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SUMMARY REPORT – WORK PERFORMED ON GRAPHITE WITHIN HTR-M PROJECT

by

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Work performed on graphite within the HTR-M project

by

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Summary

Graphite has been used as a neutron moderator in a variety of different reactors. These include the Magnox Reactors, Advanced Gas-cooled Reactors (AGRs), High Temperature Reactors (HTRs), RMBKs, Research Reactors and Materials Testing Reactors (MTRs). The amount of nuclear grade graphite currently manufactured worldwide is relatively small. However, there has recently been a renewal of interest in HTRs in the world. The European Commission is supporting a number of projects for the development of HTR technology, with a view to creating the technological basis for an industrial emergence of HTRs in Europe by 2010.

The properties of graphite in a reactor environment have been extensively studied since the early 1940s and a good understanding of the significant and complex property changes which take place in the material has been gained. Most of the available data have been obtained by irradiating small graphite samples in MTRs. Unfortunately, almost all the graphites previously irradiated are no longer available. In addition, most of the irradiation temperatures investigated will have been <550^{o}C, whereas for HTRs the graphite temperatures will be >550^{o}C. The behaviour of currently available graphites will therefore have to be determined by experiments in a MTR over the appropriate irradiation dose and temperature range.

In the past, only a small number of irradiation programmes were aimed at determining the irradiation behaviour of graphites at high temperatures, i.e. >600^{o}C. Two of the most significant in the past were for the European Dragon HTR programme, and the German HTR programme. Unfortunately most of the data obtained by other countries are confidential and cannot therefore be published in open literature. However, the data from the German HTR programme are available for publication and those concerning the graphite grade ATR-2E (manufactured by SGL Carbon Company) have been made available for the project.

An assessment of currently available graphites have been carried out following discussions with graphite manufacturers and those identified for the European HTR project have been nominated for the graphite irradiation experiments to be performed within the HTR-M1 Project.

Oxidation work on a number of graphites and CFCs have been performed to look at the performance of such materials under accident typical temperatures (approximately 1000 ^{o}C) in steam and in air. The results have been assessed in light of present understanding of the oxidation processes of such carbon based materials. The results serve as input data for advanced oxidation models for predicting burn-off rates for the materials and have been used to assess the relative merits of the different materials with regard to the penetration of the oxidation process into the porous carbon.

Introduction

This document contributes to the 5th Framework Project HTR-M, Work Package 3 on graphite and summarises the results of a technical work performed on graphite within the HTR-M Project over the first two years. The work includes the following areas of work:

- review past and current grahites and available properties and assemble within a database for application to HTRs;
- perform oxidation tests on graphites and advanced carbon based composites for air ingress accident conditions.

The Project objectives with respect to the investigation of graphite and results from the individual tasks are summarised together with overall conclusions and a summary of remaining items to be completed during the rest of the Project.

Objectives & description of work done

The need for reliable graphite data is seen as a crucial issue for existing and new HTR projects and is an important consideration for future decommissioning activities. Also, oxidation resistance of graphites at high temperature requires special attention due to its relevance for safety analyses of air and water ingress accidents, licensing procedure and normal operation.

The programme of work performed on graphite materials over this first two years of the project consists of the following.

- State of the art review of graphite materials and behaviour.
- Database of properties of graphite suitable for use by designer.
- Assess new potential graphites and needs of HTR.
- Determination of chemically kinetic data for advanced oxidation models.
- Determination of oxidation resistance of advanced C-based materials.

The work on the review and collection of graphite properties is seen as a first step in the assessment of suitable graphites for future HTRs. Most of the graphites used in previous core designs are no longer manufactured commercially and the coke used as the raw material has either run out and the manufacturer has lost his experience, or production techniques no longer exist. Review of past data and expertise is therefore seen as an important prerequisite to ensuring retention of knowledge and expertise and with some limited investigations to establish a graphite database, providing a platform of information on which to base future graphite selection investigations and assessments. This work in HTR-M is also a preliminary stage to the irradiation test work of HTR-M1 aimed at measuring irradiated graphite properties of currently available graphites and further possible future developments of new graphites (identified in the HTR-TN roadmap) to be considered for a future framework programme.

An important part of the investigations on graphite involves an assessment of the oxidation resistance in respect of accident conditions. The Work Package therefore includes test work to investigate the influence of oxidation arising from severe air ingress with core burning and an investigation of protective coatings and innovative C- based materials. Overall this Work Package is expected to provide a platform of material data for future application and selection of graphites for the HTR.

