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Definition of combined primary corrosion and Boudouard tests in NACOK II

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Summary

This document contains the description of the Boudouard tests in the NACOK II facility and the experiments in INDEX. First the theoretical background of the graphite oxidation, especially the Boudouard reaction, in case of air ingress in an HTR is given. After the description of the test facility NACOK, one will get the definition of the proposed Boudouard experiments. The first experiment is done with a block geometry, in the second experiment a pebble-bed of graphite spheres is used. Additional experiments in INDEX allow a better understanding of the flow field around pebble beds.

Approval

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1 Introduction

The overall aim of this work package is the usage of the new NACOK II facility to study the effects of the so called Boudouard reaction (a secondary reaction of air induced graphite corrosion) using state-of-the-art instrumentation systems for a better understanding of coupled fluid dynamics and reaction kinetics effects. In addition to the large scale experiments in NACOK-II with focus on the Boudouard reaction, a few small scale experiments are performed in the INDEX facility focussing on fluid dynamics phenomena.

Complementary to the original focus on the fluid dynamics of the NACOK II, the experiments extend the research activities towards graphite corrosion, especially the Boudouard reaction in different geometries in the NACOK II test facility.

The specific focus of these experiments is the Boudouard reaction, i.e. the oxidation of carbon by CO_2. In the event of an HTR air ingress accident, carbon dioxide is produced during the initial oxidation of the reactor's graphite by atmospheric oxygen in the graphite reflector, from which it could flow into the reactor core and cause damage as a result of corrosion.

The proposed experiments use the NACOK II facility, which was upgraded with new instrumentation systems, including a Particle Image Velocimetry (PIV) and better gas analytics. The secondary air-induced graphite corrosion effects are studied for a better understanding of coupled fluid dynamics and reaction kinetic effects. The graphite oxidation by CO_2 (Boudouard reaction) will be investigated without influence of the primary (air induced) reaction at a temperature level at which the Boudouard reaction can take place at significant reaction rates.

The planned experiments in NACOK II are accompanied by pre- and post-calculations with the reactor dynamics code MGT-3D. The MGT-3D code system deals with the nuclear and the thermal transient behaviour of the primary circuit of a high temperature gas cooled reactor and is a further development of the two dimensional code MGT. MGT-3D takes into account the mutual feedback effects in three-dimensional R-Z-PHI geometry. As the R-coordinate is not restricted to start at $R \approx 0$, by starting at a considerable large radial value a pseudo X-Y-Z geometry may be simulated as well. MGT contains also models for simulating air ingress into the primary circuit of an HTR. For this reason 2D and 3D models will be developed and compared.

The experiments using the INDEX test facility can provide detailed data about the velocity field and fluctuations around a single pebble or a pebble bed. This data is useful for adequate CFD validation and necessary for CFD model enhancement for pebble bed simulations.

2 Graphite oxidation

Chemical reactions in which all of the reactants are in the same phase are called homogeneous reactions, and chemical reactions between reactants that are in two or more different phases are called heterogeneous reactions. Heterogeneous reactions are much more dependent on mass transport than homogeneous reactions. Graphite-gas reactions are therefore considered heterogeneous reactions, and reactions between gaseous reactants are considered homogenous.

No.	Reaction	ΔH_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

Table 1: Reactions taking place during the oxidation of carbon in air or water vapor

Chemical reactions generally tend to depend more strongly on temperature than on mass transport by gas diffusion. The reaction rate is determined by the chemical reaction at low temperatures and by mass transport at higher temperatures. Therefore, with respect to thermal reactions between gases and porous solid materials, there are three different chemical reaction regimes, controlled respectively by the slowest of the steps involved in the reaction, that have to be taken into consideration.

At low temperatures, the slowest reaction step is the actual chemical reaction, therefore it is called chemical regime (CR) or Regime I. In a Regime I reaction, the chemical reaction progresses so slowly that mass transport simply has no influence at all. Since the reactant gases penetrating the graphite do not form a concentration profile, the corrosion affects all of the solid material largely homogeneously.

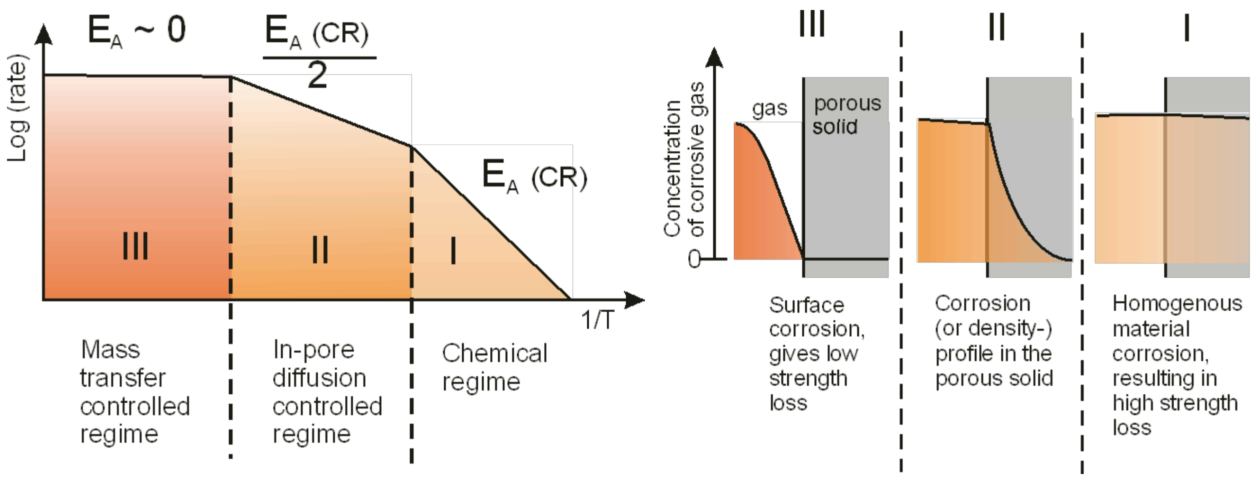

Figure 1: Graphite oxidation (heterogeneous reaction) reaction regimes

At medium temperatures, pore diffusion or Regime II determines the oxidation rate. Since at these temperatures, gas transport through the pores and the chemical reaction overlap, the reaction rate is determined by both the chemical reaction rate and pore diffusion. The high concentration profile of the reactant gases inside the solid material also leads to the formation of a corrosion profile in the graphite.

At high temperatures, the corrosion rate is determined solely by boundary layer diffusion and is therefore called boundary layer diffusion or Regime III. At these temperatures, corrosion occurs only on the graphite's surface. This temperature-controlled chemical reaction happens so quickly that the reactant gases are fully consumed at the graphite's surface long before they are able to penetrate the porous solid matter.

The temperature ranges of these different regimes strongly depend on the oxidants, their flow rates, and the graphite's porosity. The higher the purely chemical reaction rate, the lower the regimes' temperature ranges. The Regime II thresholds for CO_2 are ~1000°C to ~1300°C, while the Regime II thresholds for reactant air, which has a higher reactivity, are ~600°C to ~900°C, depending on porosity.

3 Experimental Set-Up and Instrumentation in NACOK II

3.1 NACOK II

The old NACOK (NAturzug im COre mit Korrosion) facility of the Institute for Nuclear Waste Management and Reactor Safety (IEK-6) of Forschungszentrum Jülich has been optimized, modernized and reactivated according to a new assignment of objectives (see Fig. 2). It is a 5 m high integral experiment for fluid mechanics and graphite corrosion processes under natural convection conditions or forced gas flow. The modular structure of the electrically heated ceramic flow channel allows flexible handling of samples such as spherical fuel elements and prismatic blocks. Optical access for PIV flow field measurements is provided by window segments. The new NACOK II reaches 1200°C after 1,2m entry length with normal air or defined gases and gas mixtures of N_2, O_2, He, CO_2 up to a flow rate of 50m³/h. The facility was brought into operation at the end of 2012.

