

Kinetics of O₂-Chemisorption on Chars and its Relevance to Char Reactivity

Heinz-Jürgen Muhlen, Karl Heinrich van Heek, Harald Juntgen

Bergbau-Forschung GmbH, Franz-Fischer-Weg 61, 4300 Essen 13, F.R.G.

Abstract

O₂-chemisorption on char surfaces was investigated with special regard to the time-temperature-history of the material especially pyrolysis conditions (HTT: 700,800,900°C) and surface cleaning procedures in helium at elevated temperatures before chemisorption, the chemisorption temperature and the ambient O₂-pressure. The impact of the different parameters on the maximum amount of O₂ chemisorbed and the rates of chemisorption are discussed and the results are correlated to gasification rates in 40 bar steam determined at 750, 800 and 850°C and nonisothermally up to 950°C. Moreover the effect of combustion on O₂-chemisorption will be discussed.

Introduction

Chemisorption of oxygen on char surfaces to characterize char reactivity has been investigated intensively in the past (9,10,11). Most of the authors carried out the chemisorption at temperatures ranging between 20 and 200°C for an arbitrary chosen time, e.g. 23 hours, and they found fairly well correlations between the amount of oxygen chemisorbed and the reactivity as a function of e.g., the degree of burn-off measured in oxygen, as well as in steam, CO₂ and hydrogen (9,10,11). However, only little attention was paid to the impact of the chemisorption parameters applied as there are temperature, time allowed for chemisorption, preparation modality of the char or ambient O₂ pressure. Even less the kinetics of chemisorption were taken into consideration, whether it is controlled by chemical reaction or by diffusion. Although one cannot neglect the accessibility of active sites under the conditions applied for its determination, if one tries to correlate structural or chemical attributes of a material with reactivities.

The aim of the present work is therefore to contribute to the fundamental understanding of the processes involved during O₂-chemisorption and to improve this method for char characterization.

Experimental

For this study a thermogravimetric apparatus was employed which mainly consists of a balance (Sartorius model 4406) having a resolution of .001 mg. The sample is placed in the centre of an electrically heated steel tube and flushed continuously by pure helium during the cleaning and desorption period or by a mixture of helium and oxygen (79.1/20.9) during chemisorption.

The flow rates of the gases are adjusted by means of thermal mass flow controllers to .2 l/min (5,6)

To avoid weight errors induced by buoyancy of drag forces a special time-temperature-procedure was chosen which is illustrated in Fig. 1. At the beginning of each run the temperature is adjusted to a value equal to the chemisorption temperature T_s. After the weight signal became constant, i.e. after drying the temperature is increased up to the "cleaning temperature"

T_c . The duration of this period was chosen in such a way that there are only neglectable impacts on the char structure which otherwise could decrease the porosity (12) or the internal surface area (13), an effect which is well known as "thermal annealing". To which extent this thermal annealing can influence the reactivity can be seen from Fig. 10. Therefore we chose T_c 100°C lower than the heat treatment temperature (HTT), or if HTT was too low to assure that the surface can be cleaned properly, we took the value of HTT as T_c , and limited the time of cleaning to .5 hours. This could be done because the preparation of chars included 1 hour tempering after having reached HTT. Besides former experiments (1,2) have shown that an increase of pyrolysis time affects reactivity only slightly, if the residence time at HTT exceeds 1 hour.

After cleaning the temperature is lowered to T_s again and the gas flow is switched to the He/O₂-mixture which causes a small decrease in weight due to the higher gas-density of this mixture which causes a small decrease in weight due to the higher gas-density of this mixture compared to pure helium. O₂-chemisorption is then carried out for approximately 16 hours, after which the gas atmosphere is switched back to pure helium, the desorption performed at the same temperature used during cleaning. At the end of the experiment the temperature is decreased again to T_s . This procedure has the advantage, that the amount of oxygen taken up can be determined by both the difference between the periods C and E and the difference between starting and final weight signals in period D. Besides the difference B-F represents the carbon loss due to desorption and partial combustion and the difference F-G stands for the weight of carbon oxides desorbed during period E. Analysing these values one can determine which amount of the sample has been burnt, or if not any which composition (CO₂/CO) the desorption gas has had.

