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# Behaviour of C-based materials in contact with oxidizing gases

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# Behaviour of C-based materials in contact to oxidising gases

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**Abstract** - *C-based materials are used as basic components in high temperature energy systems like HTRs and fusion reactors. Beside their favourable properties (e.g. high thermal conductivity, high melting/sublimation point, high strength, good mechanical stability up to high temperatures, low density, low neutron absorption and high moderation/reflection capability), the carbon materials show decreasing oxidation resistance with increasing temperatures. This behaviour is especially of interest in systems where high temperatures dominate in a non-oxidising environment like vacuum vessels or inert gas controlled atmospheres. An ingress of oxidising gases (air or steam) into these systems leads to corrosion of the carbon components and, at least, to a worsening of the beforementioned properties. Experimental investigations with HTR fuel element matrix graphite (A3-3), nuclear graphite (V483T5), 2D-CFC (AO5), 3D-CFC (NB31 and NS31(doped with 8 – 10 % Si)) and others were done in air and steam in order to estimate their applicability in high temperature systems. The experiments were conducted at temperatures between 623 up to 1023 K in air and between 1173 and 1253 K in steam and took place under isothermal conditions, those in steam the chemical reaction controlled regime and those in air (additionally to the chemical reaction controlled regime) also in the in pore diffusion controlled regime. As expected, the results of these experiments show different oxidation behaviour in steam and in air, but no remarkably better oxidation resistance of the CFCs in comparison to the standard materials. On the other hand, the Si-doped NS31 has a reactivity, which is a factor of nearly 2 smaller than that of NB31 in steam and in air. The investigations in air reveal oxidation rate maxima for A3-3, NB31 and NS31: For A3-3 in air, even two rate peaks were found at 5% and 40 % burn off, which are explained by a selective oxidation of binder and filler graphite. In contrast to this observation, only one pronounced rate maximum (5 % burn-off, probably binder) was found for A3-3 during oxidation in steam. All other materials show less pronounced maxima in air and in steam. The rates during oxidation in steam at 1173 K correspond to those in air at temperatures of 873 – 923 K. The activation energies in steam appear to be higher than those in air for most materials, which was expected because of the endothermal character of the C/steam reaction.*

## I. INTRODUCTION

Due to the exceedingly mechanical and thermal properties of C-based materials, the basic components of high temperature energy systems like High Temperature Reactors (HTR) are made of graphite. These properties are e.g.: high thermal conductivity, high melting/sublimation point, high strength, excellent thermal shock resistance, low density, good mechanical stability up to high temperatures, low neutron absorption and high moderation/reflection capability. In contrast to that the C-based materials show a limited oxidation resistance at high temperatures when in contact with oxidising gases (air or steam). In safety analyses this behaviour has to be considered in case of air or steam ingress accidents at high temperatures. Oxidation occurring during these events may increase fission product release, may weaken the strength of components, and even may destroy protecting structures by the explosion of flammable mixtures formed. On the one hand, the frequency of a severe air ingress is extremely small; on the other hand, the extended safety concept of modern HTRs needs safety analyses (covering also) the ‘hypothetical’ frequency range. In steam cycle HTRs, steam/water ingress accidents belong to the design basis accidents and therefore, the degree of graphite oxidation has to be known for these kinds of accidents. As a matter of fact, the character of the steam/water reaction is endothermal, a burning-like process as would be possible in the event of an air ingress cannot occur. Carbon oxidation also takes place in the normal operating reactor, due to impurities of the cooling gas. Also in view of the lifetime of the graphite components (oxidation by impurities in normal operation of HTR) a selection of carbon materials has to take into account their oxidation resistance as an important criterion.

From 1985 -1998, when only limited effort was spent into HTR development, interesting new materials were designed: Carbon fibre composites and mixed materials were developed for other purposes and are already foreseen to be used in fusion reactors. This paper deals with oxidation measurements on selected carbon materials in air and in steam, which are relevant for HTRs, and also with innovative carbon materials, i.e. CFC-materials and mixed carbon materials with Si. This will support the design and selection of C-based materials for HTRs.