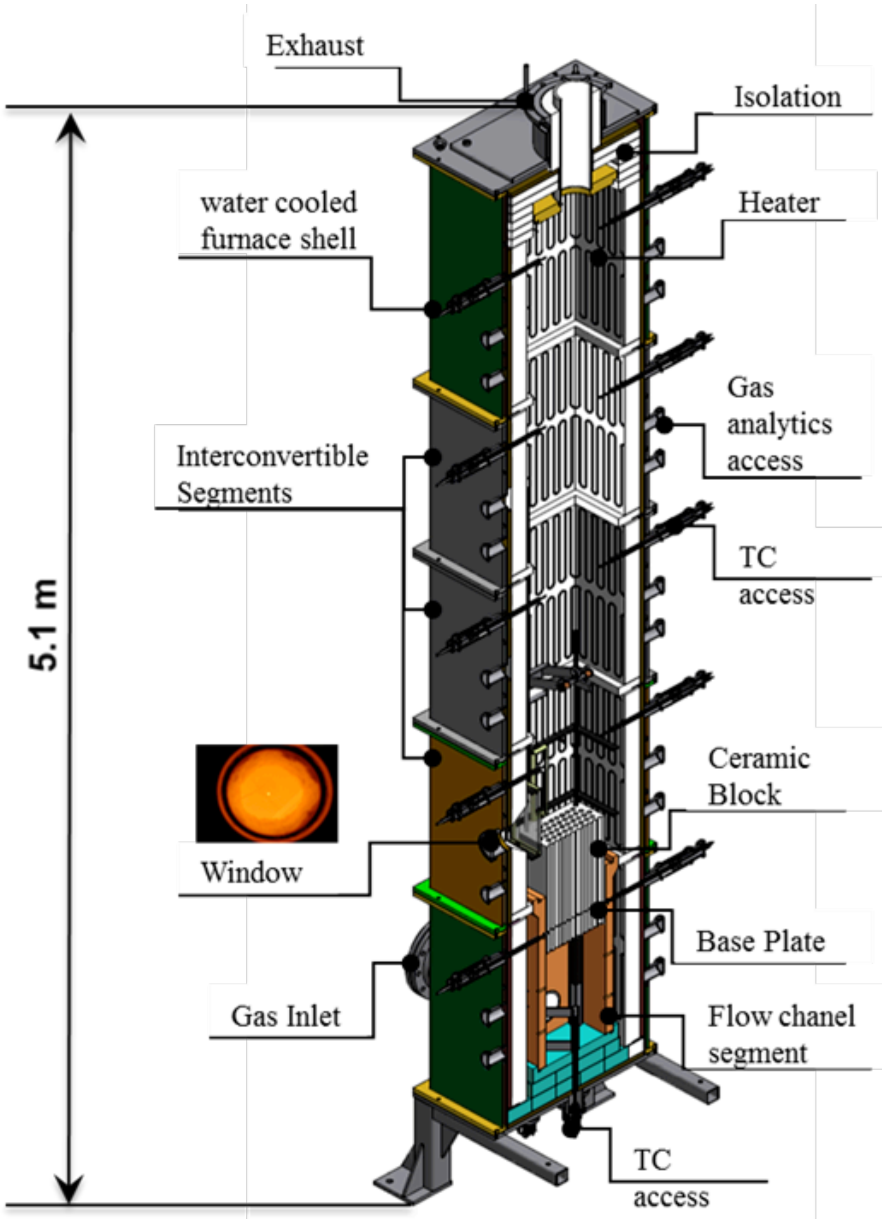

Figure 2: Schematic of NACOK II main parts

The new NACOK II has a ceramic flow channel stacked with five segments, each with a height of 0.8m and able to withstand temperatures up to 1600°C (maximal temperature of the entire facility is 1200°C). The cross section of the channel is rectangular and allows sample sizes of 300mm x 300mm. The height of those samples, like prismatic blocks, should not exceed 400mm for handling and instrumentation. The furnace shell is water-cooled and provides defined boundary conditions. The heating power of the lower three furnace segments is 40kW each, while the upper segments have a heating capacity of 25kW each. That results in a 170kW total maximum heating capacity of the furnace.

The second segment, which is interchangeable with segment three and four, is equipped with windows for optical access. This allows the implementation of Particle Image Velocimetry (PIV) to investigate the flow field above samples inside the flow channel.

Number of segments	5 (upgradeable)
Height of each segment	0.8m
Height of furnace	5.1m
Maximum temperature	1200°C
Maximum flow length to reach T_{max}	1.2m
Maximum total heating power	170kW
Maximum heating rate	30°C/h
Maximum gas flow	50Nm³/h

Table 2: NACOK II main data

The NACOK II facility has been optimized for graphite oxidation experiments. Therefore it must be assured, that no oxidation gases can enter the graphite geometry unintentionally. The water-cooled shell of the furnace allows the use of silicon seals in the cold area to get a gastight facility. There is the possibility to use pneumatic valves in the gas inlet (especially for natural convection experiments) and in the gas outlet lines. The pneumatic valve in the exhaust line has to be protected from temperatures higher than 200°C by installation of a gas cooler before the valve.

To control and monitor the gas concentration inside the flow channel and in the heating zone between ceramic flow channel and furnace heating rods, a system of gas tubes and magnetic valves was installed (see Fig. 3). This area can be ventilated with nitrogen to remove oxygen remaining from experiment preparations or in case of a leak during the experiment.