State of the Art review

Graphite has been used as a neutron moderator in a number of different reactors including the Advanced Gas-cooled Reactors (AGRs), Magnox Reactors, High Temperature Reactors (HTRs), RBMKs, Research Reactors and Materials Testing Reactors (MTRs). However the amount of nuclear grade graphite currently manufactured worldwide is relatively small, and mainly consists of graphite for AGR fuel sleeves and prototype HTRs (one in Japan and one in China).

One of the main functions of the graphite is to slow down fast neutrons, however when irradiated by fast neutrons graphite suffers crystalline damage, which results in a change in all physical and mechanical properties of the graphite. The most important property changes in this respect are strength, dimensional change (Fig. 1) and crystal coefficient of thermal expansion (CTE) (Ref. 1). Changes to thermal conductivity are also large and dependent on the irradiation temperature. The other important consequence of the crystal damage is the build up of strain energy in the graphite components (referred to as Wigner energy or stored energy). However this is not a concern in graphite irradiated at high temperatures, as in the HTRs, but more relevant to graphite irradiated at low temperatures (i.e. Windscale Piles and some small research reactors).

The properties of graphite in a reactor environment have been extensively studied since the early 1940s and a good understanding of the significant and complex property changes that take place in the material has been gained. Most of the available data have been obtained by irradiating small graphite samples in MTRs. Unfortunately, almost all the graphites previously irradiated are no longer available. In addition, most of the irradiation temperatures investigated will have been <550^{o}C, whereas for HTRs the graphite temperatures will be >550^{o}C. The behaviour of currently available graphites will therefore have to be determined by experiments in a MTR over the appropriate irradiation dose and temperature range.

Most of the graphites used in previous core designs are no longer manufactured commercially and the coke used as the raw material has either run out and the manufacturer has lost his experience, or production techniques no longer exist. The main questions are on the availability of the coke and manufacturing procedure also there are now only a few manufacturers left in the world. The decline in the ability to manufacture nuclear grade graphite in large quantities in the UK is an example of this. Two large plants, one owned by Anglo Great Lakes (AGL now SGL) and the other by British Acheson Electrodes Ltd (BAEL, later known as Union Carbide and presently called UCAR) manufactured all the Gilsocarbon graphite used in the UKs AGRs. Neither plant now exists. Todays HTGR projects - HTTR (Japan) and HTR-10 (China) - use a Japanese graphite (IG-110). This graphite, with its high strength, should be taken into account for exchangeable core components where low fast neutron fluences and hence low total doses apply.

It was found that only a small number of irradiation programmes carried out in the past were aimed at determining graphite behaviour at the high operating temperatures associated with HTRs, i.e.>600^{o}C. Two of the most significant were for the European Dragon Project and the German HTR programme. Unfortunately most of the data obtained by other countries are confidential and so far not published in open literature. However data from the German HTR programme are available for publication and have been made available for the project.

Database of properties

The graphite core is a key component that affects safety and operability of the reactor. As well as acting as a neutron moderator and shield, it is a structure that generally provides channels for the passage of fuel and control devices, and coolant flow. The problem is that when irradiated by fast neutrons, graphite suffers damage to the crystallite structure. The resulting damage causes a change in all the physical and mechanical properties of the graphite e.g. strength, coefficient of thermal expansion (CTE), and thermal conductivity.

Ideally, the graphite chosen for HTR designs should be reasonably isotropic, exhibit small dimensional change behaviour, and have a low CTE, a high thermal conductivity, a high irradiation creep constant, a low Young's modulus and a high strength. The problem is that many of these properties are not compatible in practice for normal commercial graphites e.g. graphites with high strength also have a high Young's Modulus. Other factors affecting the choice of graphite would be impurity levels, cost and machinability.

Most of the available irradiated materials data are obtained from various materials test reactors and often it is not possible to complete an irradiated materials property database for a particular graphite in advance of design and construction phases of a reactor. In such cases design databases can be used to arrive at the required information, developed from previously irradiated graphites of similar microstuctures, and an understanding of irradiation damage in the polycrystalline graphites. R & D activities have been undertaken in a number of countries to investigate graphite properties. The IAEA International Irradiated Graphite Database Technical Steering provides a valuable forum for the exchange of information and opinion on graphites and has recently held seminars to review the current situation.