## II. EXPERIMENTS

The experimental investigations were done in different facilities, depending on temperature, oxidising gas and the needed gas flow rate: Long term experiments at low temperatures in air (673 – 773 K) were performed in an annealing furnace with natural gas convection. For higher temperatures (833 – 1253 K) and a gas flow rate between 6 – 12 l/h (< 0.01 m/s) a thermogravimetric apparatus (THERA) was used (Fig.1).

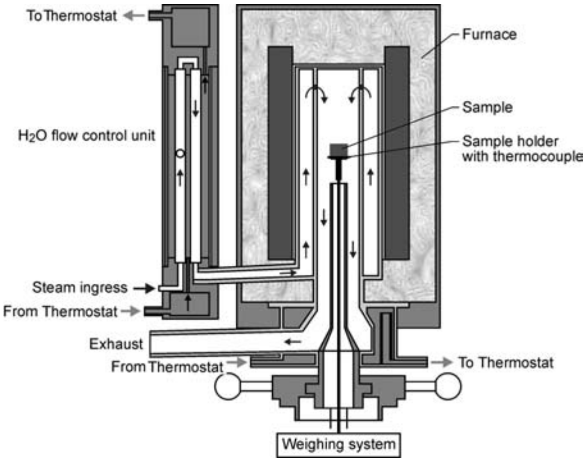

**Fig. 1:** Scheme of the experimental unit of the THERA facility

This facility is an simultaneous thermal analyser where the experimental unit is coupled with the weighing system. So the weight loss of the investigated material can be measured directly during oxidation. The samples used in THERA are small roughly cube shaped pieces of maximum 250 mg. Experiments with higher gas flow rates (up to 310 l/h = 0.5 – 1 m/s in the specimen) take place in the INDEX facility (Fig. 2). This apparatus is an inductive heated oxidation experiment and was used for investigations in steam at 1273 K. The INDEX-samples are tube shaped with an outer diameter of 20 mm, an inner diameter of 10 mm and a total length of 30 mm. Here the oxidation reaction takes place at the surface of the inner borehole and the total weight loss is defined –due to preferential surface oxidation- by the weight difference in relation to the oxidation surface.

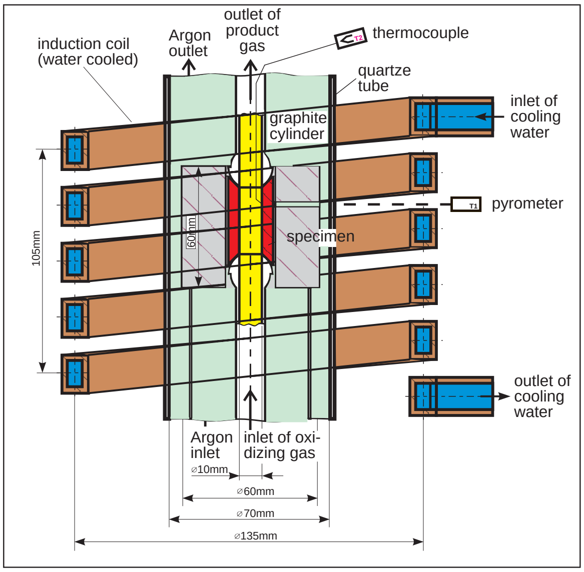

**Fig. 2:** Scheme of the central part of the oxidation facility INDEX

All experiments are executed under isothermal conditions. During experiments the composition, flow rate and partial pressure of the reaction gas are held constant. The investigations were done in the chemical reaction controlled regime I (THERA) and in the in pore diffusion controlled regime II (INDEX) (see box). In regime I the experiments were performed between 673 – 1073 K in air and between 1173 – 1253 K in steam. Regime II measurements in steam are done at 1273 K. Former regime II measurements in oxygen [1,2,3] cover a temperature range of 923 – 1123 K. The partial pressures diversified between ambient in the annealing furnace and (THERA /INDEX) 1 bar in air respectively a slightly overpressure of 1.05 / 1.1 bar in steam to inhibit air ingress into the cavity. Experiments in THERA and in the annealing furnace were stopped after achieving a total weight loss of about 60 – 90 % which corresponds to a run time between 8 – 1300 h in air and between 18 – 45 h in steam.

Carbon oxidation:

In reactions between gases and homogeneous porous solids with gaseous products 3 reaction zones have to be distinguished [4,5,6]:

Regime I: at low temperatures the chemical reaction itself is the rate limiting step and the material is oxidised homogeneously within the pore system, which leads to a severe loss of mechanical strength. A strong dependence of the volume related rate on burn-off with a maximum is found, because of the changing of the reactive surface during oxidation.

