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## **Burn-out behaviour of organic matter in the ceramic mass of honeycomb bricks depending on the firing conditions**

### **Introduction**

The reduction of energy demand for the production and improvement of functional properties of ceramic building materials is still a current problem in the ceramic industry. Both objectives can be achieved by adding carbon or organic compounds such as Styrofoam, sawdust, coal slag, recovered stock from the paper industry etc. to the ceramic mass.

The conversion of these additives leads to hollow spaces improving the thermal insulation. In addition, energy for the combustion process is released by conversion of the organic substances.

During the short firing cycles of highly perforated bricks in particular, the possibility now exists to selectively withdraw the energy released through the smouldering effect using optimised flow conditions in the kiln and thereby avoiding the temperature peaks in the stone and reducing the consumption of primary energy.

At the beginning of this paper, a short explanation of the technological background will be presented. Then first results from the thermogravimetric examinations on laboratory-scale will be discussed. The significant objective of these laboratory tests is the determination of reaction kinetic parameters. Pyrolysis coke was used as carbon substance in the investigations. The concentration of pyrolysis carbon in the ceramic mass, temperature, gas atmosphere and flow rate were varied.

The results allow first qualitative and quantitative statements concerning the weight change behaviour with respect to characteristic values such as burn-out behaviour or degree of combustion, combustion time etc. in dependence upon the composition of input material, the temperature profile, and the composition of the reaction gas. The formation/release of gas components during the conversion of clay-carbon material in isothermal and non-isothermal combustion time periods, the evaluation of compression strength measurements and the porosity of the combustion samples upon the independent variables will also be discussed.

### **Objectives**

Main objectives are to achieve:

- a general reduction of the energy demand in the burning process of bricks by reduction of the burning temperature
- the saving of primary fuels and raw material resources by use of substitute burning materials and clay materials with relatively high carbon content
- to ensure the product quality of the honeycomb bricks.

The detailed objectives of this project are the following:

- fundamental thermogravimetric and mass spectrometric investigations concerning the reaction behaviour of the solid and the release of reaction gases from the particular components clay Nordhausen and pyrolysis coke
- estimation of the reaction kinetics and process parameters
- optimising the heating-time-programme and the reaction gas atmosphere to achieve an effective burning-out degree of the pyrolysis coke additive
- determination of quality parameters such as compressive strengths, density of the burned sample etc.

## General Aspects of Ceramic Formation

The burning process influences all required and desired properties of the final ceramic product depending on the composition of raw materials. Important qualitative objectives for the building ceramics described in this publication are compressive strength, bulk density, thermal conductivity, colour of the product and thermal fatigue resistance (freeze-thaw-cycling resistance). Furthermore, a more extensive reduction of the energy demand of the burning process is necessary.

Due to the sintering process, alterations in structure/texture of the material affect the properties mentioned above. For example the sintering process is associated with shrinkage and occurrence of fluid phases. E.g. molecule distances decrease or the strengthening and compaction increases respectively. These processes also result in higher thermal conductivity.

To improve the thermal insulation of honeycomb bricks (Fig. 1) in particular, so-called pore-forming materials are used during the burn-out and corresponding pores remain. For example, in ceramics, carbonaceous materials such as sawdust or coal are used as pore-forming materials. Materials with low bulk density such as Styropor are used preferably.

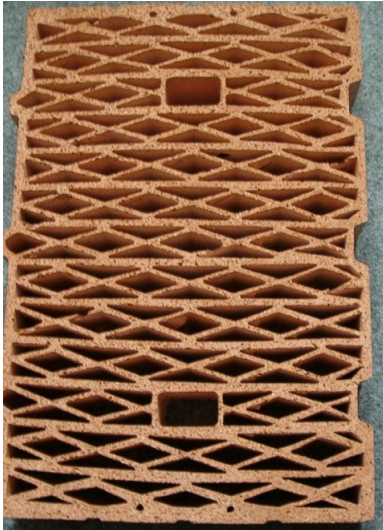


Fig. 1. Honeycomb brick.