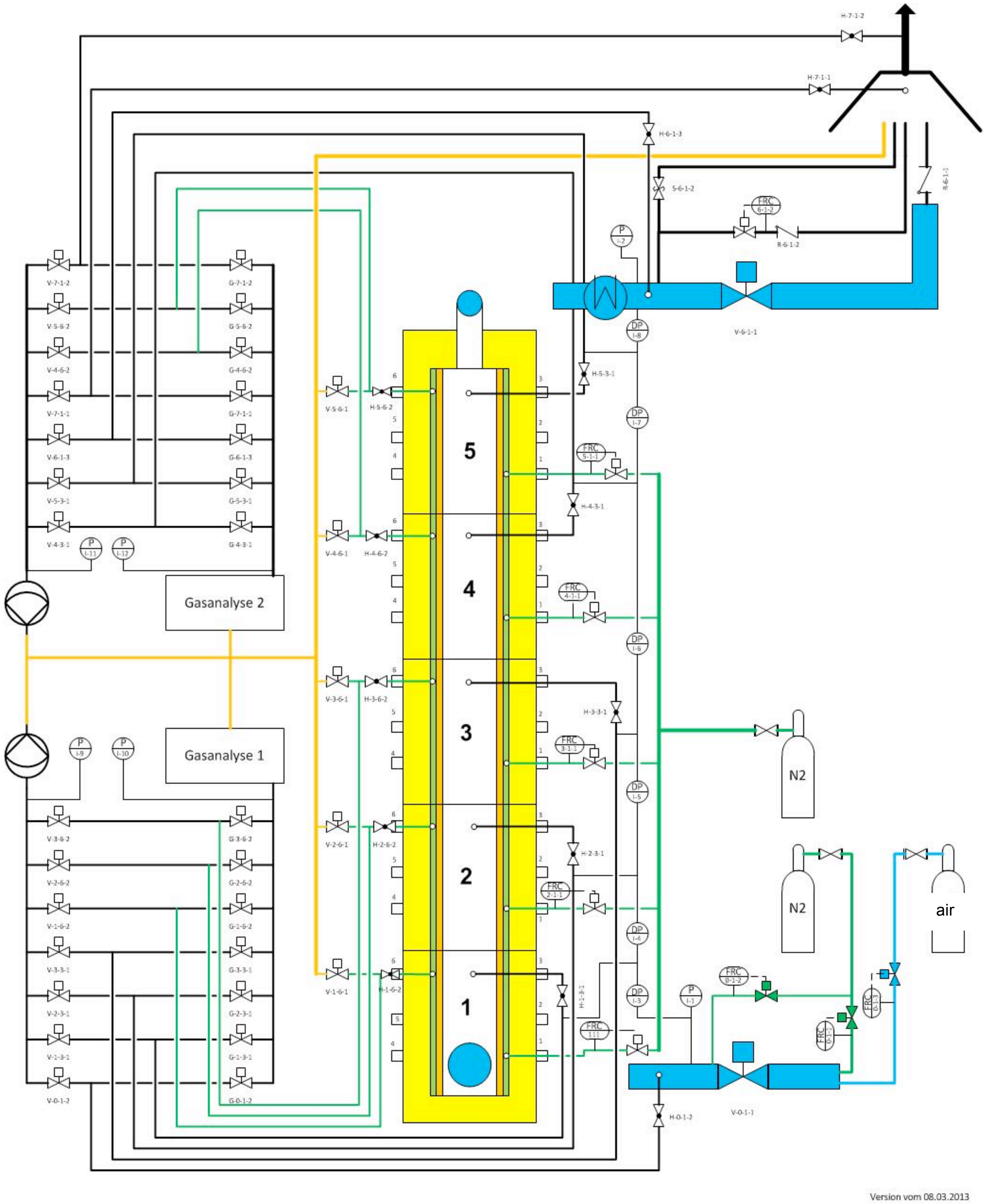

Figure 3: Schematics of gas analysis and gas flow

3.2 First experiment: Block Geometry

For the first experiment in NACOK, we define the following set up: Five graphite blocks (NBG-18) with boreholes are stacked inside the flow channel with an overall height of 2m. The furnace heats the graphite up to 1100 - 1200°C with a constant nitrogen gas flow of 7 m^3_N/h to vent out remaining oxygen in the system. After having reached stable conditions at the desired temperature, the oxidation starts when a mixture of 21 Vol.-% CO_2 in Nitrogen enters the system with a flow rate of 7 m^3_N/h. Temperatures and gas concentration are measured during the oxidation.

Due to the high temperatures in an HTR, the exothermic primary reaction ($C + O_2 \rightarrow CO_2$) would occur immediately in case of an air ingress, producing the carbon dioxide for the secondary so called Boudouard reaction ($C + CO_2 \rightarrow 2CO$, endothermic). To study the effects of the Boudouard reaction separately, the oxidation gas is a mixture of CO_2 in nitrogen. For stability reasons the experiment is stopped at a maximum weight loss of 25% at the lowest block.

The samples in the first experiment are block-shaped allowing for instrumentation with thermocouples and gas analytics. In this geometry it is possible to measure the gas concentration at different heights of the stacked blocks. An additional advantage of the block-shaped geometry over a pebble bed is the stability of the measurement points. Depending on the oxidation regime, there can be significant material loss due to oxidation. In a pebble bed, the set up may change and start to move downwards unpredictably with increasing material loss. For the block-type geometry the measurement points stay in place, even when significantly corroded. The borehole geometry is defined by the base plate, so the gas can flow through the channels without further disturbances. For mechanical treatment, handling, and instrumentation, the 5 graphite blocks are cut in two parts (so-called block 1.1 and 1.2 from block 1, block 2.1 and 2.2 from block 2 etc.) and stacked above each other.

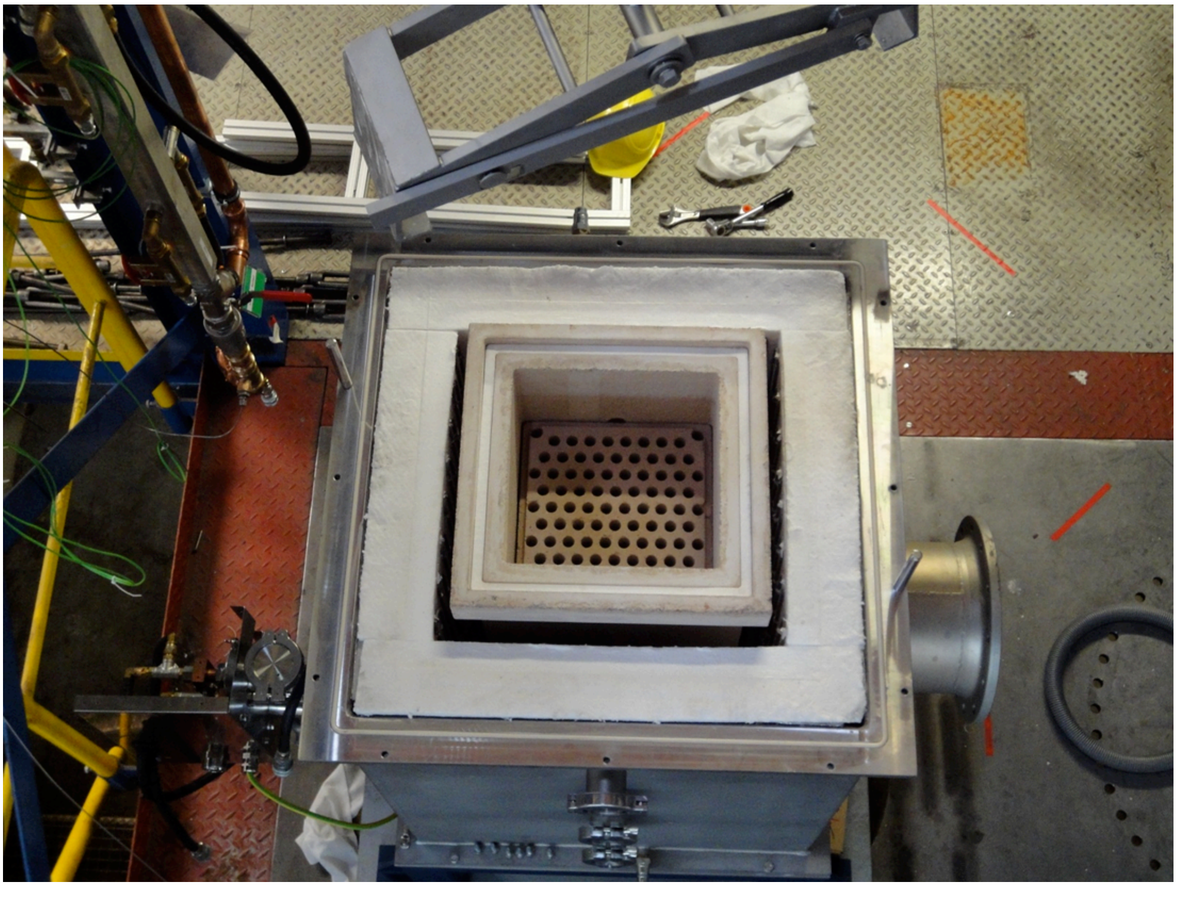

Figure 4: View into the ceramic flow channel during set-up, looking at the base plate

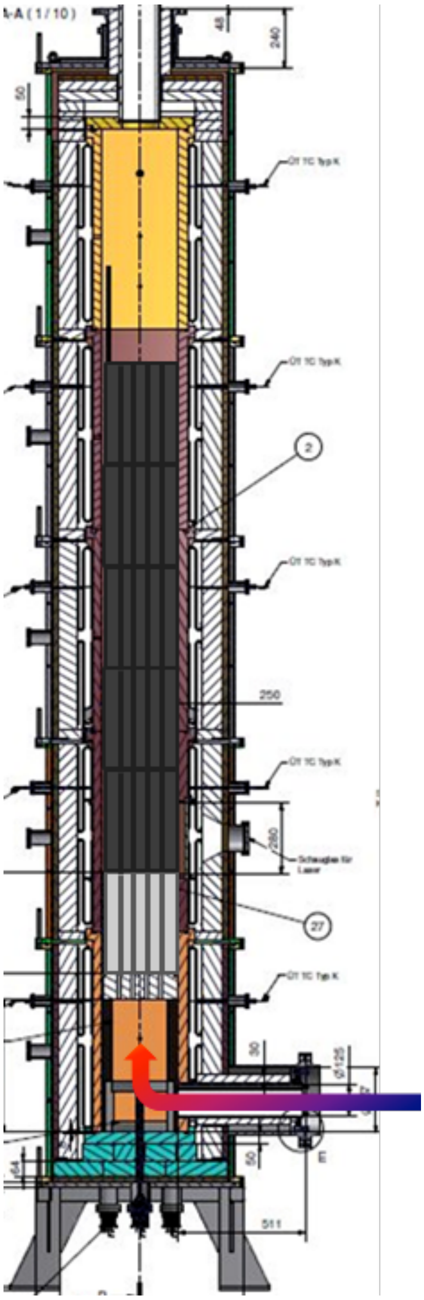

Figure 5: Schematic of sample set up and gas flow

The oxidation gas enters the flow channel and is heated up in the lower part. For a good investigation of the Boudouard reaction the temperature of all graphite blocks should be in the same range. To ensure this, an additional ceramic block is implemented in the geometry below the graphite blocks for heating of the oxidation gas before entering the graphite-zone. At 1100 - 1300°C, the Boudouard reaction is in the in-pore diffusion controlled regime. Due to the endothermic character of the investigated reaction, the oxidation should start at preferably high temperatures (1100 – 1200°C). The Boudouard reaction reduces the temperature in the graphite geometry. The relatively low flow rate of 7m³N/h is recommended to allow the Boudouard reaction to take place in the whole test section for a better investigation of this effect.