For the purpose of this investigation the char of a German bituminous coal "Westerholt" was ground to 100-315 microns and preoxidized in a fluidized bed under air for 24 hours at a temperature of 200°C in order to reduce the caking properties. Thereafter pyrolysis was carried out feeding the material into a preheated (700, 800 and 900°C) fluidized bed under argon. After a residence time of 1 hour the char was removed and stored. Proximate and ultimate analyses of the chars and the parent and preoxidized coal are given in Table 1.

To investigate the influence of the cleaning temperature on O₂-chemisorption the char prepared at 900°C was used after cleaning at temperatures ranging between 600 and 900°C. To investigate the temperature dependence of chemisorption the conditions were varied between 150 and 250°C for all chars. Lower and higher temperatures were not applied in order to avoid physisorption effects (8) and to keep the amount of char burned as small as possible. Moreover the partial pressure of oxygen was reduced in some experiments to determine the reaction order of chemisorption concerning oxygen.

RESULTS

Influence of cleaning temperature

In Fig. 2 the increase in weight as a function of time is shown for the different cleaning temperatures. It should be mentioned that the time for cleaning was such that as long as the weight signal needed to attain a

constant value. Therefore one would assume that after cleaning all active sites are available for the oxygen, however, Fig. 3 points out, that there still are occupied sites even after cleaning at 800°C. The total amount of O₂ taken up still raises, if T_s is increased from 800 to 900°C. This is shown in Fig. 2 which demonstrates further, that there exists a nearly linear relation between T_s and the amount chemisorbed during the first 16 hours. Also noteworthy is the fact that the shapes of all weigh curves seem to be identical, with the exception of the beginning.

Influence of chemisorption temperature

How chemisorption temperature influences the amount of oxygen taken up is shown in Fig. 4. For this series of experiments we fixed the cleaning temperature at 800°C for the 900°C char and at 700 for the 700 and 800°C chars. Starting with 150°C we varied T_s in intervals of 25°C up to 250°C. No higher temperatures were applied as during the chemisorption at 250°C almost 5% of the carbon has reacted and desorbed. Regarding the shapes of the weight curves can state that the sorption process is faster and that after 16 hours the slope of the curves has leveled off more the higher the temperature, indicating a more completed chemisorption. It can, however, not be deduced from these results whether or to which extent the equilibrium coverage with oxygen depends on temperature.

Influence of oxygen partial pressure

For the determination of the reaction order concerning oxygen, experiments were carried out using oxygen concentrations of 29.9, 10.5 and 5.3%. The results indicate that the reaction order is less than 1 as shown in Fig. 5 where the amount of oxygen taken up until the end of the run is plotted against the O₂-concentration of the He/O₂-mixture.

Discussion

Regarding the course of chemisorption, i.e. that the curve does not level off even after 16 hours at a temperature of 250°C, one can hardly imagine that all of the sites which are being covered after some hours or not yet after 16 hours are correlatable with reaction rates at temperatures twice as high than T_s.

Therefore we calculated the chemisorption rates on the basis of the weight curve and plot the logarithm of the rates as a function of time. As can be seen from Fig. 6, there is a fast reaction just at the beginning followed by a slower one indicated by the linear decrease of the graph after a time of 250 minutes. In order to determine the kinetics of these two reactions, i.e. to identify the processes involved, we tried to fit several kinetic models (3,4,8,9) and found that after approximately 20 minutes of chemisorption the weight curve can be described fairly well, assuming that diffusion is rate controlling. According to the study of Baumann, Klein and Juntgen (3,4) who have investigated the diffusion controlled chemisorption in the beginning as a square root law of time:

$$n(t) = n_{\infty} - \frac{12}{d} \sqrt{\frac{D_s \cdot t}{\pi}} \quad (1)$$

With:

$n(t)$ = O_2 -coverage at time t ; n_{∞} equilibrium coverage
 d = particle diameter; D_s = diffusion coefficient

and via an exponential function at the end of the sorption process.