By burning out pore-forming materials, reaction products and a specific amount of energy is released in the inside of the ceramic batch. This means that there will be a certain gas atmosphere and a corresponding temperature in the batch.

Sintering processes are time-dependent. They are largely influenced by the surrounding gas atmosphere. During the sintering process, an equilibrium state will not be reached. That represents the ongoing processes by extension or repetition of material treatment. It should be noted, that an optimal burning curve is a specific temperature-time-function for each product and can be influenced by the material properties (conditions of the starting materials/batch), the processing parameters of the material treatment (partial pressure of oxygen, temperature, residence time,

gas atmosphere) and by the type of additive (e.g. carbonaceous admixtures).

As mentioned above, the objectives to consider are the reduction of energy consumption in general and the saving of energy and material resources respectively. Objective of the

treatment is the control the burning process of a certain starting material (batch) in such a manner that the intended product quality can be achieved and energy released during the burn-out process inside the batch can be used.

However, the difficulties are situated in conventional burning processes of carbonaceous batches in tunnel kilns. The burning out of carbon in a ceramic body is a process which is diffusion-controlled over wide ranges [e.g. 1-3]. When the conversion of carbon takes place too quickly an immediate rise in temperature is possible. Tensions can then occur in the ceramic body which can also lead to stress cracking. Furthermore, a reducing gas atmosphere can appear locally. In a reducing gas atmosphere, a reduction of oxides such as  $\text{Fe}_2\text{O}_3$  or  $\text{TiO}_2$  is possible. This way mix-crystals (solid solutions) of  $x\text{FeO}\cdot y\text{Ti}_2\text{O}_3$  can occur which results in a discoloration from blue to green. However, the formation of so-called „black cores“ under reducing conditions is also possible. The formation of "black cores" is not immediately related to the unburned coal. IR-analyses of these dark layers show carbon contents of  $< 0.1$  mass-%. This indicates that carbon exists in a very finely dispersed form. This result is however rather implausible [4]. Perhaps one can assume that the discoloration is caused by reduction of oxides or by the formation of corresponding compounds. In the dark layers, distinctly higher concentrations of divalent iron (Fe II) was analysed. Investigations using scanning electron microscopy showed darkly coloured rhombohedral crystals (possibly  $\text{SiC}$ ,  $\text{Fe}_2\text{O}_3$ ) [4]. In addition to the dissimilar coloration mentioned above, the „black cores“ lead to laminations with corresponding differences of compressive strength. Colour and strength are important criteria for pro-duct quality.

The objective is to control process conditions and to structure the batch. The release of reaction products and energy must be adjusted carefully to the different steps of ceramic conversion by means of process control. Variation parameters are special gas atmospheres and special temperature-time-functions (e.g. heating rates). The faster the burning product is heated, the higher the shifting of e.g. reactions in the batch to higher temperatures and/or the superposition of different reaction ranges.

When this type of process control is possible, carbon-containing raw material could be used in addition to the direct dosage of carbon-containing materials. This way the range of appropriate raw material will be shifted from the current „clean“ clays (carbon content  $< 1$  mass-%) to starting materials with correspondingly higher carbon contents. An important contribution could then be given in the sense of resource conversation.

## **Experimental Investigations**

The strips in honeycomb bricks are of a thickness in a range of 6 mm up to 10 mm. The advantage of these are relatively good gas flow conditions in burning aggregates. This provides uniform heat and mass transfer conditions especially for fast burning processes. In a first step it is possible to carry out investigations on specimens with smaller dimensions. Thermoanalytical methods are well suited for reaction kinetic investigations. With these methods, reaction conditions e.g. compositions of raw materials or the batch, temperature-time-functions (e.g. heating rate, constant burning temperature and residence

time, gas atmosphere) can be varied. Furthermore, the specimens obtained under special burning conditions can then be used for material investigations.

