

The low values found for the activation energy should therefore be particularly regarded from the aspect that at  $623^{\circ}$  K only one measurement is available in each case. If one considers the scatter found at  $673^{\circ}$  K (see Fig.9), which probably increases towards lower corrosion temperatures, then considerably higher values for the activation energy may result. It will only be possible to provide reliable information after an appropriately large number of experiments have been performed.

### 3.1.3 Comparison with results from external organisations

In the temperature range from 500 to  $900^{\circ}$  K only relatively few measurements are available for corrosion rates in air and gas mixtures with a high oxygen content. There are a somewhat greater number of values available in the literature for small oxygen partial pressures.

In the following comparison of measuring results, only those literature values are used from which values corresponding to our experimental conditions could be calculated by interpolation.





#### a) Measurements at BNL (1957) /5/

The measurements on AGOT and AGHT reactor graphites (well-graphitized materials) cover a range from 520 to 720° K. They were performed in pure oxygen and also in air. In particular, the corrosion of irradiated specimens was investigated as well as the significance of  $\gamma$ -radiation-induced reactions.

At 623° K a corrosion rate of 0.15 w/o/100 d was found and at 673° K a rate of 3.09 w/o/100 d in air – a value that was also found in the range of reaction rates for well-graphitized materials measured by us. The measured activation energies were in the region of 205 kJ/mol. Apart from a slight rise in the corrosion rate with burn-up, no pronounced influence of burn-up on corrosion events appeared in these BNL experiments. It was found that both radiation damage due to neutron irradiation and also  $\gamma$ -radiation during corrosion increased the burn-up rate.

#### b) Measurements at BNL (1961) /6/

These measurements were also performed on AGOT graphite, namely at temperatures of  $673^{\circ}$  K and at temperatures above  $920^{\circ}$  K. The influence of oxygen partial pressure on the corrosion rate at O<sub>2</sub> partial pressures of 0.25 to 2 atm was investigated. An order of reaction of 1 was derived from the experiments. For the activation energies, values were given that corresponded to the values from 1957 specified above – taking into consideration a scatter of 25 %.

By converting the given surface corrosion rates to bulk corrosion, values of approx. 1 w/o/100 d are obtained for 673° K with corrosion in air, although the corrosion times were only 5 days. The deviation of the corrosion rate from the experiments discussed above can probably be attributed in part to the influence of the burn-up.

#### c) Measurements on French reactor graphites (1964) /7/

Corrosion experiments were performed in air on French reactor graphites. In particular, it was attempted to determine the order of reaction. A reaction rate of 170 w/o/100 d was found at  $773^{\circ}$  K, which is in the range of the values for structural graphite extrapolated from our experiments. The order of reaction was given as 0.7 to 0.9.

#### d) Measurements at AERE Harwell (1964) /8,9/

Corrosion experiments on moderator graphite (British Pile Grade A) were performed in air at temperatures between 708 and  $758^{\circ}$  K. Only CO<sub>2</sub> was found as the reaction product. An activation energy of 185 kJ/mol and an apparent order of reaction of 0.6 were derived from the measurements. If



the reaction rates measured at 708° K are extrapolated to  $673^{\circ}$  K then values in the region of 0.5 w/o/100 d are obtained. However, these comparatively low burn-up rates are only valid for small burn-up values (0.1 – 0.3 w/o).

Similar measurements in the temperature range from 848 to 928° K also yielded an order of reaction of approx. 0.6. At 848° K, reaction rates of 480 w/o/100 d were found in air.

In later work at AERE /19/, the reactivity was measured on a material whose starting material displayed pile grade A quality, but whose binder was apparently not graphitized and where there was no impregnation, that is to say, which displayed the same fabrication features as our matrix materials. For  $633^{\circ}$  K, a conversion rate in air of approx. 11 w/o/100 d was given, which is somewhat higher than our burn-up rate determined at  $623^{\circ}$  K for the matrix.

#### e) Investigations at BNL on irradiated graphites (1965) /10/

Corrosion experiments in air were performed on AGOT and AIA graphites in the temperature range from 623 to 773° K. "Low-temperature annealing" was performed between neutron irradiation and corrosion in order to anneal the radiation damage.

An activation energy of 210 kJ/mol was found. For AIA graphite, corrosion rates of approx. 0.1 - 1.5 w/o/100 d were obtained (little burn-up dependence), and for AGOT material values of 2 - 3 w/o/100 d. These data are comparable with our results on pure structural materials.

