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Industrial oxygen measurement under air deficiency – a paradox?

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Industrial oxygen measurement under air deficiency – a paradox?

Apart from the generation of heat, fuel is also used to produce inert gas atmospheres in certain technical processes. Hereby, interesting thermo-chemical and thermo-physical reactions are exploited for the purpose of process optimization. Quality assurance expects repeatable process results, which can only be achieved via interventions in the process control system. Such a combustion application for the reduction of metals is discussed below, and is then illustrated in the form of a control diagram.

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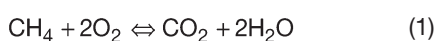
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Introduction

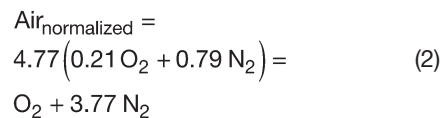
In general, the term «combustion» is associated with the generation of heat, rather than with the oxidation or molecular conversion of a fuel. During such a conversion or reaction, new substances are created, which have nothing in common with the original product – they have other physical and chemical properties. A typical example in this context is the change in volume frequently encountered with gases.

With certain thermal processes, such as e.g. firing of ceramics, annealing of metals, etc., combustion is coupled directly with the heat treatment process. Hereby, combustion is subjected to conditions that support the process or are even prerequisites for it. In order to make qualitative assessments, e.g. by means of a system analysis, the actual combustion process must be separated from the engineering process. All the properties required for the engineering process should be listed next to the properties that characterize the combustion process, enabling the overlap to be determined.

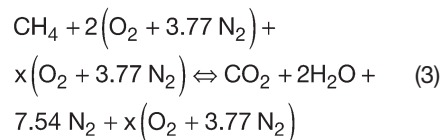
This article describes the reduction of a metal oxide by means of combustion gases. Using this approach, combustion is examined in more detail, whereby, for the sake of simplicity, pure methane gas is assumed as fuel. The following basic reaction will then result:



Consequently, during the combustion with (normalized) air, this leads to:

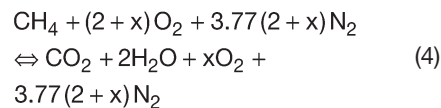


If excess air x is assumed, we get:

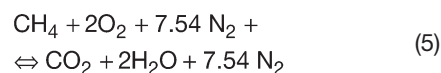


From this, 3 cases can be derived:

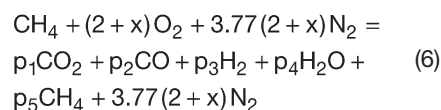
1. Case: Over-stoichiometric combustion with $x > 0$



2. Case: Stoichiometric combustion with $x = 0$



3. Case: Sub-stoichiometric combustion with $-2 < x < 0$



whereby

$$p_i = f(\vartheta).$$

Consequently, the obvious procedure is to assess the quality of this reaction by means of an oxygen measurement. This applies in particular, if the technical process depends on the oxygen or its reactivity, or if the energy balance of the combustion is to be evaluated.

For Case 1, investigating the oxygen activity by means of an oxygen measurement is self-explanatory. In Case 2, it is possible to assume a condition of “no oxygen”. However, in Case 3, in which no free oxygen is present, an oxygen measurement seems to be out of the question at the first glance. But this problem can be solved elegantly by the use of oxygen sensors based on the principle of potentiometric zirconium oxide.

Oxygen measurement principle

At temperatures above 600 °C, zirconium dioxide, a ceramic material, is used as an oxygen ion conductor. Hereby, oxygen ions are formed on a conductive layer, which usually consists of platinum.

As the oxygen concentration in a gas sample determines the number of ions generated, it is therefore decisive for the measure of oxygen activity.

The basic design of a sensor involves an ion conductor with contact surfaces on both sides. One side is in contact with a reference gas, e.g. air, and the other side with a sample gas. The sensor's mecha-

nical construction prevents the two gases from mixing.

Depending on the application, heated or unheated sensors are used. Unheated sensors are used mainly in furnaces, whilst heated sensors are required for applications in which the temperatures of the sample gases are below 600... 700 °C (the measurement principle requires a minimum temperature of 500...650 °C).