The oxidation progress in the experiment is monitored with a dense grid of thermocouples (at least 7 per block, up to 17 in the lower part) and with gas analytics to measure the gas concentration of oxygen, carbon dioxide, and carbon monoxide at the upper part of every block. By integrating the measured carbon dioxide and carbon monoxide, the mass loss of every block can be monitored during the experiment. The oxidation gas is stopped, when 25% mass loss in the lowest block is reached, which would compromise the structural integrity. The oxidation must also be stopped, if the cooling rate in the ceramic part is higher than 30°C/h. As the first experiment is already finished with release of this paper, in Table 3 are the planned as well as the experimentally reached features listed.

Feature	planned	first experiment
Number of graphite blocks	5 (10 half blocks: x.1 and x.2)	5 (10 half blocks: x.1 and x.2)
Type of graphite	NBG-18 (from SGL)	NBG-18 (from SGL)
Height of graphite block	0.4m (0,2m for half block)	0.4m (0,2m for half block)
Overall height of stacked graphite	2.0m	2.0m
Flow channel diameter	15.9mm	15.9mm
Number of flow channels	82	82
Graphite temperature at start	1100-1200°C	1185°C
Gas flow	7 Nm³/h	7 Nm³/h
Oxidation gas	21Vol.-% CO_2 in N_2	21Vol.-% CO_2 in N_2
Inert gas (heating and cooling phase)	Nitrogen	Nitrogen
Maximum heating rate	30°C/h	30°C/h
Heating power	170 kW	170 kW
Heating time to stable state before oxidation	48h	49h
Cooling down phase	72h	>72h

Table 3: Oxidation experiment main data

Figure 6 shows a block before the instrumentation with thermocouples. 82 boreholes with a diameter of 15.9 mm and four slots for guiding the thermocouples in the corners are presented. Figures 7-11 provide an overview of the positions of the thermocouples in the different graphite blocks. The instrumentation of the lower graphite blocks (1.1 and 1.2) is denser than in the upper blocks to ensure a good knowledge of the temperature distribution. This is of special interest in the lower part, because there heated oxidation gas enters first and we assume the reaction to have the highest rate in this part.

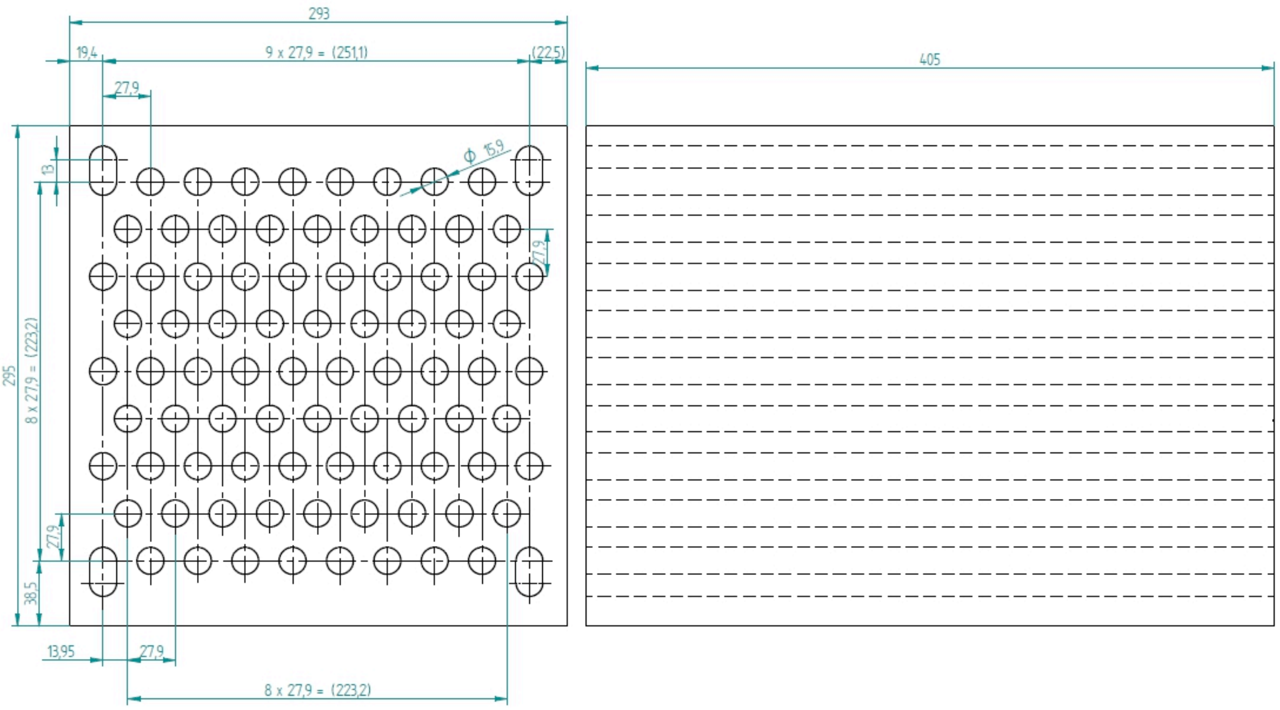

Figure 6: Geometry of sample shape (before cutting into two parts)