#### f) Work at General Atomic (1973) /11/

The corrosion rates of H-327 graphite (fuel element graphite from the Fort St. Vrain reactor) were investigated in air at 653 to 843° K, also under  $\gamma$ -irradiation. No influence of  $\gamma$ -radiation on the corrosion rate was found. The activation energy was given as 170 kJ/mol. A corrosion rate of 2 w/o/100 d was found for 673° K, although no information can be derived on burn-up dependence from the data available to date. The mean corrosion rate for the well-graphitized, very pure H-327 graphite was close to the values we determined for comparable German materials.

#### g) Work at HRB (1975 – 1980) /12,13,14,15/

At HRB, corrosion experiments were performed at low oxygen partial pressures ( $\geq 5$  torr) on A3 matrix materials between 833 and 953° K. The apparent orders of reaction were in the region of 0.6 – 0.7.



Since under these conditions pore transport processes are probably of considerable significance, it is not meaningful to perform an extrapolation to compare them with our measurements.

Corrosion experiments up to a burn-up of 0.7 w/o were performed on irradiated A3-3 fuel elements at  $673^{\circ}$  K in a mixture of 50 v/o air and 50 v/o helium. The corrosion rate was approx. 6 - 7 w/o/100 d (level of precorrosion 0.1 w/o), which is in adequate agreement with our corrosion rates for A3 matrix for low burn-up rates.

Corrosion experiments at a maximum oxygen partial pressure of 0.02 bar and temperatures between 697 and 897° K were performed on ATR-2E. An extrapolation to 0.2 bar oxygen partial pressure and 673° K yielded a corrosion rate of 1.7 w/o/100 d at a burn-up of up to 1.1 w/o, and at a burn-up of up to 21 w/o a rate of 5.7 w/o/100 d. The extrapolation was performed with the measured activation energy of 180 kJ/mol and the measured order of reaction of 0.6. The burn-up rates that we found at 673° K for a burn-up range of less than 3.5 w/o were between these two values, which can be regarded as good agreement in view of the uncertainties due to the extrapolation.

V483T graphite was also examined in a similar parameter range to that for ATR-2E. For  $673^{\circ}$  K, corrosion rates from 1.25 to 1.4 w/o/100 d were obtained for burn-ups of approx. 1 w/o (after an extrapolation from 0.023 to 0.2 bar oxygen partial pressure with an order of reaction of 0.6 as well as an extrapolation from 699° K to  $673^{\circ}$  K with an activation energy of 185 kJ/mol), which is also in good agreement with our data.

#### h) Work at NUKEM (1973) /1/

At NUKEM, corrosion experiments were performed on A3 matrix at temperatures above 720° K in an atmosphere containing oxygen. The burn-up / time curves obtained for our measurements indicating a reactivity maximum at burn-up values below 6 w/o were also measured here. In air, a mean corrosion rate of 25 w/o/100 d was found in the burn-up range of 0-5 w/o for 723° K at NUKEM and at 773° K a rate of approx. 100 w/o/100 d. An activation energy of 115 kJ/mol can be derived from this – a low value in comparison to the above-mentioned activation energies of the well-graphitized materials (see 3.2.1). A corrosion rate of approx. 5.5 w/o/100 d was obtained by extrapolation to 673° K in the above-mentioned burn-up range. In comparison to our results for 673° K, this value is lower by about a factor of 4. No explanation for this deviation can be given up to now.



#### 3.2 Influence of catalysts on corrosion in air

#### 3.2.1 Experiments on doped matrix spheres

In order to gather our own experience of the catalytic efficiency of some characteristic metals, A3-3 matrix spheres impregnated with CsNO<sub>3</sub>, AgNo<sub>3</sub> and Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O according to the method described in Section 2.2 were corroded in air at 623° K. The results of the investigations are shown in Fig. 10 in comparison to an undoped sphere. The catalyst concentrations are not directly related to accident considerations for HTRs. They were initially set at such a high level for experimental reasons.



Fig. 11: Catalyst efficiency at 623° K

The high efficiency of caesium nitrate is striking. This was first discovered when the sphere doped with caesium nitrate was to be removed from the furnace after just under a week for the weight to be measured and only graphite dust was found. The weight loss was 82 %. This led to the considerations on sphere disintegration described in Section 4.