Regime II: at intermediate temperatures consumption of oxidising gases within the pores becomes important and the oxidation attack becomes smaller in depth of the material. The temperature dependence of the chemical process is much larger than that of the competing in pore gas diffusion, which together leads to a decrease of the activation energy compared with regime I. A concentration and a burn-off gradient within the carbon is found.

Regime III: at high temperatures external mass transfer to the outer surface is the rate limiting step and the reaction is restricted to the geometrical surface only; the kinetics is not influenced by properties of the solid.

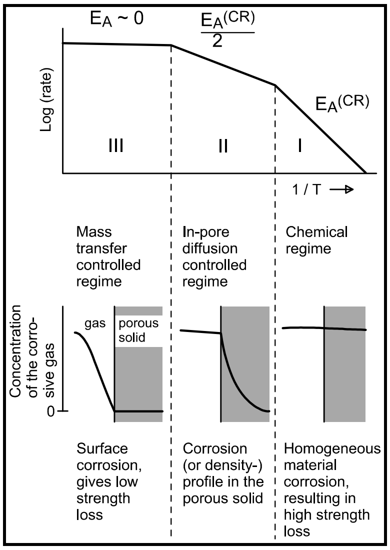

**Fig. 3:** Schematics of oxidation regimes

*II. A. Investigated material*

The investigated C-based materials are listed in Tab. I with their Si-content. All graphite materials are fine grained and consist of about 90 % matrix graphite and 10% of different binder material, the latter being coked but not graphitised in A3. In case of the V483T and the ASR-graphites the filler and binder materials are formed of the same pitch coke.

The CFC materials have, according to the direction of the fibres, to be subdivided in two-directional (2D-CFC)and three-directional (3D-CFC) materials. These materials are the 2D-CFC AO5, and the 3D-CFCs N31/NB31, NS31 (doped with 8 – 10 % Si), INOX A14 (+ 40% Si) and NOVOLTEX (+ 40 % Si). The doping of Si into the CFCs, as well as into the SiC 30 mixed graphite during fabrication by injection of liquid silicon implicates a higher density and lower porosity. This doping is agreed to increase the oxidation resistance of the material by formation of an impermeable $SiO_2$ layer in course of oxidation.

**Tab. 1:** Investigated material

| **Material** | **Density [kg/m$^3$]** | **Ash-content** | **Si-content [%]** |
|---|---|---|---|
| HTR-graphites | | | |
| **A3-3** | 1730 | ≤ 60 ppm | - |
| **A3-27** | 1740 | ≤ 60 ppm | - |
| **V483T** | 1810 | 200 – 340 ppm | - |
| **ASR-1RG*** | 1790 | 1500 ppm | - |
| **ASR-1RS*** | 1820 | 200 ppm | - |
| Mixed graphite material | | | |
| **SiC 30** | 2650 | < 0,1 % | 30 |
| CFCs | | | |
| **AO5** | 1870 | < 200 ppm | - |
| **N31/NB31** | 1920 | < 0,1 % | - |
| **NS31** | 2120 | < 0,1 % | 8 - 10 |
| **INOX A14** | 2100 | < 0,1 % | 40 |
| **NOVOLTEX** | >2000 | < 0,1 % | 40 |

* = published in [7]

## III. RESULTS

The experimental investigations in air and in steam show clearly a different oxidation behaviour as well material as oxidising gas dependent.

*A3-27 / A3-3:*

These two fuel element matrix graphites are, as is visible in Tab. 1, very similar and can be considered together. During oxidation in air two rate maxima can be observed at 5 and 35 % burn off in regime I at the whole temperature range between 673 – 1023 K. The observed rate maxima can be explained by a selective binder-filler oxidation: Because of the incomplete binder graphitisation, its reactivity is higher than that of the well graphitised filler; so the oxidation behaviour of two different materials are portrayed: The first peak at 5% burn off is due to the oxidation of the binder, at 35% burn off the second peak shows the oxidation of the filler graphite. This behaviour is given at the example of A3-27 in Fig. 4.