The work on review and collection of graphite properties (Ref.1) has considered the information within the IAEA database, internal information and published information at seminars and conferences. Two of the most significant experimental programmes in the past were for the European Dragon HTR programme, and the German HTR programme. Unfortunately most of the data obtained by other countries are confidential and so far are not published in open literature. However, data from the German HTR programme have been made available for publication and for the project. These data are being collated onto spreadsheets (see Table 1) in a set format (Ref. 2) for use within the project and as for the steels will be considered for insertion into the JRC alloys-DB for housing the information on the web. It is proposed that the data is to be presented in the form of recommended 'design curves' for each required material property.

Selection of new graphites

Generally, the most important material property change from the point of view of core lifetime integrity is dimensional change. Graphite initially shrinks but then undergoes shrinkage reversal, i.e. growth. This is referred to as 'turnaround'. The exact form of the dimensional change curve varies with irradiation temperatures. Normally, the higher the temperature the lower the peak shrinkage and the lower the dose at which turnaround occurs. Different graphites can have significantly different dimensional change curves at the same temperatures.

The validation of the through life performance of the graphite core structure is critically dependent on the knowledge of graphite properties and the way they vary under fast neutron irradiation. It is essential therefore that its behaviour is fully understood and investigated up to at least the peak design dose and over the appropriate temperature ranges

The final choice of graphite for the core should therefore be based on a number of factors, although the most important will be the effects of fast neutron irradiation on it's properties up to the peak doses envisaged. Given the best graphite available, it is the task of the core designer to produce a design that will operate safely over the design life of the reactor. The most important considerations are component integrity and changes in core geometry, both of which are affected by the dimensional change. For example, graphite shrinkage could lead to disengagement of individual components and between the core and interfacing structures and to a loss of control of the core geometry; graphite growth could lead to the take-up of design clearances and large forces between structures; and differential shrinkage/growth in a component could lead to high stresses and failure by cracking.

Assessment of available graphites have been made (Ref. 3) following meetings and discussions with graphite manufactures and five of the currently available graphites have been selected for the irradiation test programme to be performed within the HTR-M1 Project. These have been made available by UCAR (Graftech), SGL and Toyo Tanso who have offered extruded and iso-moulded graphites and for a range of grain sizes (1mm down to 10 μm). Under 5th Framework Programme funding the graphites will be initially irradiated in a high flux MTR to low/medium fluence. Hopefully this will be continued to the full life peak fluence with funding from the 6th Framework Programme.

Corrosion experiments

The graphite oxidation work involves two principal tasks relevant to safety analysis and licensing of HTRs for normal operation.

- The improvement of experimental database for advanced graphite oxidation models.
- Experimental investigation of innovative C-based materials with respect to their application on HTRs.

The experimental work contained in Work Package 3 uses the thermo-gravimetric facility THERA and the in the induction furnace facility INDEX (Figure 2) housed at FZJ.

Graphite burning under severe air ingress accidents, is assessed by computer models, based (up to now) on isothermally measured kinetic equations that consider in-pore diffusion and chemical reaction mechanisms. The data requirements for such models are burn off dependent chemical (regime 1) reactivities and in-pore diffusion coefficients. THERA was used for the regime 1 (see figure 2) and INDEX for regime II where higher flow rates are needed. Long term experiments at low temperature in air were done in an annealing furnace.

Although material development for HTRs almost ceased in Germany in 1985 development of C-based materials for Fusion Reactors continued. These included innovative concepts such as Carbon Fibre composites, and mixed materials (Si, Ti content) which show a high heat conduction and high strength. A second series of experiments were performed using the THERA and INDEX facilities to look at the performance of such materials under accident typical temperatures (approximately 1273 K) in steam and in air. Some results are presented in figure 3 for the materials investigated (see table 2). Oxidised gas flowed through the inner bore hole of the tube with flow rates sufficiently high to suppress the influence of boundary layer mass transfer on kinetics. Oxidation effects were measured by mass spectrometric analysis of the product gases and by weight loss of the sample. Experiments were also performed to determine properties of CFC materials irradiated and non-irradiated (up to 1dpa). These include measurements of strength, dimensional change, thermal diffusivity and heat capacity.

Kinetic data for Oxidation models

Measurements were made on the kinetics of a German A3 fuel matrix graphite (type A3-27) and for a typical structural graphite (V483T fine grain graphite) for temperatures between 400 and 800^{o}C in air and between 900 and 1000^{o}C in steam. The partial pressures were between ambient pressure (annealing furnace), 1 bar in air and 1.05/1.1 bar in steam.