## 3.2.2 Data from the literature

There are still extremely great uncertainties with respect to the mode of action and the effectiveness of individual catalysts, as shown by an overview of the literature by HRB /16/. It has been known for a long time that alkaline metals, especially caesium compounds, catalyse the gasification reactions of graphites. For high-purity graphites at 673° K, an increase in reactivity by a factor of 64,000 was observed due to 0.13 w/o caesium /17/. However, a corresponding increase in reactivity is not to be expected for A3 matrix due to the higher initial reactivity so that the increases of 200 to 600 found at 623° K certainly appear plausible.

The high increase factors for manganese (86,000) or silver (1340) given in /17/ were not even approximately found in our experiments. The increase in reactivity due to 0.06 to 0.08 w/o of the respective metal was in the range of a factor of 10.

There are apparently no experiments on reactor graphites which would permit a quantitative comparison with the catalytic efficiencies measured by us. Attention should be drawn to the DRAGON experiments, in which a reactivity increase of more than one order of magnitude was obtained at 773° K in air by 2000 ppm of silver in grade 9 graphite /18/.

# **4 DISINTEGRATION OF MATRIX SPHERES**

### 4.1 **Disintegration experiments**

As described, particularly in the case of the corrosion of spheres doped with caesium nitrate (at  $623^{\circ}$  K in air), it was observed that they lost strength relatively rapidly and ultimately disintegrated. This led to the idea of using this phenomenon for the disintegration of HTR fuel elements. The main idea was that it should be possible to decompose the fuel elements with as little chemical burn-up as possible, to separate the – if possible undamaged – coated particles and to process the remaining graphite dust into a weak- or medium-active product ready for final disposal. In the following, initial experiments on disintegration will be presented.

Fig. 12 gives an impression of the nature of the corrosion attack. The figure shows an A3-27 sphere, doped with approx. 0.11 wt % CsNO<sub>3</sub>, removed from the annealing box after 44 hours corrosion in air with a burn-up of 34 %. During the first 30 hours, the temperature was 623°K. Due to a damaged regulator, the temperature then rose to 697° K, which is why the results of the experiment could not be



evaluated. However, what the picture does show clearly is that the corrosion attack reaches into the material bulk, indicating that the mechanical bond completely disintegrates – probably due to preferential corrosion of the binder – without this becoming visible at the surface. The piece of the original surface of the sphere remaining after removal of the sphere from the furnace shows clear striations.



Fig. 12



The corrosion attack is more uniform the lower the reaction temperature is. The fragments of an undoped A3-27 matrix sphere in Fig. 13 show that the fracture surfaces also pass through the centre of the sphere. The sphere was corroded for 99 days in a convection furnace at 673° K and let drop onto a stone floor from a height of approx. 1 m while it was being removed for weighing. At this point in time it had a burn-up of 13.4 %.

Reaction times such as those mentioned above would, of course, be far too long for an industrial headend process. The process can be speeded up either by increasing the reaction temperature or, if lower temperatures are required, by using catalysts. In both cases, however, the corrosion attack becomes more homogeneous. It is increasingly restricted to regions close to the surface.

The other experiments therefore concentrated on the question of whether disintegration of the sphere without an increase in total burn-up could be accelerated significantly. To this end, experiments were performed in such as way that the respective sphere was removed from the furnace after a relatively short corrosion time and the loosened outer layer was scraped off with a glass rod. This was repeated in further corrosion steps until the sphere disintegrated.



Fig. 14 shows the disintegration of an undoped A3-3 sphere which was corroded at 833° K. At the first time of removal after 24 hours, the weight loss due to combustion amounted to 8.4 %, and it was possible to scrape 11 % off in the form of powder. The residual sphere was returned to the furnace. After a total corrosion period of 45 hours, the weight loss amounted to 20.4 %, whereas the quantity of powder removed had already reached 53 %. After 69 hours the remaining sphere had disintegrated. The total weight loss was 30.3 %. The quantities of powder scraped off are shown in Fig. 15.



Fig. 14







Fig. 15 shows the remains of an A3-3 sphere doped with 0.11 wt % caesium nitrate that was disintegrated in two steps at 623° K. It was removed with 27.7 % burn-up after 91 hours. 48.3 % of the original mass was scraped off in the form of powder. The residual sphere was further corroded. It was finally removed after a total time of 185 hours. The fragments had practically no strength and the total burn-up of the sphere was 32.2 %.