$$1 - \frac{n(t)}{n_{\infty}} = \frac{6}{\pi^2} \exp \left[-4\pi^2 \frac{D_s \cdot t}{d^2} \right] \quad (2)$$

Both fitted the present data sufficiently which, however, is not significant enough. To confirm this assumption we plotted the logarithm of the rates concerned against temperature. In accordance we plotted the logarithm of the rates concerned against temperature. In accordance to theory the temperature dependence of the diffusion coefficient which in this case should be proportional to the rate can be described by:

$$D_s \sim T^{1.75} \quad (3)$$

Fig. 7 verifies this assumption. Since it is not correct to correlate chemical reactivities with amounts of oxygen taken up diffusion controlled, we focused our interest on the fast reaction subtracting the weight increase due to diffusion from the total increase in weight. One resulting weight curve is shown representatively in Fig. 8.

It is also interesting to examine the influence of cleaning temperature on chemisorption rate and to see whether it affects only the number of sites available or also their accessibility. For this purpose "diffusion coefficients" and diffusion corrected O_2 uptakes are compared in Table 2. Besides Fig. 9 shows the increase of the "diffusion coefficients" as a function of the amount of gases having evolved during the cleaning procedure. As can be seen from the picture this relation turned out to be fairly linear, whereas the "diffusion coefficients" seem to level off with increasing cleaning temperature. This means, that beyond a certain temperature a further increase in temperature only increases the number of sites available during chemically or diffusion controlled chemisorption.

Correlation with reactivities in steam

The reactivities of the chars under investigations were determined both isothermally and nonisothermally in 40 bar steam. A typical result is shown in Fig. 10 where the reaction rate

$$r_s = \frac{dX}{dt} (1-X)^{-2/3} \quad (4)$$

X = Degree of burn-off

is plotted as a function of burn-off for a gasification temperature of 750°C. The results depict that only in the beginning the reaction rates differ from each other and that after a certain time they narrow. An effect due to either thermal annealing of the char structure during gasification or the fact that in the beginning the unstable sites are gasified preferably and that already in the range of medium burn-off the structures of the different

chars became similar. These effects again point out how important it is to choose the correct cleaning time and temperature not to change the material under investigation.

For comparison we plotted therefore the first reaction rates versus the oxygen uptake during the fact chemisorption step as a function of cleaning temperature (s. Fig. 11). The relation seems to be linear in both cases for a cleaning temperature of 600 and 700°C. Both curves show similar slopes but different intercepts, as could be expected from the above mentioned. Next time it is planned to extend these correlations to a broader range of cleaning and chemisorption temperatures.

Conclusion

It could be shown that the O₂-chemisorption yield on chars produced from a German bituminous coal is affected to a large extent by diffusion processes and that its magnitude is influenced by the cleaning procedure which is absolutely necessary before chemisorption is carried out. Nevertheless the chars produced in different ways seem to behave similarly, i.e. whether they are cleaned at 600 or 700°C, the correlation with reaction rates depicts nearly the same slope. Therefore up to the time being only relative change in the reactivity of the chars originating from the same parent coal can be forecasted by chemisorption results, not the absolute magnitude of reactivity.

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| | Original coal raw | Original coal ox. | Pyrolysis temperature [°C] | | |
|--------------------|-------------------|-------------------|----------------------------|------|------|
| | | | 700 | 800 | 900 |
| Proximate analysis | | | | | |
| Moisture % | 2.1 | 3.3 | 0.6 | 0.4 | 0.2 |
| Ash, df % | 3.9 | 3.7 | 5.5 | 5.6 | 5.9 |
| VM, daf % | 37.4 | 34.6 | 4.1 | 3.6 | 1.5 |
| Char % | 62.2 | 63.2 | 89.8 | 92.8 | 95.0 |
| Elemental analysis | | | | | |
| C, daf % | 77.8 | 73.6 | 86.5 | 89.4 | 90.0 |
| H, daf % | 5.14 | 3.6 | 2.5 | 1.8 | 1.6 |
| N, daf % | 1.32 | 1.38 | 1.41 | 1.54 | 1.64 |
| O, daf % | 8.3 | 21.8 | 5.7 | 3.4 | 3.2 |
| S, daf % | 1.12 | 1.1 | 1.1 | 1.1 | 1.1 |