For these investigations, a thermogravimetric high-pressure apparatus with coupled mass spectrometer was used (Fig. 2). The equipment is suitable for thermoanalytical investigations of chemical and physical processes with solid-gas, fluid-gas, gas-gas and solid-fluid-gas reactions. With this apparatus it is possible to determine the mass changes of a sample and the quantitative changes of gaseous components released during the reaction in various reaction gas atmospheres at pressures up to 100 bar and at temperatures up to 1100°C. Thereby temperature-time and respective pressure-time conditions can be realised which are then used in fundamental research as well as in industrial processes. The main parameters and variations of the investigation programme are given in Fig.3.

As basis for the measurement analysis, the mass change-time-curves, the corresponding

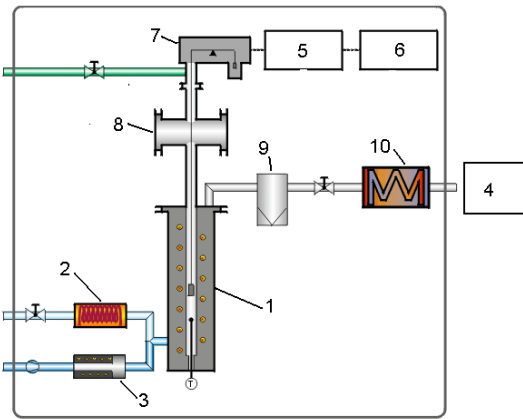


Fig. 2. Scheme of the HP-TGA\_MS-Equipment.

1 – tube reactor; 2 – reaction gas supply and mixing unit; 3 – steam generator; 4 – gas analyser (mass spectrometer); 5 - data uptake; 6 – on-line analysis; 7 – micro balance; 8 – sample lock; 9 – high-pressure filter; 10 – cooler.

sample form and size	powder
	specimen (cylinder)
	diameter d [mm]: 4 and 6
	length l [mm]: 30 ... 50
sample weight m [g]	powder form: 0.750 ... 0.900
	specimen: 1.300 ... 1.900 and 2.300 ... 3.200
carbon content [mass-%]	0 ; 1 ; 3 ; 6
temperature treatment:	non-isothermal: heating rate [K/min]: 4 and 10
	isothermal: residence temperature $\vartheta_H$ [°C]: 750 , 850
carrier / reaction gas flow [cm <sup>3</sup> /min]	600 and 300
carrier / reaction gas atmosphere	argon, synthetic air

Fig. 3. Investigation programme, main parameters and their variations.

gas concentration-time-curves in the outgoing gas flow of TGA and the compressive strength of the thermally treated specimen<sup>1</sup> are used.

As starting material, clay from Nordhausen was used for the investigation. The carbonaceous additive pyrolysis coke came from a plant in Freiberg (Fig. 4).

<sup>1</sup> The authors would like to thank Dipl.-Ing. Walter, Institut für Fertigteilechnik und Fertigung e.V., Weimar, for carrying out the compression strength measurements.

<b>Chemical Analysis</b>		
<b>Characterisation</b>	<b>Clay Nordhausen</b>	<b>Pyrolysis coke Freiberg</b>
Mark of the samples	K/1 - 99	K6 - 99
Measured values of chemical analysis	mass-%	mass-%
SiO <sub>2</sub>	64.81	23.78
Al <sub>2</sub> O <sub>3</sub>	15.68	3.74
Fe <sub>2</sub> O <sub>3</sub>	4.89	12.95
CaO	1.03	8.53
MgO	2.56	1.13
K <sub>2</sub> O	3.98	0.55
Na <sub>2</sub> O	0.18	0.33
SO <sub>3</sub>	0.04	6.94
Ignition loss (1000 °C)	5.64	39.70
C <sub>org</sub>	0.10	31.69
H <sub>org</sub>	< 0.02	1.33
CO <sub>2</sub> /carbon	< 0,05	6.59
H <sub>2</sub> O + hydrate	5.50	<0.05
<b>Mineral Analysis</b>		
Method / analysed components	Qualitative	Qualitative
X-ray analysis:		
CaCO <sub>3</sub> as Calcite		++
CaSO <sub>4</sub> as Anhydrite		++
Iron oxide as Magnetite (Fe <sub>3</sub> O <sub>4</sub> )		++
SiO <sub>2</sub> as Quartz	+++	++++
Illite	+++	
Montmorillonite	++	
Chlorite	+	
Kaolinite	+	
Feldspar	+	++

Fig. 4. Characterisation of clay (Nordhausen) and pyrolysis coke (Freiberg).