Another A3-3 sphere doped with 0.15 % caesium nitrate was removed after 20.5 hours at 723° K with a weight loss of 33 %. 24 % of the powder fell off or was scraped off. This experiment, which was not originally intended to determine the disintegration but rather to determine the burn-up / time diagram, was not continued. It merely serves to underline the observation that with increasing temperature the corrosion is concentrated on a thinner and thinner layer close to the surface. If the aim is to disintegrate the sphere with low burn-up then the loosened layers must be scraped or brushed off at short intervals or, best of all, continuously, and removed from the furnace area.

Fig. 16 and 17 show the results of disintegration experiments on one A3-3 and one A3-27 sphere each doped with CsNO<sub>3</sub>, corroded at 673° K and removed from the furnace five times. The burn-up at the end of the disintegration process was 29.2 and 24.2 w/o, respectively.



The disintegration process for one undoped A3-3 and one undoped A3-27 sphere corroded at 853° K is shown in Fig. 18 and 19. After being removed 5 times, the burn-up at the end of the experiment amounted to 20.4 and 22.4 %, respectively.





Fig. 18

Fig. 19

It was only possible to perform a disintegration experiment on fuel element spheres with coated particles on a sphere containing TRISO particles (natural  $UO_2$  kernel). The sphere was taken from an experimental production batch and did not correspond to the usual specifications.

The sphere was corroded at 833° K (without being doped with catalyst). It was removed a total of 3 times in order to separate the powder or the particles (Fig. 20). After 54 hours the sphere had disintegrated completely and the burn-up was 18.6%. As far as could be seen with the naked eye, the particles did not display any damage. Part of the overcoating was still visible, but when the particle was touched it fell off.



![](_page_24_Figure_9.jpeg)

![](_page_25_Picture_1.jpeg)

Material	Temp /K/	Fraction	Corrosion	No. of times	Burn-up /w/o/
		CsNO <sub>3</sub> /w/o/	time /h/	removed	
A3-3	623	0.11	185	2	32.2
A3-3	673	0.15	63	5	29.2
A3-27	673	0.11	62	5	24.2
A3-3	833		69	3	30.3
A3-3 (with	833		54	2	18.6
TRISO)					
A3-3	853		61	5	20.4
A3-27	853		61	5	22.4

The essential data of the sphere disintegration experiments are compiled in Tab. 3.

Tab. 3: Disintegration experiments on spheres

In conclusion, attention should be drawn to the fact that well-graphitized materials can also apparently be disintegrated according to the method described. A cube of reactor graphite with an edge length of 60 mm originating from a former critical facility at Kernforschungsanlage Jülich (specifications unknown) was doped with 1.2 wt % caesium nitrate and corroded at 673° K. After 23 hours, the burn-up amounted to 24.1 % and it was possible to scrape 28.5 % off in the form of powder. Fig. 21 shows the residual cube (edge length 45 mm) and the powder.

![](_page_25_Figure_6.jpeg)

Fig. 21

![](_page_26_Picture_1.jpeg)

# **5 CONCLUSIONS**

The following conclusions can be drawn from the experiments described:

- 1. It is possible with only partial combustion of the matrix at low temperatures to loosen the graphite structure in such a way that the residual, unburnt graphite can be separated from the coated particles in powder form. Process-related damage to the TRISO particles can be practically ruled out. Particles coated solely with PyC will probably not be corroded due to their high chemical inertness in comparison to the matrix /20/. This will thus prevent fission products from entering the matrix material. The graphite powder itself remains weak- or medium-active. The off-gas flow also retains its low activity and is considerably reduced in comparison to the previous combustion head end.
- 2. If particularly strongly corroded layers in the vicinity of the geometric surface of the spheres are continuously removed from the reaction space into a zone with temperatures below about 470° K then it is expected that the chemical burn-up required for complete disintegration of the fuel elements can be restricted to values of less than 20 %
- 3. Optimum temperatures for the disintegration of undoped spheres in air are probably between 820 and 870° K. The required total reaction time thus remains less than 3 days.
- 4. If lower process temperatures are desired then the same effect can also be achieved at reaction temperatures between 620 and 679° K if the spheres are doped with a catalyst. If caesium nitrate is used then 0.1 to 0.2 w/o is sufficient.
- 5. Homogeneous pre-corrosion may be an adequate step to increase the efficiency of other segregation methods for the head end of HTR spent fuel reprocessing plants.