At the required temperature, the ratio of the oxygen partial pressures on both sides of the oxygen ion conductor results in a voltage.

This voltage can be calculated according to the following formula (Nernst equation):

$$EMF = \frac{R \cdot T}{4 \cdot F} \cdot \ln\left(\frac{P_1}{P_2}\right) \quad (7)$$

whereby:

R = 8,31 J/mol K

T = temperature in Kelvin

F = 96493 As/mol

P₁ = oxygen partial pressure of the reference gas at 0.20946 bar

P₂ = oxygen partial pressure of the sample gas

EMF = electromotive force in volts

In a practical test setup with an oxygen measuring device, the oxygen measurement value represents the process, and is therefore of interest. This value is determined from (7) as:

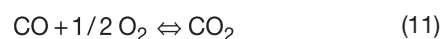
$$P_{O_2} = 0.2094 \cdot 10^{\frac{-20.166 \cdot EMF}{T}} \quad (8)$$

whereby P_{O₂} is the oxygen partial pressure in bar or, if multiplied by 100, a percentage of atmospheric pressure. For all further considerations in this report, the logarithmic value of the oxygen partial pressure will be used.

$$\log P_{O_2} = -0.68 - 20.166 \cdot \frac{EMF}{T} \quad (9)$$

This mathematical conversion permits a graphical representation of the oxygen "concentration" to be made, starting with percentage values, through ppm values, down to molecular values. Oxygen measurement in the sub-stoichiometric area in order to establish a relationship with the oxygen partial pressure for Case 3, the relevant reaction equations will now be drawn up.

$$\frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{0.5}} = k_1 \quad (10)$$



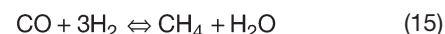
with

$$\frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{0.5}} = k_2 \quad (12)$$



These equations show the oxygen partial pressure that corresponds with all the reaction partners. Consequently, it can be considered as a basic value.

$$\frac{P_{CH_4} \cdot P_{H_2O}}{P_{CO} \cdot P_{H_2}^3} = k_3 \quad (14)$$



k_i = f(θ) (to be found in the pertinent books of tables [1])

The partial pressures p_i are then calculated with the help of these equations, whereby the aggregated material balance (ψ_C, ψ_H, ψ_O) for C, H, and O, as obtained from equations 10-14, must be resolved, thus supplying additional equations for the equation system. The method of finding a solution is very complex, so that the result will only be shown graphically. Hereby, "lambda" is introduced as a new value for the x-axis, which is defined as

$$\lambda = \frac{\text{effective air qty.}}{\text{theoretic air qty.}}$$

The lambda scale of the x-axis is linear, and covers the entire range from oxidizing to reducing combustion. The advantages of this representation (Fig. 1) become evident during signal recording and for control purposes.

If the lambda definition is applied to equations 4 and 5, it is easy to determine lambda.

leads to λ > 1 for x > 0; λ = 1 for x = 0, λ < 1 for -2 < x < 0

$$\lambda = \frac{2(O_2 + 3.77 N_2) + x(O_2 + 3.77 N_2)}{2O_2 + 7.54 N_2} \quad (16)$$

The y-axis represents the oxygen partial pressure that is measured with an oxygen sensor or is calculated according to (9). When all the components have been calculated according to the above equations, conclusions can be drawn about the amount of applied oxygen or air. The next step for determining lambda is then just a simple calculation of percentage.

Note:

The above description assumes that the equation system is based on standard pressure, mol volume or standard volume, and on thermodynamic equilibrium.

Practical application example

In a practical example, a metal oxide is to be reduced at 800 °C. This can be done with a medium that has a moderate