## Results

- **Investigation of the reaction kinetics**

During the measurement programme ca. 50 experiments were carried out. A brief summary of the results attained from these investigations is given here. Special attention is paid to the variations in the gas atmosphere and the residence time.

Based on the reaction rate–time–curve of a cylindrical specimen treated in oxidising atmosphere (synthetic air: 78 vol.-% argon and 22 vol.-% oxygen) and at a heating rate of 4 K/min (Fig. 5), the results show the beginnings of carbon conversion at temperatures of about  $\vartheta \approx 300^\circ\text{C}$ . This process is complete at  $\vartheta \approx 550^\circ\text{C}$ . However, the beginning of the real

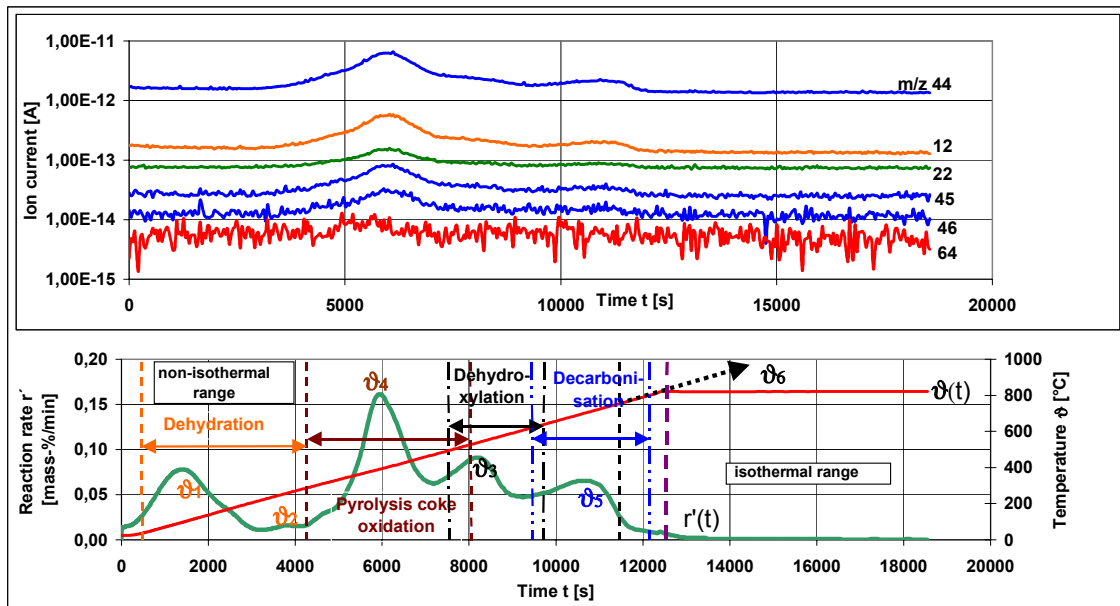


Fig. 5. Test 918: Oxidising, 4 K/min, cylinder.

sintering processes takes places at a higher temperature range. Increasing the heating rate from 4 K/min to 10 K/min did not shift the carbon conversion into the range of the ceramic sintering process sufficiently. Therefore, the change from initially inert gas atmosphere (argon) to an oxidising gas atmosphere (air) was investigated in the next step. This allowed for the shift of the carbon conversion into the temperature range of ceramic sintering. Fig. 6 clearly shows a peak at ca.  $t=17,000s$  caused by changing the inert atmosphere to oxidising atmosphere and the associated conversion of carbon. The gas analysis shown in Fig. 6 confirms this, e.g. the release of carbon dioxide is apparent at amu 44, 45 and 46.