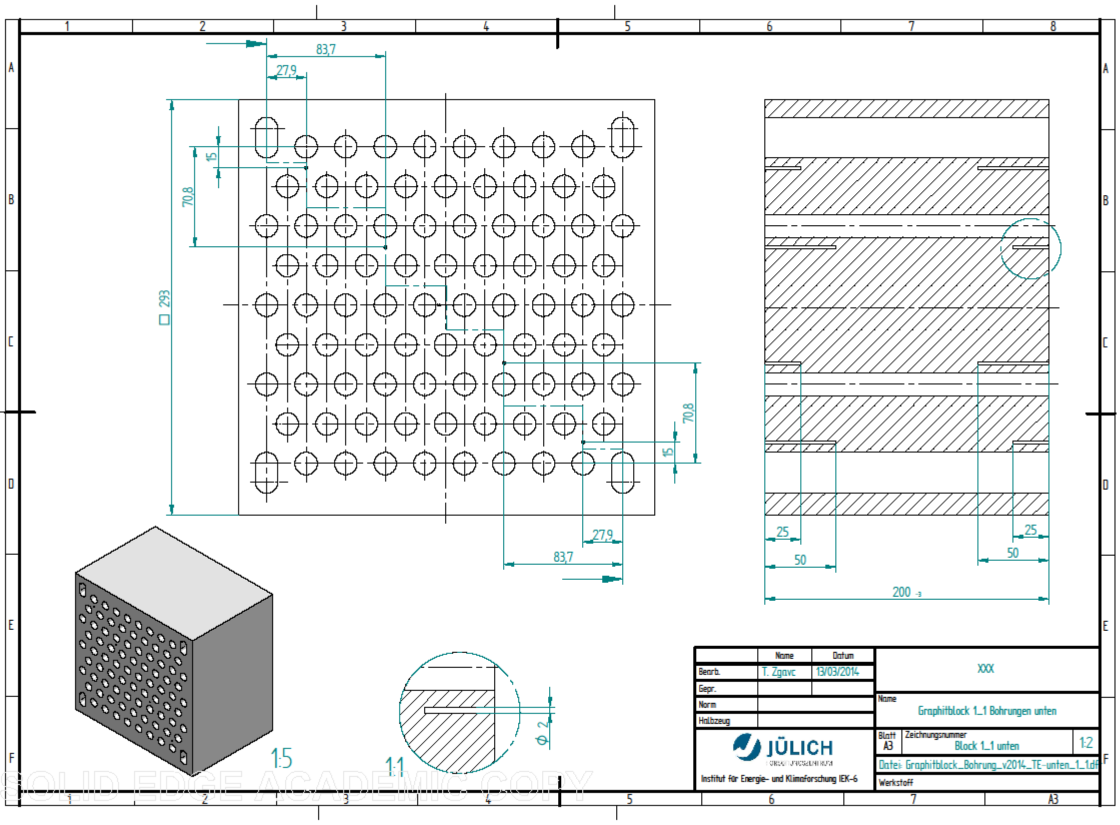

Figure 7: Position of thermocouples at the bottom of block1.1

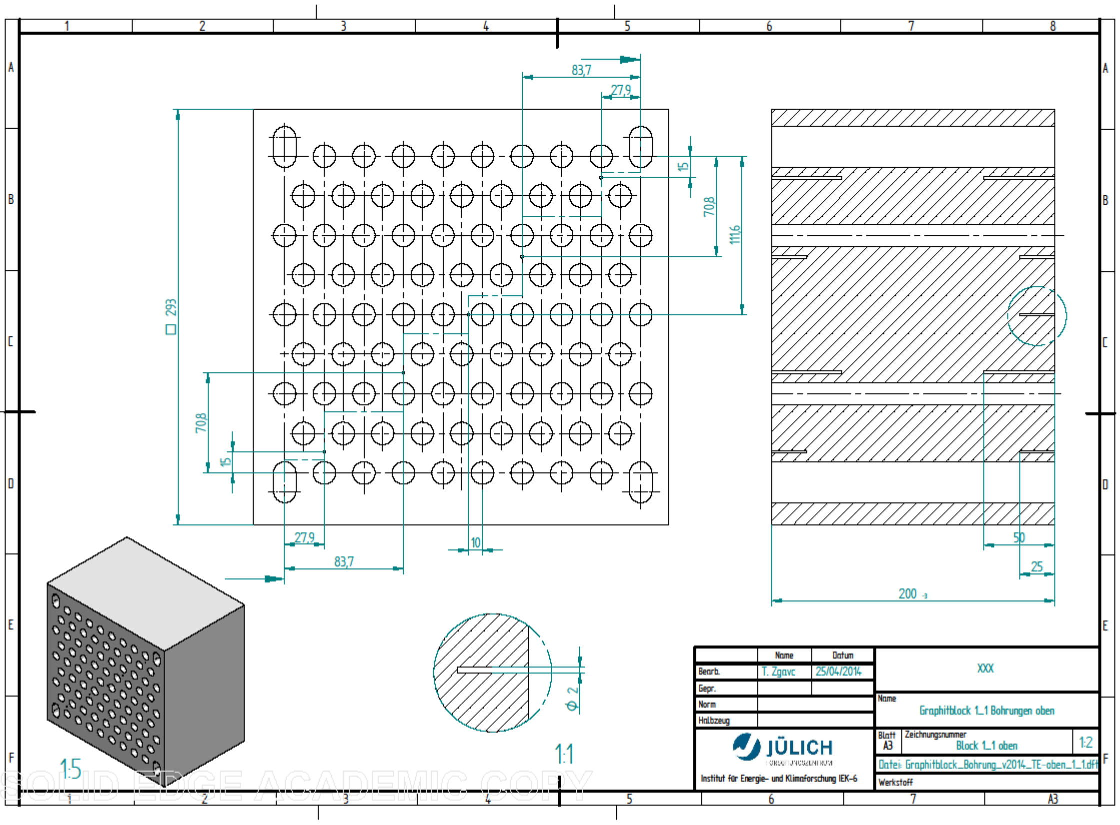

Figure 8: Position of thermocouples at the upper part of block 1.1

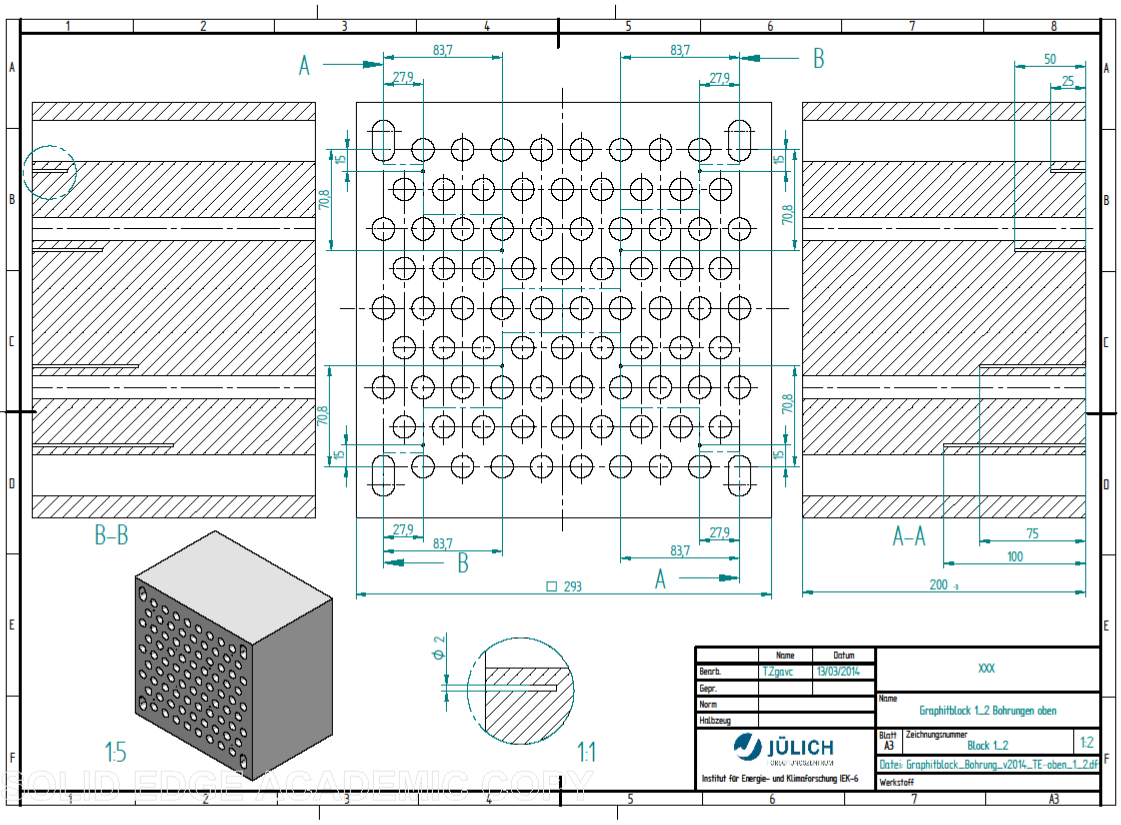

Figure 9: Position of thermocouples at top of block 1.2

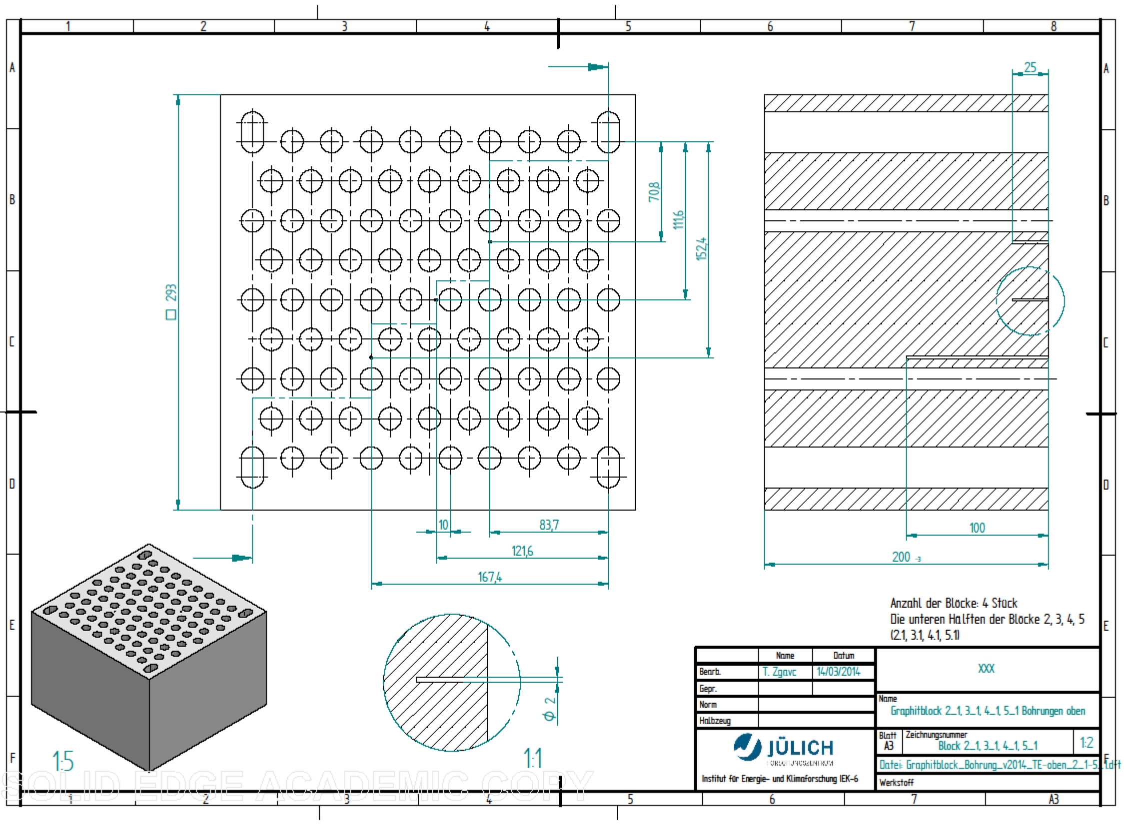

Figure 10: Position of thermocouples at top of block 2.1 – 5.1

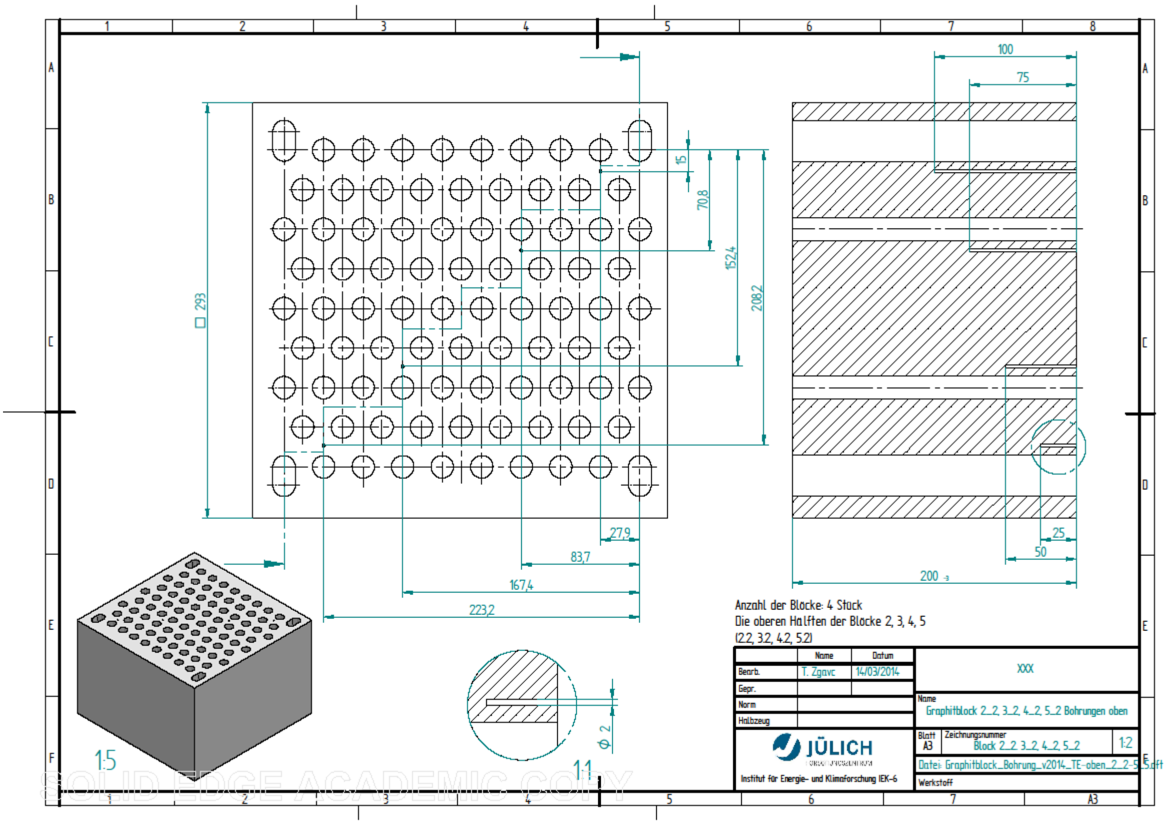

Figure 11: Position of thermocouples at top of block 2.2 – 5.2

To get an idea of the instrumentation a prepared block is shown in Figure 12.

Figure 12: Example assembly of thermo couples in an experimental set up for fluid dynamics investigation done in NACOK II previously

3.3 Second experiment: Pebble-Bed Geometry

The second experiment in NACOK II is complementary to the first one, but uses a pebble-bed geometry instead of the stacked blocks. For a good comparison between the two experiments the second experiment is done under the same boundary conditions as the first experiment (21Vol.-% CO_2 in nitrogen, 7m³N/h, 1100 - 1200°C). In addition to the direct comparison between both geometries, the set of these two NACOK experiments provides data for the Boudouard reaction, which is less well known compared to the primary corrosion reaction.