![](_page_27_Picture_1.jpeg)

![](_page_27_Picture_2.jpeg)

# 6 References

/ 1/ H.J. Becker, F.J. Herrmann : Untersuchungen der Oxydation von A3-Graphit und der Eindringtiefe des oxydativen Angriffs; NUKEM-147, 1973

/ 2/ R. Moormann, J. Anhalt, P. Ashworth, H.-K. Hinssen, W. Katscher : Investigation of the kinetics of the interaction between oxygen and reactor graphitic materials; Proc . 5th London Int. Carbon and graphite Conf. (1978) 108-115

/ 3/ R. Aris : On shape factors for irregular particles 1.Chem . Eng . Sci . 6 (1957) 262

/ 4/ S. W. Churchill : A generalized expression for the effectiveness factor of porous catalyst pellets; AICh E J . 23 (1977) 208

/ 5 / W.C. Kosiba, G. J. Dienes : The effect of radiation on the rate of oxidation of graphite; US/UK Graphite Conf. {1957}, London, USAEC-Rep. TID 7565 Pt . 1 (1959)

/ 6/ D.G. Schweitzer, R .M . Singer : Oxidation and heat transfer studies in graphite channels III. The chemical reactivity of BNL graphite and its effect on the length of channel cooled by air; Nucl. Sci. Eng. 12 (1962) 51

/ 7/ F.M. Lang, P. Magnier: Ordre des reactions air-graphite (500°C) et CO<sub>2</sub> -graphite (620-670°C) entre la Pression atmospherique et 18 bars. C.R. Acad. Sc. Paris 258 (1964) 889

/ 8/ P. Hawtin, J.A. Gibson, R. Murdoch, J. B. Lewis: The effect of diffusion and bulk gas flow on the thermal oxidation of nuclear graphite I; Temperatures below 500°C; Carbon 2 (1964) 299

/ 9/ J.B Lewis, P. Connor, R. Murdoch : The order of reaction for the oxidation of nuclear graphite in dry oxygen-nitrogen mixtures. Carbon 2 (1964) 311

/10/ D. G. Schweitzer, R. M. Singer: Oxidation rates of alternately irradiated and annealed graphite. J. Nucl. Mat. 16 (1965) 220

/11/ D. Jensen, M. Tagemi, C. Velasquez: Report GA-A 12493 (GA-LTR-7) (1974)

/12/ H. Jauer, P. Kubaschewski, H. Werthmann: The depressurisation accident in steam cycle HTR's . Graphite corrosion in core and its consequences for reactor safety. CSNI spec . meeting on high temperature gas-cooled reactor safety, Petten (1975)

/13/ P. Kubaschewski: Graphitkorrosion bei Lufteinbruch; HRB-Bericht DA 0086 (HHT) (1979)

/14/ Heinrich/Weimann : Messungen zur Luftkorrosion an ATR-2E Graphit; HRB-Bericht BE 0266 (HBK) (1980)

/15/ Heinrich/Weimann : Messungen zur Luftkorrosion von V483T-Graphit; HRB-Bericht BE 0319 (HBK) (1980)

/16/ Heinrich : Katalyse der Graphit-Korrosion, Literaturübersicht;HRB--Arbeitsbericht E II-75/61 (NRW) (1975)

![](_page_28_Picture_1.jpeg)

/17/ H. Amariglio, X. Duval: Etude de la combustion catalytique du graphite; Carbon 4 (1966) 323

/18/ M.L. Pointud, W. Karcher, N. Pollit, J. Lothe : Catalytic influence of different metals on corrosion rate of graphite; DRAGON Proj. Rep. 332 (1965)

/19/ P. Hawtin, J.N. Gibson: The effect of diffusion and bulk gas flow on the thermal oxidation of porous carbons Ungraphitised carbons; Carbon 4 (1966) 501

/20/ H. Pirk, U. Tillessen: Kalte Pilotanlage für die Graphitverbrennung als head end zur Wiederaufarbeitung von HTR-Elementen; Reaktortagung Bonn, 1971

/21/ W. Katscher, R. Moormann, H.-K. Hinssen, B. Stauch, Kernforschungsanlage Jülich GmbH, Institute for Nuclear Safety Research: Experiments on Graphite Corrosion in Air at Temperatures below 873K; Proposal for Modifying the Combustion Head End for HTR Fuel Elements; Internal Report KFA-ISF-IB-2/82; February 1982

/22/ Verfahren zur Abtrennung des Strukturgraphites vom Kernbrennstoff bei
Kernreaktorbrennelementen (Process for separation of structural graphite from fuel particles);
Patent DE 31 49 795 C2, submitted 16.12.1981, granted 15.05.1986; H.-K. Hinssen et al.,
Kernforschungsanlage Juelich