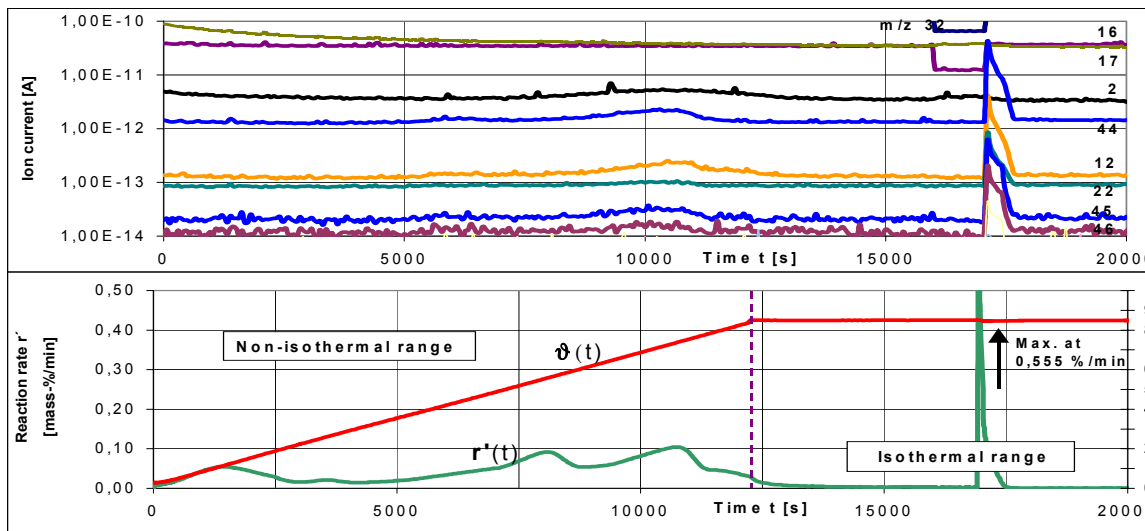


Fig. 6. Test 930: Reducing/oxidising, 4 K/min, cylinder.

## Temperature measurement inside the specimen

In experiments such as test 930 with an isothermal burning temperature of  $\vartheta=850^{\circ}\text{C}$  for

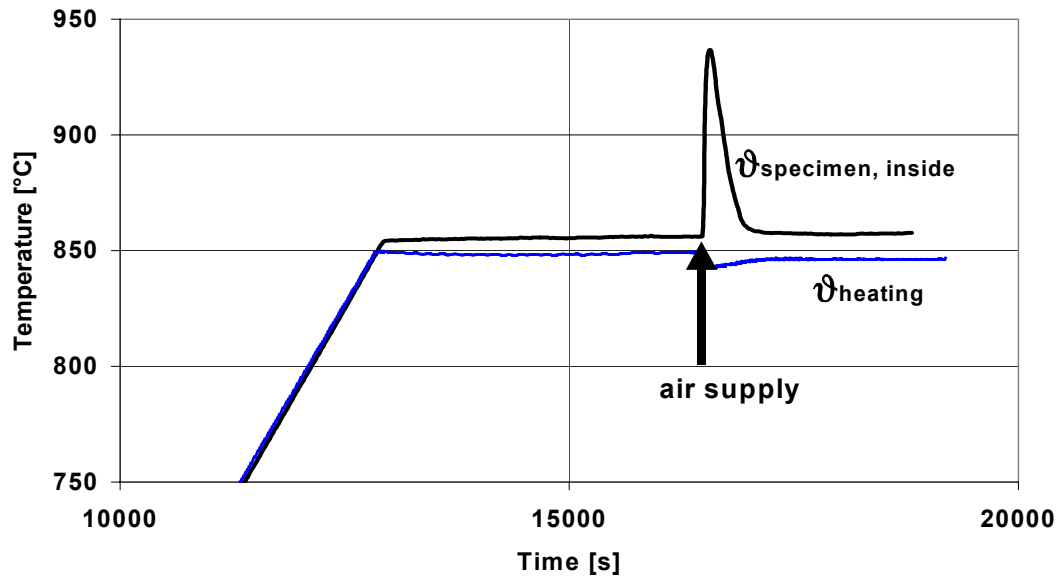


Fig. 7. Temperature inside of the specimen (process conditions similar to test 930, compare with Fig. 6).