From the results of the work (Ref. 4) the following conclusions were drawn.

<u>Experiments in air:</u>

- There was a strong dependence on temperature as expected. For the lower temperatures a long run time was needed (800-1300h) to reach burn-off values of 50%. Note that the 50% burn-off level was not reached with VT 483T within the experimental lifespan.

- In regime 1 the nuclear graphites showed slow rate increases with burn-off (up to 40% burn-off) at low temperature followed by a nearly linear decrease. This behaviour at can be explained by the kinetics of carbon oxidation.

- For A3-27 the fuel matrix graphite experienced two peaks in regime 1, which could be explained by selected binder-filler oxidation. The first peak (around 5%) was thought to be due to the binder oxidation and the second (35%) due to the filler oxidation. At higher temperatures the second peak becomes more pronounced and the first peak vanishes.

<u>Experiments in steam:</u>

- There was a volume loss and increased porosity after steam oxidation in regime 1 (900 & 980^{o}C). The overall decrease in sample size was however low as expected.

- The samples show roughly the same oxidation vs. burn-off behaviour in steam at both temperatures.

- With increasing burn-off the reaction rates in steam decrease.

- The carbon oxidation mechanisms of different materials are in detail different in air and in steam.

- The exact shape of rate vs. burn-off curves is different in both gases.

Oxidation resistance of Advanced Carbon based materials

Measurements were made on five different CFC materials (AO5, N31/NB31, NS31, INOX A14, NOVOLTEX) under isothermal conditions for temperatures between 500 and 750^{o}C in air and between 900 and 1000^{o}C in steam. The partial pressures were between ambient pressure (annealing furnace), 1 bar in air and 1.05/1.1 bar in steam.

From the results of the work (Ref. 5) the following conclusions were drawn.

Experiments in air:

- As expected there was a strong dependence of reaction rate. Again long run times were needed (800-1300h) to reach burn-off values above 50% for some materials.

- As with graphite, in regime 1, a slow rate increases with burn-off (up to 30% burn-off) at low temperature was typically observed followed by a nearly linear decrease. This again can be explained by the kinetics of carbon oxidation

- For the Si doped NS31 the rate change maxima occurred at 15% burn-off in regime 1 with the weight change possibly due to the generation of solid SiO_2 and C-burn off.

Experiments in steam

- Again, as with graphite, there was a volume loss and increased porosity after steam oxidation in regime 1 (900 & 980^{o}C).and the overall decrease in sample size was again low as expected.

- For 3-D CFCs oxidation along the inside of single fibres does not cause a breakdown of the structure and a slight strength loss is observed after regime 1. For 2-D CFCs the carbon matrix is preferentially oxidised and the fibres are relatively unaffected. This results in a high strength loss after oxidation.

- A rate maximum for the CFCs, which was found in air, is not seen in steam.

- The steam rates at 900^{o}C correspond to those in air at 600 – 650^{o}C.

- The activation energies in steam are higher than those in air. Despite its Si-content, the oxidation resistance of NS31 is not remarkably better than that of other examined materials (but a factor of 2 better than the CFC without Si).

Properties of CFC materials

PARIDE experiments deal with the evaluation of properties of CFC materials after irradiation (0,2 & 1.0 dpa) at 200°C in the HFR at Petten. PIE includes 4-point bend tests, measurement of thermal diffusivity and dimensional change. Mean values of SEPcarb NS31 have been derived to-date and some thermal diffusivity results are shown in figure 4. The results will be compiled and introduced into the database when completed.

Conclusions

Graphite has been used as a neutron moderator in a variety of different reactors, and there has recently been a renewal of interest in its use for HTRs in the world. In particular the European Commission is supporting a number of projects for the development of HTR technology, with a view to creating the technological basis for an industrial emergence of HTRs in Europe by 2010.

Most of the available data on the irradiation behaviour of graphite have been obtained by irradiating small samples in MTRs. Unfortunately, almost all the graphites previously irradiated are no longer available. Before embarking on the planned irradiation programme for the European HTR project it was first of all necessary to carry out a review of the situation regarding graphite data.

It was found that only a small number of irradiation programmes carried out in the past were aimed at determining the irradiation behaviour of graphites at the high operating temperatures associated with a HTR, i.e. >600°C. Two of the most significant in the past were for the European Dragon HTR programme, and the German HTR programme. Unfortunately most of the data obtained by other countries are confidential and so far are not published in open literature. However, data from the German HTR programme are available for publication and some have been included in this report.