Tab. 1: Proximate and ultimate analysis of coal Westerholt and the concerning chars

| Cleaning temperature °C | Slope in the $w(t) - \sqrt{t}$ -diagram | Diffusion corrected amount of O ₂ mg / 100 mg C | Total amount of O ₂ mg / 100 mg C |
|-------------------------|---|--|--|
| 600 | $9.65 \cdot 10^{-3}$ | 0.347 | 0.778 |
| 700 | $1.73 \cdot 10^{-2}$ | 0.51 | 1.03 |
| 750 | $2.73 \cdot 10^{-2}$ | 0.561 | 1.16 |
| 800 | $3.94 \cdot 10^{-2}$ | 0.584 | 1.17 |
| 850 | $3.86 \cdot 10^{-2}$ | 0.655 | 1.42 |
| 900 | $3.67 \cdot 10^{-2}$ | 0.725 | 1.54 |

Tab. 2: Comparison of diffusion corrected and total O₂-uptake. Char Westerholt Chemisorption temperature 200 °C

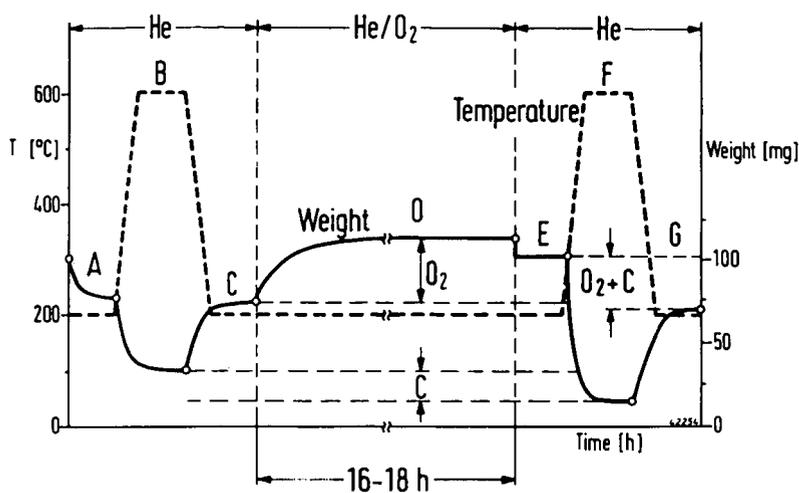


Fig. 1: Time-temperature-procedure for the determination of O_2 -chemisorption

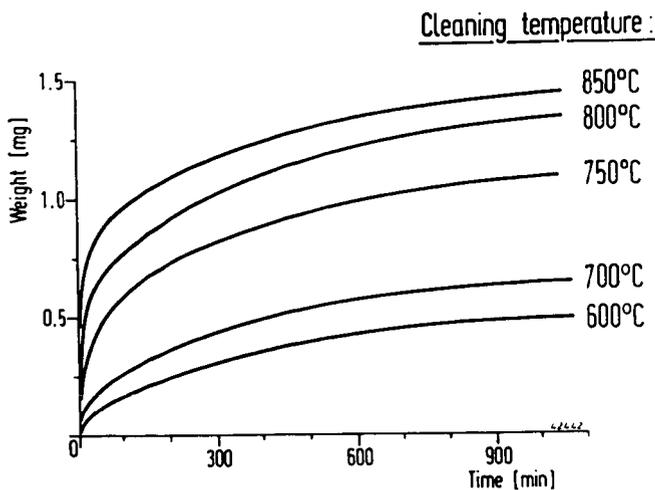


Fig. 2: Weight increase during O_2 -chemisorption on char Westerholt (HTT 900 °C) as a function of cleaning temperature