Based on the results of the first experiment, the stability of the graphite after the Boudouard reaction is quite good. The stability of the pebble-bed geometry should also be assured if the reaction takes place in the in-pore diffusion regime and if the duration of the oxidation part of the experiment is similar to the first experiment.

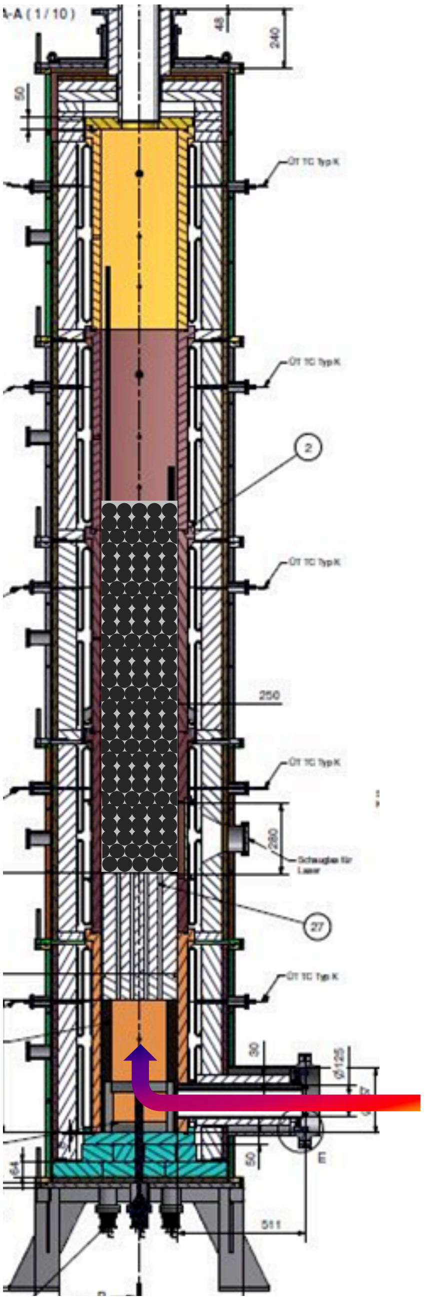

Figure 13: Schematic of the sample set up with pebble-bed geometry

The oxidation progress in the experiment is monitored with a dense grid of thermocouples and with gas analytics to measure the gas concentration of oxygen, carbon dioxide, and carbon monoxide above the pebble bed. Concentration measurement within the pebble-bed geometry is not possible. By integrating the measured carbon dioxide and carbon monoxide, the mass loss in the geometry can be monitored during the experiment. The oxidation gas is stopped after a comparable oxidation rate or time of oxidation. It must also be stopped if the cooling-rate in the ceramic part is higher than 30°C/h.