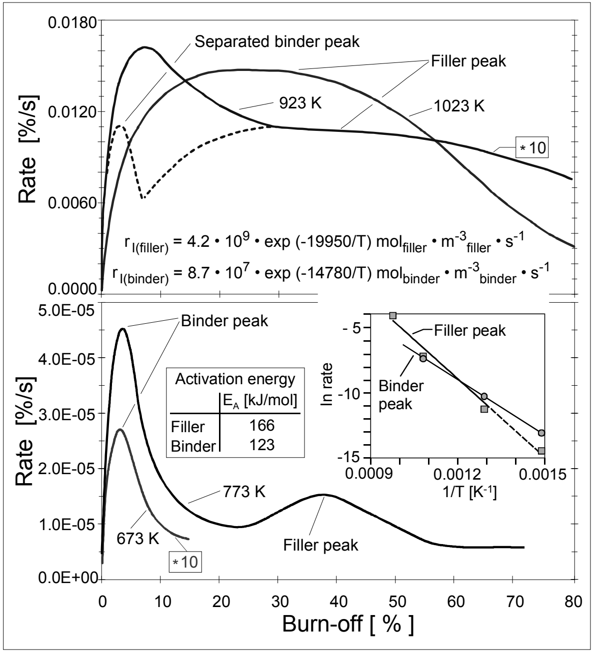

**Fig. 4:** Oxidation in air of matrix graphite A3-27 [4]

At higher temperatures the second peak becomes more pronounced and the binder peak vanishes. The activation energies are different for binder and filler graphite (Fig. 4). Here the lower activation energy of the binder is responsible for the vanishing of the binder at higher temperatures. Experiments in air in regime II [4] reveal apparent activation energies substantially larger than one half of the values of regime I reported here, which is not in line with the respective (simplified) theory.

The oxidation behaviour of A3-3 in steam is not as easy to explain: There is a maximum at 5 % burn-off, which is obviously connected to the binder, but the activation energy associated to these peaks (191 kJ/mol) is not -as expected- smaller than that at high burn-off (filler) but higher in comparison to the activation energy of the binder in air. A pronounced filler peak is not observed (Fig. 5).

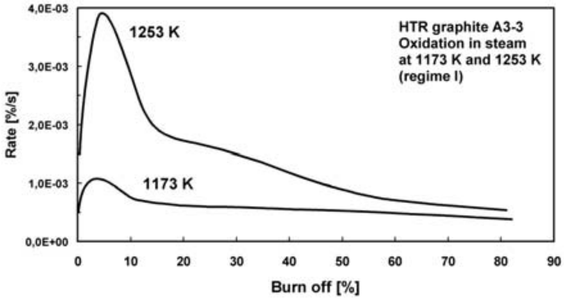

**Fig. 5:** A3-3: Burn off vs. rate at 1173 and 1253 K (steam)

*V483T:*

This HTR graphite shows at oxidation in air a rate increase up to 40 % burn off followed by a linear decrease in regime I (Fig. 6). Here an increase factor of 4 between virgin material and rate maximum can be observed. The activation energy is 166 kJ/mol. For low burn off values at a temperature of 773 K the lowest reactivity of all materials examined was found for the V483T.

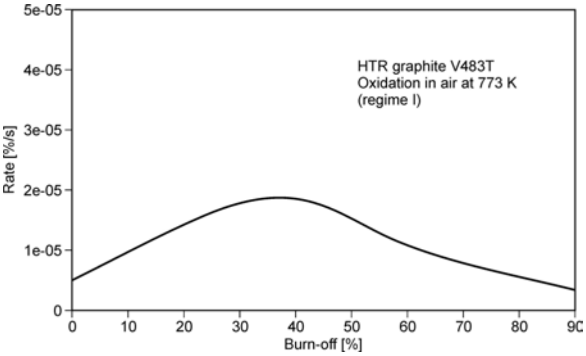

**Fig. 6:** V483T: burn off vs. rate (relative) at 773 K (air)

In steam the V483T5 shows a very less distinct maximum at burn off rates of 50 % at 1173 K (Fig. 7). Here the curve progression is –except of the binder peak – very similar to that of the A3-3 at the same temperature (see Fig. 5).