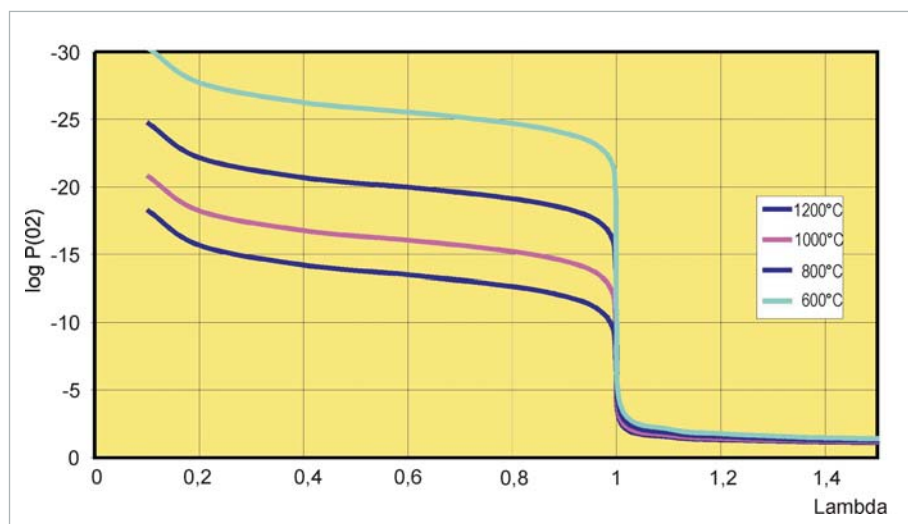


Fig. 1: Curves for oxygen partial pressure versus excess air ratio "lambda" (λ)

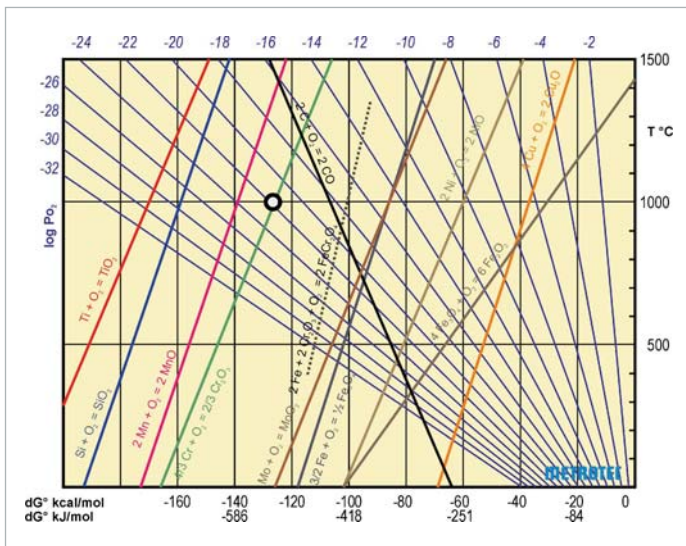
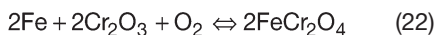
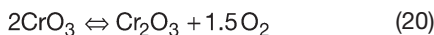
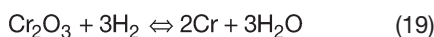
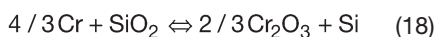


Fig. 2: Nomograph of oxygen partial pressure versus the mol-specific enthalpy

Ti, Si, and Mn. Moreover, Fig. 2 can be used to establish that other reaction partners, as mentioned in (22) for example, will shift the equilibrium of oxygen partial pressure by several orders of magnitude. It is therefore important to know which material is used with what alloy percentages (mol fraction), and which oxidation stage is to be achieved.

The resulting value of -21.83 from (25) means that this is the neutral point regarding the metal/metal oxide reaction. In other words: Neither will a metal be converted to an oxide, nor will a metal oxide be reduced. To reduce a solid metal oxide, the oxygen partial pressure existing in the atmosphere at 1000 °C must be less than -21.83 (and more for its oxidation).

tendency to oxidation, e.g. chromium, as will be used in our example. For this, the following reactions are listed as possibilities for reduction:



Using (21) and a temperature of 1000 °C for a better representation, we will demonstrate how the chromium reduction quality can be determined by means of a mathematical evaluation without taking the reaction kinetics in a pure

chrome/chromium oxide system into account.

Using the relationship (23) $\Delta G^0 = \Delta H^0 - \Delta S^0 \cdot T = -744 + 0.167 \cdot T \rightarrow$ at 1000 °C -531 (J/mol) [thermodynamic data from book of tables, e.g. [2]] as well as (Equ. 24) $\Delta G^0 = -R \cdot T \cdot \ln P_{\text{O}_2}$, and equating ΔG^0 plus resolving to $\ln P_{\text{O}_2}$ results in a P_{O_2} of $1.59 \cdot 10^{-22}$ (bar O_2) or (25) $\log P_{\text{O}_2} = -21.83$.