Feature	First experiment	Second experiment
Number of graphite blocks	5 (10 half blocks: x.1 and x.2)	
Overall height of stacked graphite	2.0m	
Flow channel diameter	15.9mm	
Number of flow channels	82	
Graphite surface	8,192m²	8,200m²
Pebble diameter		60mm
Number of pebbles		725 (fits 29 layers)
Height of pebble-bed		1.5m
Type of graphite	NBG-18 (from SGL)	MLRF-1 (from SGL)
Graphite temperature at start	1185°C	1100 - 1200 (1185) °C
Gas flow	7 Nm³/h	7 Nm³/h
Oxidation gas	21Vol.-% CO_2 in N_2	21Vol.-% CO_2 in N_2
Inert gas (heating and cooling phase)	Nitrogen	Nitrogen
Maximum heating rate	30°C/h	30°C/h
Heating power	170 kW	170 kW
Heating time to stable state before oxidation	49h	48-50h
Cooling down phase	>72h	>72h

Table 4: Comparison of the main data of both experiments

There are more thermocouples in the lower part of the pebble-bed to get a good knowledge of the temperature distribution in the geometry. The lower part is of special interest, because here enters the heated gas the graphite structure and the oxidation takes place with higher reaction rates. As there is no possibility to measure the gas concentration within the pebble-bed, the temperature drop in the geometry gives an impression of the progress in oxidation for the different layers.

Figure 14 shows 8 layers of the pebble-bed geometry. The first layer is 5x5 spheres, like the third, fifth, and every other odd layer of the pebble-bed. In the second layer are 4x5 intact spheres, and 5 spheres cut into half, laying on two sides. Also the fourth layer are 4x5 intact spheres and 5 spheres cut into half, but now with a 90° rotation with respect to the second layer. The sixth layer is the same like the second, the eighth layer is like the fourth and so on. The total height of the pebble-bed is 29 layers (1.5m). With this well-defined geometry it is also possible to calculate the filling factor.

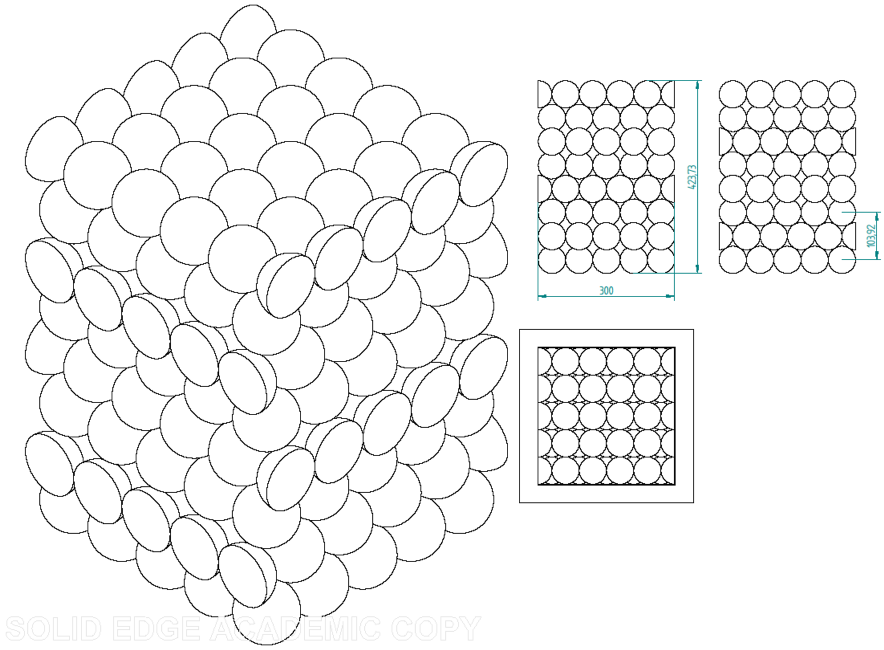

Figure 14: Geometry of the pebble bed

4 The INDEX test facility

Complementary to the large scale facility NACOK the small scale experiment INDEX is used to investigate fluid dynamics phenomena.

4.1 Experimental Set-Up and Instrumentation

The INDEX (INDuction EXperiment) facility (Fig. 15) is a glass flow channel in which a geometry of graphite can be inductively heated up. The coil is optimized for a mass of 200g graphite (one graphite sphere, d=60mm), the sample shape can be varied from a single pebble to a prismatic block like shape to a pebble bed. The geometry can be overflown with several gases like nitrogen, helium, air, carbon dioxide and their mixtures.

In the rectangular part of the flow channel a PIV (Particle Image Velocimetry) measurement system can be adapted to measure the flow field in this region. Depending on the current experimental setup, the flow field below and above the geometry can be measured. By removing the inductive coil out of sight around the pebble bed, to a certain degree, depending on the geometry also wall effects can be investigated.

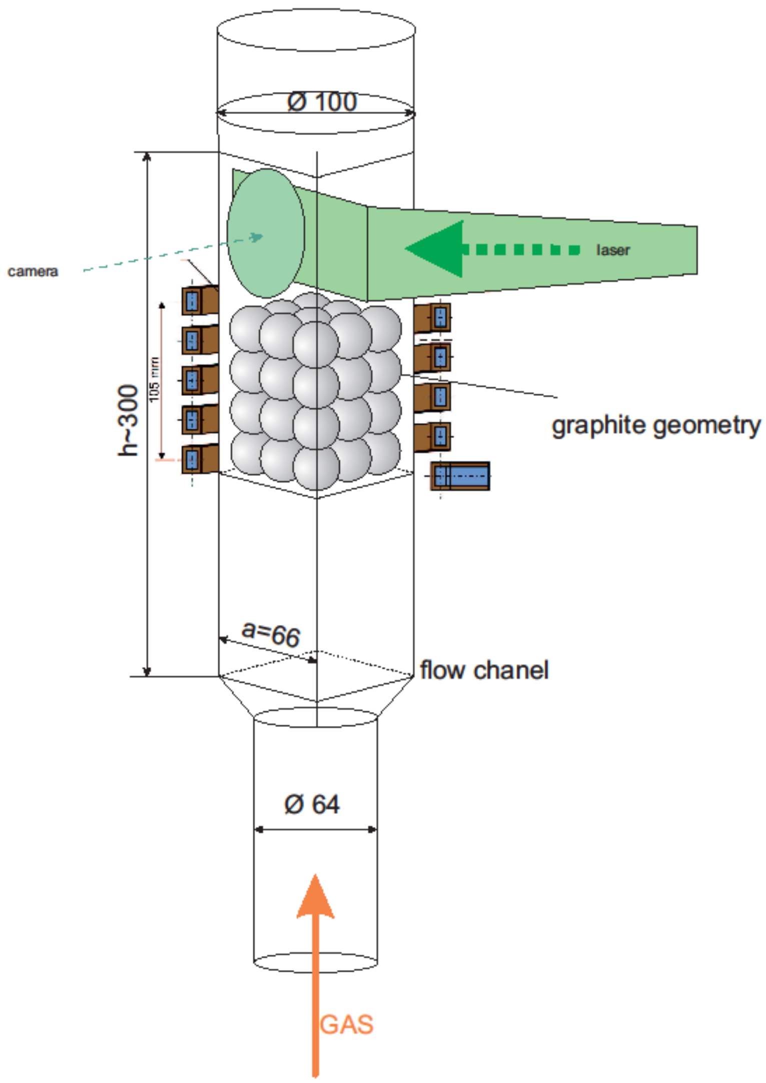

Figure 15: Schematic of INDEX

The lower part of the glass channel is a tube with an inner diameter of 64mm and a length of 1100mm. Above this cylindrical part the flow channel becomes a rectangular profile with an inner dimension of 66 x 66mm and a length of 300mm (Fig. 16). For good handling, the geometries can be inserted, using a second, inner rectangular glass channel (Fig. 17), inner dimension: 61 x 61mm, length: 300mm. The geometry is located inside this inner glass channel.