the carbon conversion, a short-time temperature increase was reached with a maximum of ca.  $\vartheta\approx 940^{\circ}\text{C}$  corresponding to a temperature difference of ca.  $\Delta\vartheta\approx 80\text{K}$  to  $100\text{K}$ . The course of the temperature of the specimen was measured in a separate experiment under process conditions identical by those of test 930 (Fig. 6 and 7).

- **Compressive strength and bulk density**

The results are summarised in Fig. 8 with regard to the bulk density and compressive strength of the burnt specimens as an important objective.

Fig. 8 shows that the compressive strength of a specimen, which was burnt in inert atmosphere at first and then oxidised at isothermal temperatures in the range of ceramic burning, reaches values corresponding to the strength required for the product quality [6]. These specimens, characterised by filled triangles, circles or squares in Fig. 8 show higher values of compressive strength and slightly higher bulk densities than the specimens (blank triangles, circles or squares) burnt in an oxidising atmosphere from the beginning of the test. Furthermore, it can be seen in Fig. 8 that the specimens burnt only in inert gas atmosphere (filled black triangles, circles or squares) have high strengths which are still in fact above the values mentioned before. However, this burning behaviour does not have any practical importance because of the residual carbon content remaining after burning process.

For a further comparison of the results with the conventional burning process under oxidising atmosphere at temperatures of ca.  $\vartheta=1000^{\circ}\text{C}$ , the corresponding results

(black square in Fig. 8) can be used. The highest values of compressive strength and bulk density can be reached by applying this type of thermal processing. In both the continuously oxidised burning and the combined thermal mode of operation

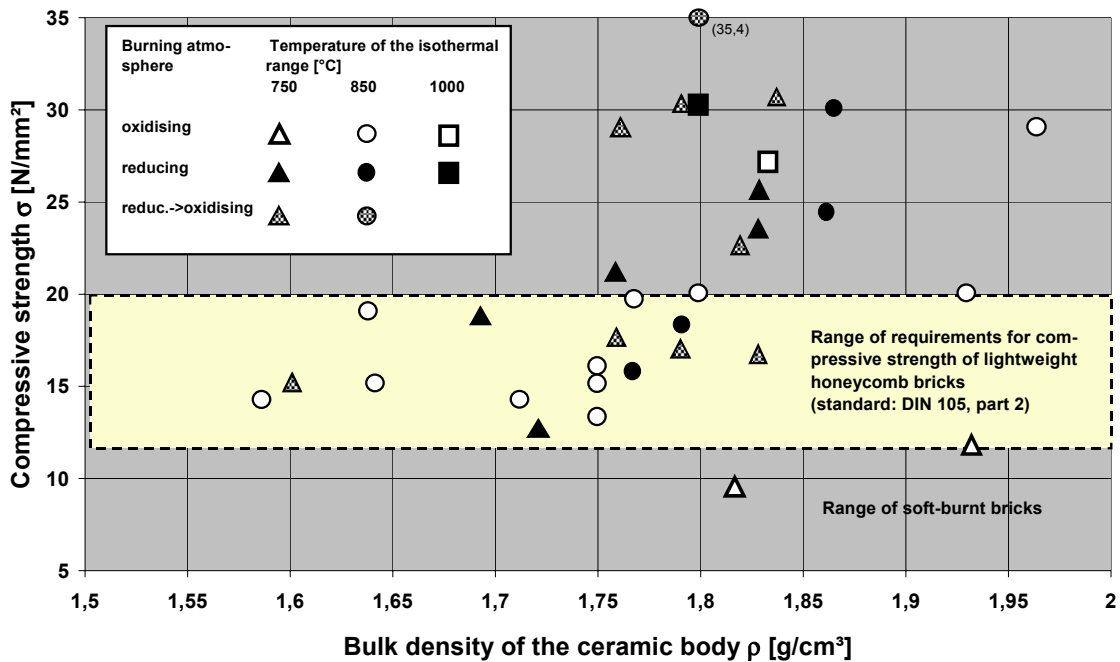


Fig. 8. Compressive strength of burnt specimen vs. bulk density.