The need for reliable material data and properties is a key issue in the development of HTR technology and is especially important for those areas where safety considerations are upper-most. The work done within the HTR-M project on graphite behaviour aims to provide a platform on which to develop the future HTR technological basis within Europe. The work done provides a first step towards building an understanding of the behaviour and manufacturing requirements for some of the new graphite materials that will be needed for such developments.

An assessment of currently available graphites have been carried out following discussions with graphite manufacturers and those identified for the European HTR project have been nominated for the graphite irradiation experiments to be performed within the HTR-M1 Project.

Oxidation work on a number of graphites and CFCs have been performed to look at the performance of such materials under accident typical temperatures (about 1000 °C) in steam and in air. The results have been assessed in light of present understanding of the oxidation processes of such carbon-based materials. The results serve as input data for advanced oxidation models for predicting burn-off rates for the materials and have been used to assess the relative merits of the different materials with regard to the penetration of the oxidation process into the porous carbon.

Further tasks to be completed

Assemble graphite data within database formats. This will largely consist of data obtained from the graphites used in the irradiation experiment of HTR-M1

Transfer results from oxidation experiments into a suitable form for future application and assessment of air ingress transient.

Data from corrosion and PARIDE experiments to be included within the database for future HTR application of graphites and carbon based composites.

References

Ref	Title
1	M. Davies & G. Haag State of Art review of graphite materials behaviour Report No. HTR-M 02/6-D-3-1-37
2	M. Davies Report on database of properties suitable for use by designer Report No. HTR-M 02/6-D-3-1-38
3	M. Davies Assess new potential graphites and needs of HTR HTR-M 02/11-D-3-2-53
4	K. Kuhn, H-K Hinssen, R. Moormann Report on chemical kinetic data for advanced oxidation models HTR-M 02/12-D-3-3-56
5	K. Kuhn, H-K Hinssen, R. Moormann Report on oxidation resistance of advanced C-based materials HTR-M 02/12-D- 3-3-55

Table 1 Recording of irradiated sample dimensions/properties

Irradiation temperature (oC)	Dose EDND (x10E22)	Irradiated properties							
		Length L (cm)	Diameter D (cm)	Volume V (cm3)	Mass M (g)	Density ? (g/cm3)	Young's modulus E (GN/m3)	CTE a (x10-6/oC)	Thermal conductivity K (W/m/oC)

Table 2 Materials Investigated in steam in corrosion tests

Sample	Description	Density [kg/m^3]
A3-3	HTR fuel element matrix graphite consists to 90 % of a filler graphite and 10 % of a coked resin binder	1735
NB31	3D-CFC	1920
NS31	3D-CFC infiltrated with 8 – 10 % liquid silicon	2120
AO5	2D-CFC	1870
V483T5	fine grain nuclear graphite	1810
RG	well graphitised standard HTR graphite with a low ash content	~1750