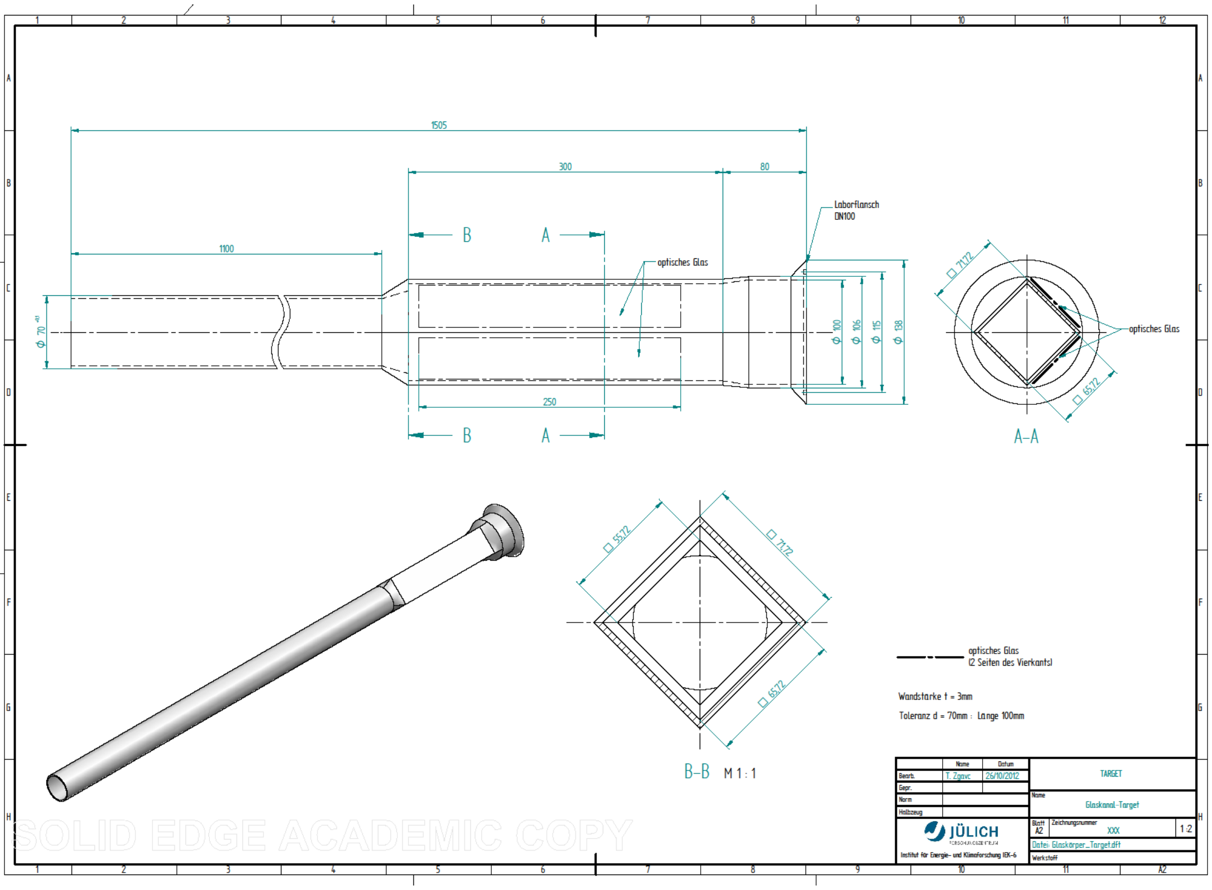

Figure 16: glass channel

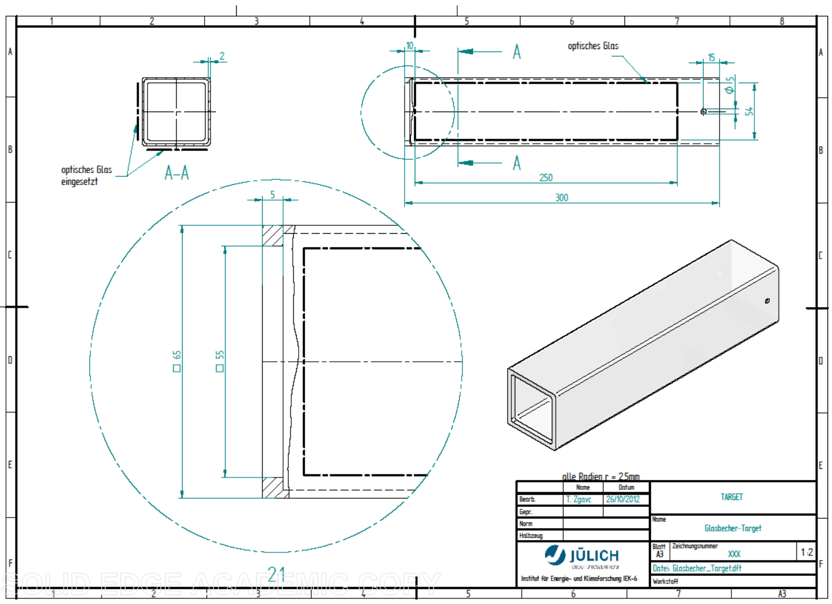

Figure 17: inner glass channel

4.2 Planned Experiments

The set of experiments in INDEX consists of six experiments with different geometries at two different flow velocities, defined as following:

- **Empty channel, low velocity:**
  In the first experiment, information about the flow profile without geometry are generated

- **Pebble bed (10mm spheres, disordered), low velocity:**
  In the second experiment, the flow profile with a pebble bed of graphite spheres with 10mm diameter is investigated

- **Pebble bed (30mm spheres, disordered), low velocity:**
  In the third experiment, a disordered pebble bed geometry (30mm diameter spheres) at low velocity is used

- **Pebble bed (30mm spheres, BCC), low velocity:**
  In the fourth experiment, a sorted geometry (BCC, body centered cubic, see Fig. 18) with 30mm diameter pebbles is investigated at low velocity

- **Empty channel, high velocity:**
  The fifth experiment is in the same setup like the first experiment, but with higher velocity.

- **Pebble bed (30mm spheres, BCC), high velocity:**
  The sixth experiment is complementary to the fourth experiment (BCC geometry with 30mm diameter pebbles) at higher velocity.

Figure 18: BCC geometry

The gas of interest is helium, so all experiments are done in helium atmosphere. In order to the comparability of the experiments, they are done at room temperature. The different geometries would couple in differently to the induction field and the experiments would not be comparable.
The BCC geometry is of special interest for the CFD code validation at NRG, so this design is investigated at two gas velocities. The BCC geometry is manufactured, containing defined points of contact, so this geometry can later be modelled in CFD (Fig. 19).

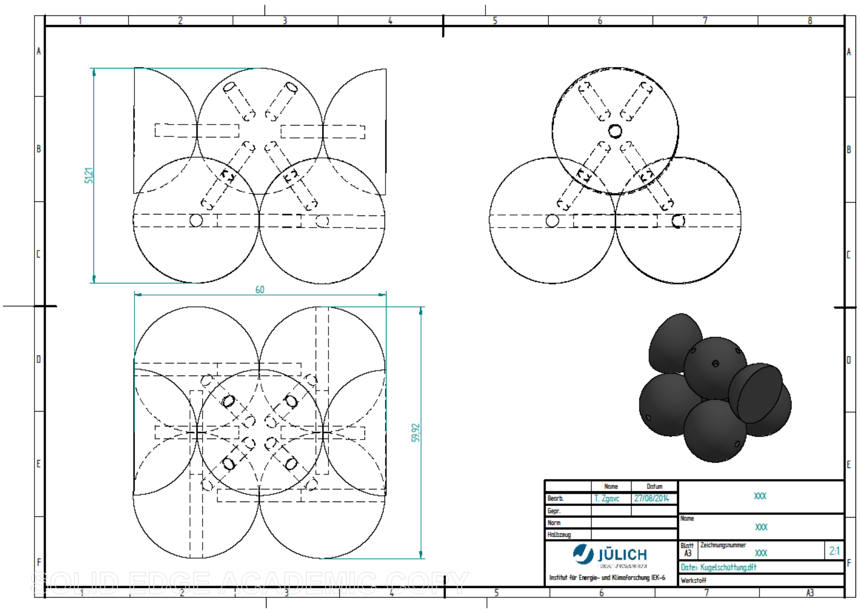

Figure 19: BCC geometry, defined points of contact