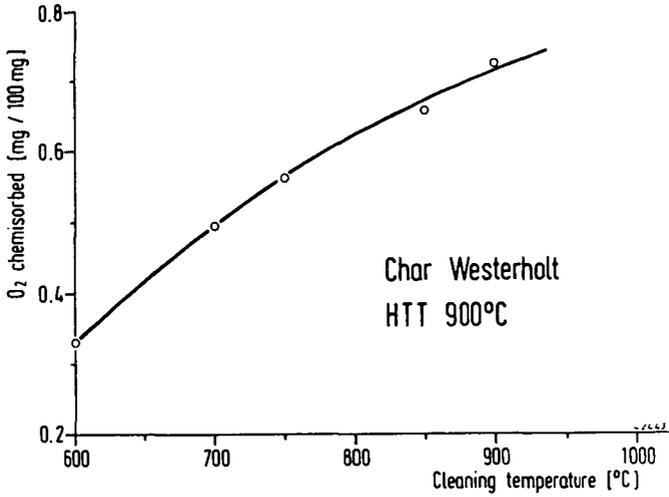


Fig. 3: Effect of cleaning temperature on the amount of O₂-chemisorption yield. Char Westerholt, HTT 900 °C, chemisorption temperature 200 °C

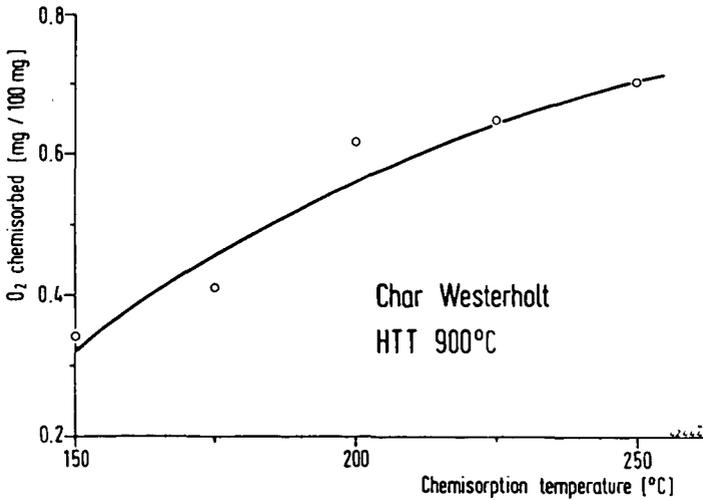


Fig. 4: Effect of chemisorption temperature on the amount of O₂ chemisorbed. Char Westerholt, HTT 900 °C, cleaning temperature 800 °C

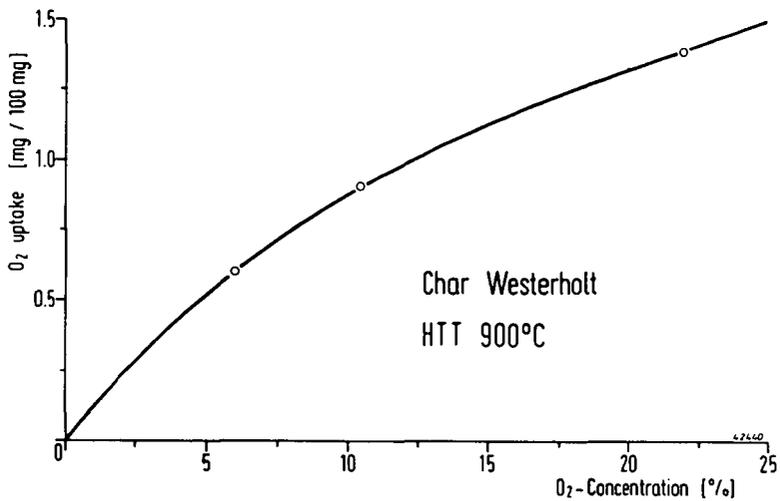


Fig. 5: Total O₂-uptake as a function of O₂-concentration. Char Westerholt, HTT 900°C, chemisorption temperature 200 °C