with initially inert followed by a second oxidising atmosphere, the carbon content of the specimen will be converted completely. The analysis of the burnt specimens shows carbon contents of < 0.05 mass-%. When the continuous inert mode of operation is applied to temperature from  $\vartheta \approx 300^\circ\text{C}$  to  $800^\circ\text{C}$ , a small amount of carbon reacts with the reaction products of the ceramic burning process (e.g. water from the dehydration of clay minerals,  $\text{CO}_2$  from the dissociation of calcium carbonate).

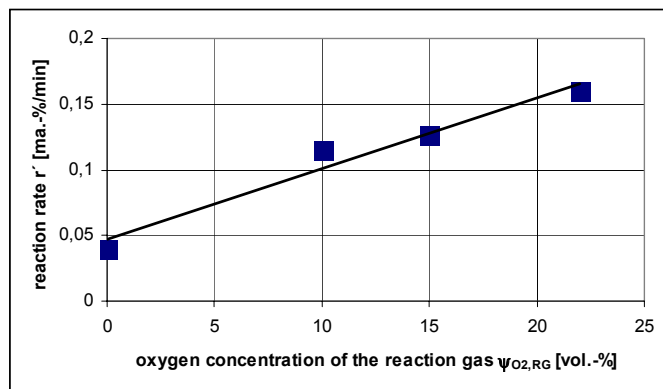


Fig. 9. Reaction rate vs. oxygen concentration.

The inert thermal processing of specimens with starting carbon contents of ca. 3.5 mass-% result in residual carbon contents (TOC) in the range of 2.4 and 2.7 mass-%. The dependence of the maximal reaction rate of the carbon conversion for continuously oxidised thermal treatment as function of the oxygen concentration  $\psi_{\text{O}_2}$  in the reaction gas is of interest with respect to the reaction mechanism. The linear dependence of the reaction rate vs. the oxygen concentration (Fig. 9) at the same temperature level ( $\vartheta_{\text{RG}} \approx 450^\circ\text{C}$ ) indicates that the reaction is diffusion-controlled (see for this e.g. [1, 2]).

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## Conclusions

From the investigations, two main conclusions can be drawn:

First, it appears impossible to obtain pore formation in the ceramic body and save primary energy without problems through the addition of pyrolysis coke to the ceramic batch in conventional tunnel kilns under continuously oxidised atmosphere with high oxygen concentration (e.g. air).

The reactions related to the carbon conversion are diffusion-controlled. However, they run in temperature ranges of  $\vartheta \approx 300^\circ\text{C}$  to  $550^\circ\text{C}$  in which the basic ceramic formation processes are just beginning or are not finished. This leads to a high risk of e.g. tension and consequently crack formation.

To reach the objective of pore formation in the body by addition of carbonaceous materials (e.g. here pyrolysis coke was used) with simultaneous reduction of primary energy demand, a corresponding variation of the process flow in thermal treatment is necessary. That means burning under inert gas atmosphere at first and then in oxidising gas atmosphere in a subsequent burning section. As the experiments show for such burning conditions, high strengths complying with the standards are attainable.

For the subsequent investigations of reaction mechanisms and of the influence of carbon addition, more laboratory experiments are needed before practical realisations can be carried out. This could result in new burning technologies.

It must be mentioned that the tunnel kiln technology - with oxidising mode of operation and use of treated and nearly carbon-free clay materials - developed in the last century to the state-of-the-art with regard to the history of burning bricks could be considered as a borderline case.

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Ausgabe August 1989.

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