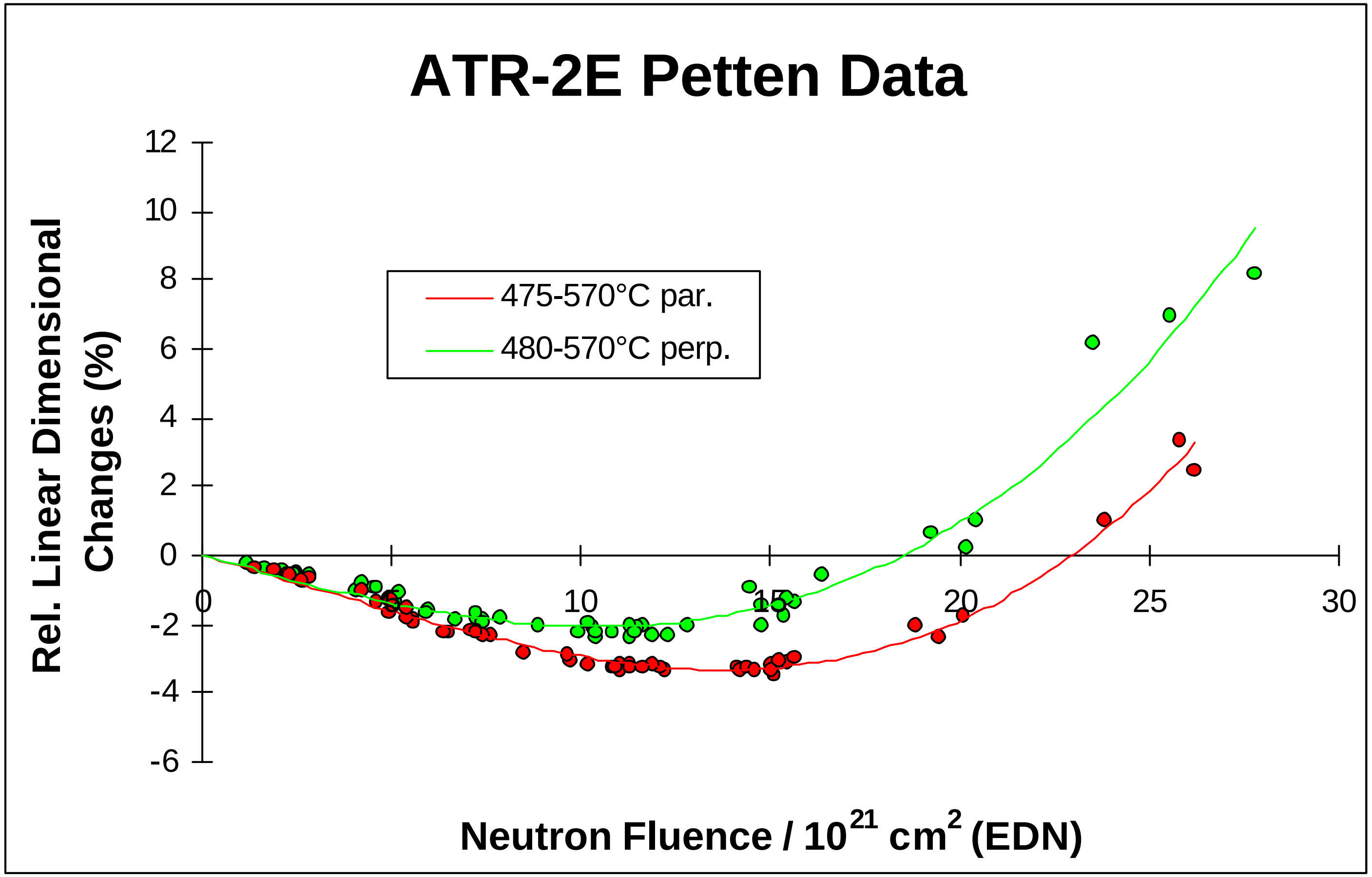


Figure 1 Relative linear dimensional change (%) - 475-570°C