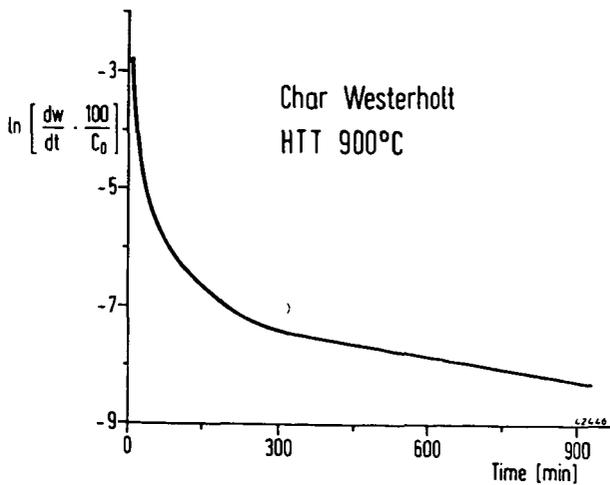


Fig. 6: Logarithm of weight increase with time during chemisorption at 200 °C. Char Westerholt, HTT 900 °C

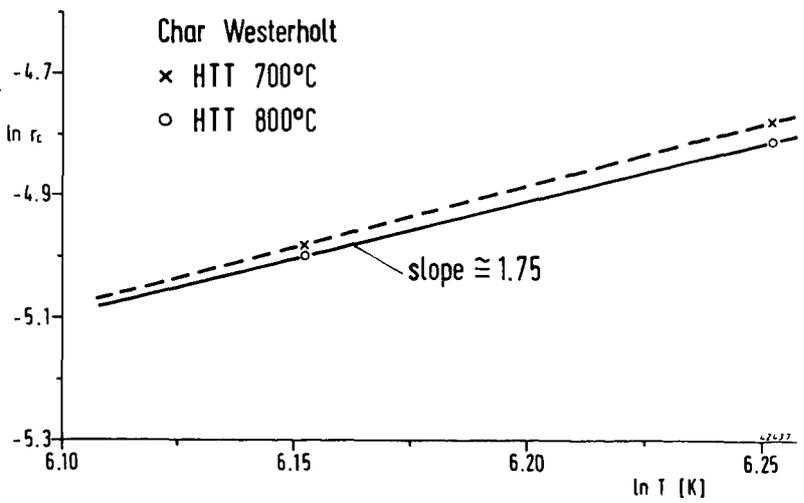
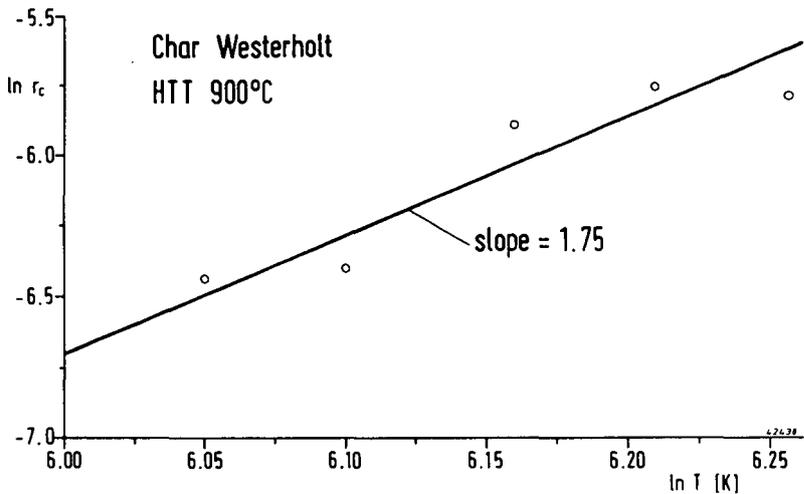


Fig. 7: Temperatur dependence of diffusion coefficients of chars prepared at a) 700, 800 °C; b) 900 °C

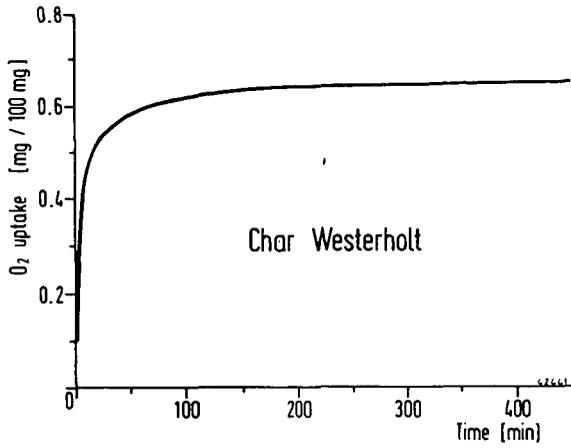


Fig. 8: Diffusion corrected weight increase during O₂-chemisorption on char Westerholt. Cleaning temperature 700 °C, chemisorption temperature 200 °C