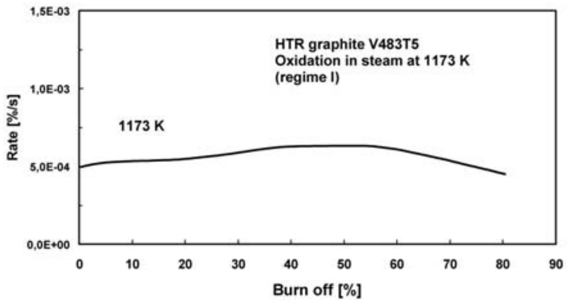

**Fig. 7:** V483T5: Burn off vs. rate at 1173K (steam)

*SiC 30:*
The Si-doped SiC 30 shows at intermediate and high burn-off the lowest reactivities at 773 K in air. In long term experiments with a run time of 1300 h this material reaches only 10 % burn off. Here it should be noticed, that at low temperatures and burn off values > 5 % the doping of Si is leading to substantially improved oxidation resistance compared to the other investigated graphites without Si.

*AO5:*
During oxidation in air a rate increase with increasing burn off can be observed. An example for this behaviour is given in Fig. 8 for 1032 K. In this case the rate increase of AO5 is about a factor of 2.2 to a maximum of 30 % burn off. The activation energy is 150 kJ/mol.

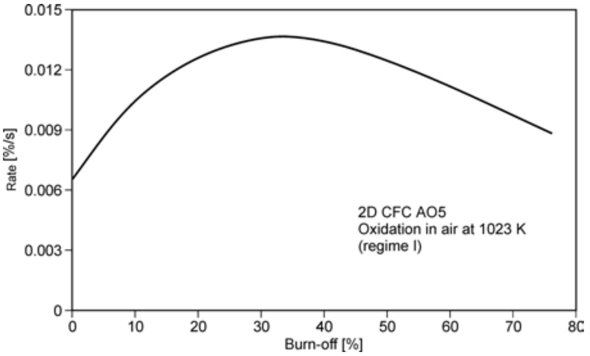

**Fig. 8:** AO5: burn off vs. rate at 1023 K (air)

In steam a less pronounced rate maximum was determined for AO5 at 1173 and 1253 K (Fig. 9). These values are very close to that of the 3D-CFC NS31 (see Fig. 12) and obviously smaller than that of the NB31 (Fig.10).

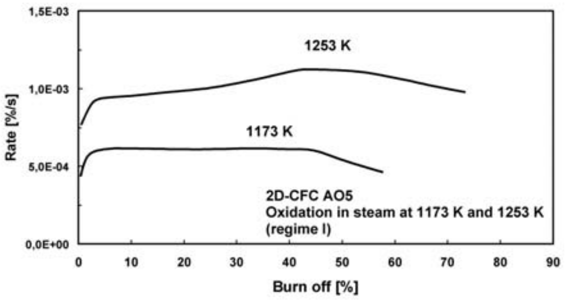

**Fig. 9:** AO5: burn off vs. rate at 1173 and 1253 K (steam)

*N31/NB31:*
The 3D-CFC materials show at investigations in air at 773 K relatively high burn off values in relation to other investigated HTR graphites and CFCs. In long term experiments a burn off value of 70 – 80 % was reached between 800 – 1000 h, whereas the other materials reach at maximum 50 % burn off in the same time span. This comparatively high rate is probably due to the low heat treatment temperature of the matrix.

In steam this material shows a pronounced maximum at 20 % burn-off for 1253 K, whereas this maximum is less pronounced at 1173 K (Fig. 10). The activation energy for 20 % burn off is 216 kJ/mol.

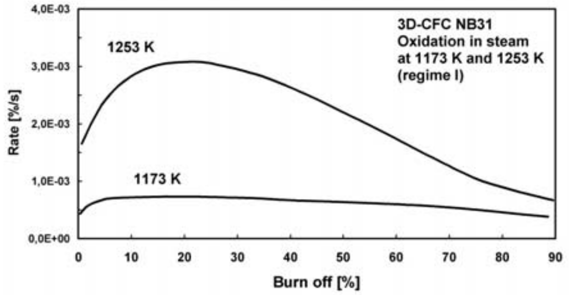

**Fig.10:** NB31 burn off vs. rate at 1173 and 1253 K (steam)

*NS31:*
Experiments on the Si-doped 3D-CFC reveal a rate maximum at 15 % burn off at 1023 K in air in regime I (Fig 11). Here the weight change stems from C burn off and from the generation of solid $SiO_2$. An activation energy of 175 kJ/mol was evaluated for the rate maximum. The oxidation rates of NS31 are not smaller than that of AO5 or V483T, but a factor of 2 smaller than that of the undoped 3D-CFC N31.