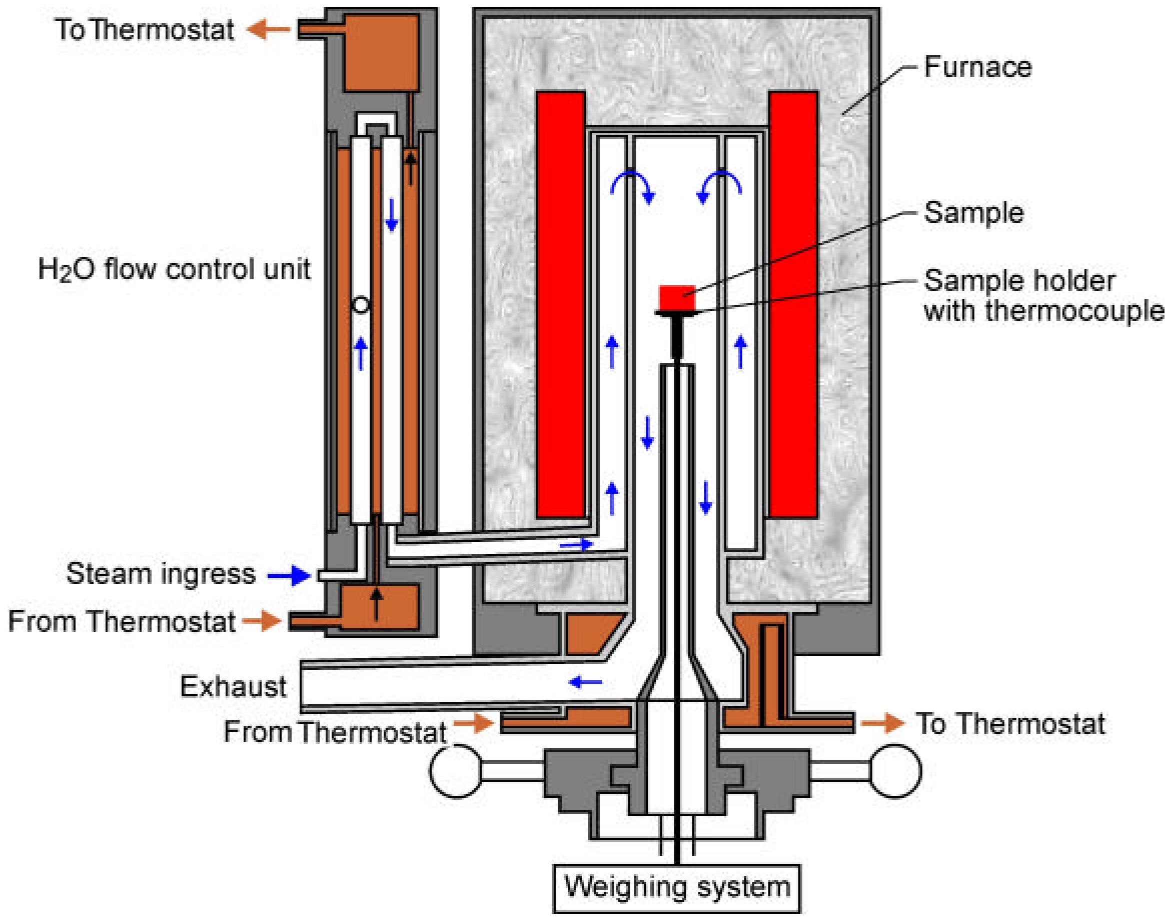


Figure 2 Scheme of facility THERA to be used for kinetic data generation in regime I:

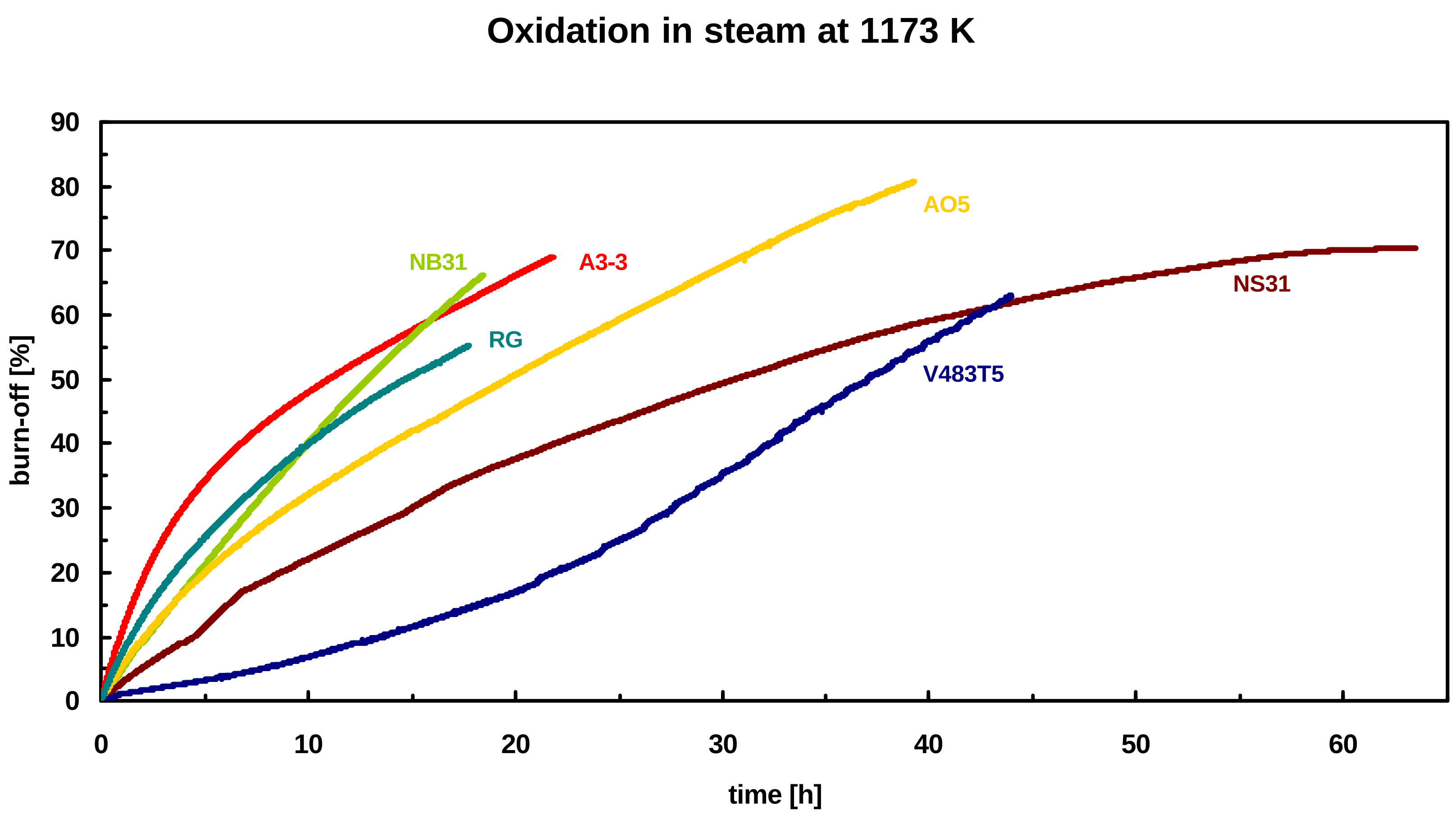
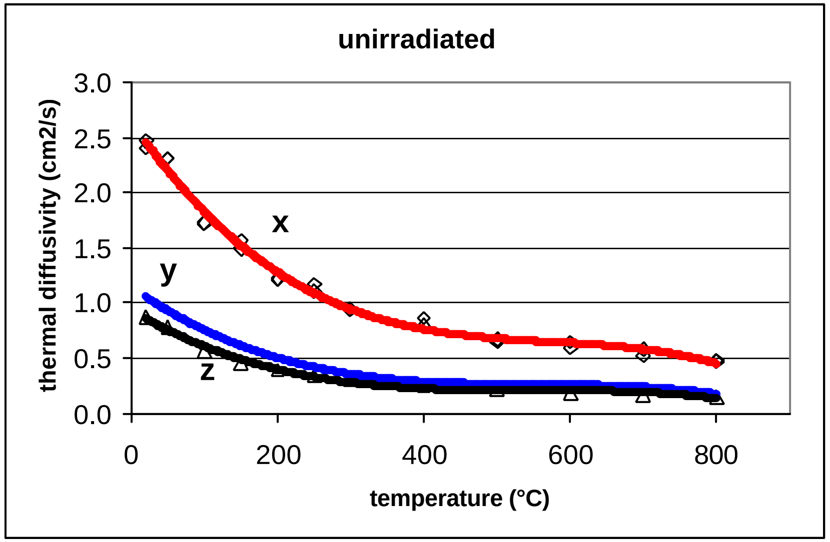


Figure 3 Oxidation in steam at 1173°K



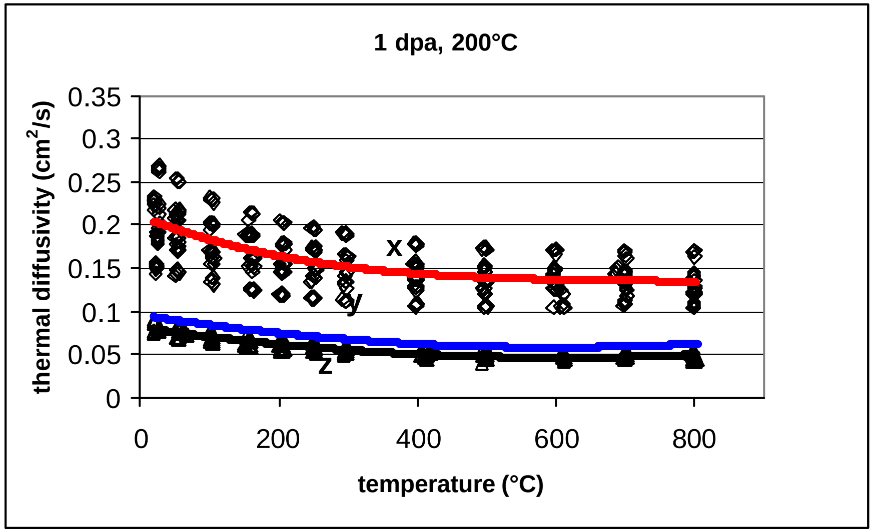


Figure 4 Thermal diffusivity of SEPcarb NS31 (mean values)