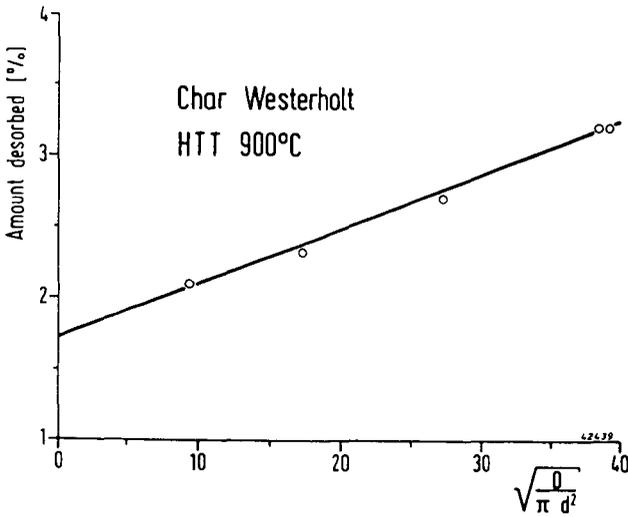


Fig. 9: Correlation between the slope of the $w(t) - \sqrt{t}$ - diagram and the extent of cleaning. Char Westerholt, HTT 900 °C

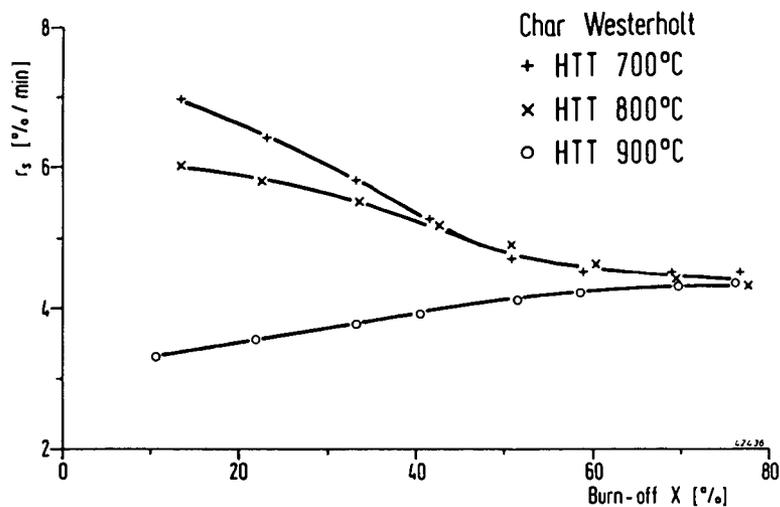


Fig. 10: Reaction rates of chars prepared at different HTT in 40 bar steam at 850 °C

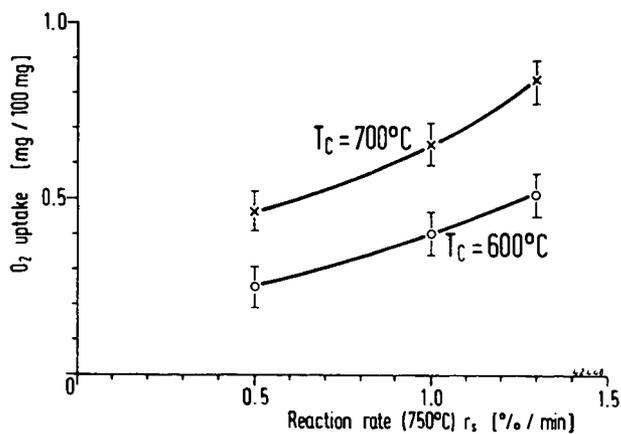


Fig. 11: Correlation of O_2 -uptake with initial reaction rates (750 °C) of chars prepared at 700, 800 and 900 °C. Cleaning temperatures 600 and 700 °C