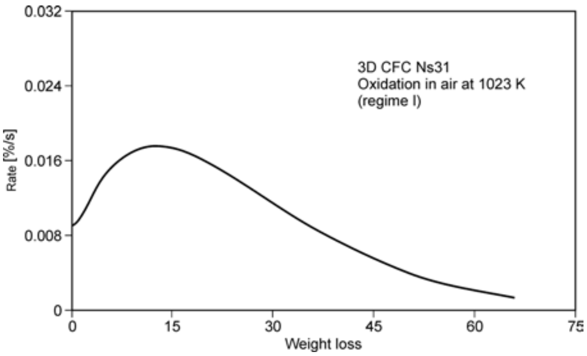

**Fig.11:** NS31: weight loss vs. rate at 1023 K (air)

Except by the rates being a factor of about 2 smaller the behaviour of NS31 in steam is very similar to that of N31/NB31 (Fig. 12). Here the maximum is less pronounced at 1253 K. The activation energy is only 160 kJ/mol at 10 % burn off.

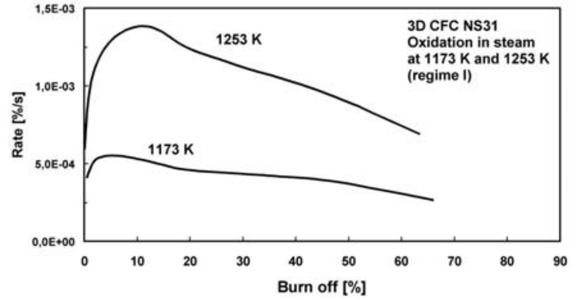

**Fig. 12:** NS31 burn off vs. rate at 1173 and 1253 K (steam)

*INOX A14 / NOVOLTEX and others(regime II):*
For INOX-A14 and NOVOLTEX only experiments in steam at 1273 K (regime II) are available up to now. In Fig. 13 the results are compared with those of other materials.

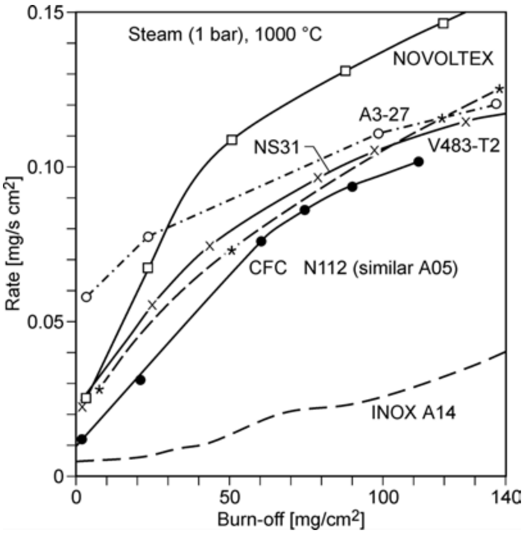

**Fig. 13:** regime II experiments in steam at 1273 K

A remarkable low reactivity in steam was found for INOX A 14. The NOVOLTEX (with a similar Si-content) did not show this low reactivity. Rates of NOVOLTEX are by far too high, compared with all other materials, which means, that this material is not yet optimised in the development stage examined here. Rates of NS31 are similar to those of V483T2 (which is an earlier development stage of V483T5 and shows a higher reactivity).

## IV. CONCLUSIONS

The experimental investigation of the oxidation kinetics show:

- Ungraphitized binder/matrix has to be treated as a separate component because of its remarkably different oxidation behaviour.
- Not only the amount of Si determines its ability for oxidation protection, but also its distribution within the material.
- The oxidation behaviour of homogeneous materials in regime I is charaterized by a continuous rate versus burn off curve with one (more or less pronounced) maximum.
- Whereas the shape of rate versus burn off curves is roughly similar in air and in steam, the rates differ remarkably: Achieving similar rates in regime I as in air requires for steam oxidation about 250 K higher temperatures.
- Inhibition by hydrogen/CO remains to be measured for steam oxidation.

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