This result is comparable with the value found in the diagram (Fig. 2) at the intersection of the straight line for chrome/chromium oxide at 1000 °C with the oxygen partial pressure line. Similarly, the diagram can be used to determine the reduction with media that have a moderate tendency to oxidation. This includes all the substances that can be entered to the left of the chrome/chromium oxide line, whereby Fig. 2 shows

To resolve a technical processing task, in which a certain oxidation potential must be obtained in the atmosphere by means of gas combustion, it is now possible to establish a link with reductive combustion. The measured oxygen partial pressure, which was linked to the lambda, as demonstrated above, can thus be used for a qualitative evaluation and to reproduce this process condition.

The described basic procedures can be applied easily to similar processes and tasks that go beyond the case examined here (Fig. 3).

Control engineering concept

In the following, we will discuss only the control system for the reducing atmosphere (Fig. 4). All other associated control loops, e.g. for stocking, control and batching of feedstock, various filter sta-



Fig. 3: Prototype of a plant. Since the process had not been implemented before, this project was executed as a pilot plant with support from the Ministry of Economics of the Federal State of Saxony (photo by courtesy of Industrieofenbau Aue GmbH, Mentec GmbH)

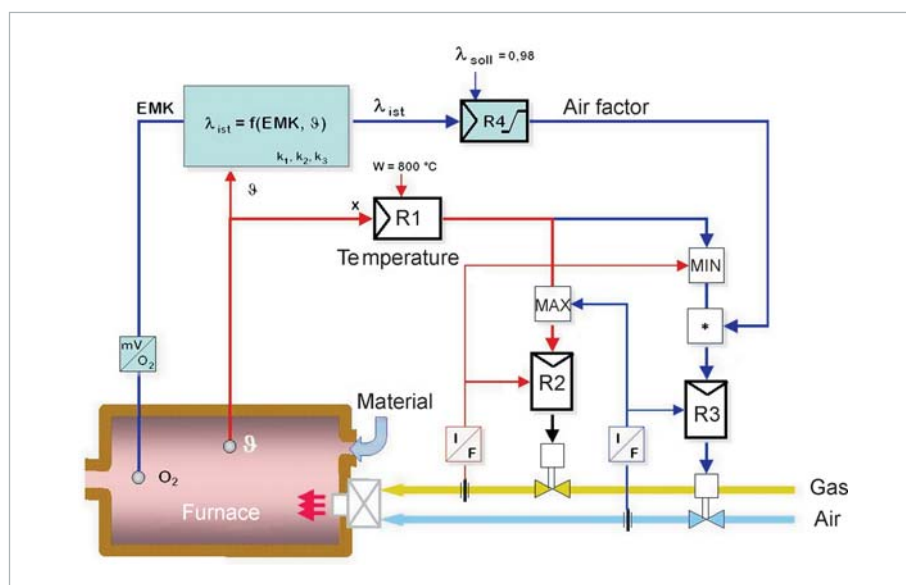


Fig. 4: Control concept of the reduction process

ges, afterburner, heat exchanger, etc., will not be dealt with. Similarly, limit monitoring and sequential process control will not be considered.

The purpose of control technology is to create a furnace atmosphere with specified, uniform properties within tight tolerance limits, thus enabling reliable results to be obtained for process quality and performance. The atmosphere's reduction potential will be selected as a quality benchmark, which can be influenced by means of the air ratio factor $\lambda = f(O_2, \vartheta)$.

Based on the oxygen measurement (EMF), the coefficient k_i and the equations for the partial pressures p_i the ratio factor λ will be calculated as described, and applied to the controller R4 as process variable. First, however, the process must be brought to a constant temperature (preparatory phase). This is

handled by the master temperature controller R1, which demands more/less air from the coupled gas/air ratio controllers (R2 / R3).

Extremely important hereby is that a corresponding air deficiency is always present in the atmosphere. I.e., when the temperature controller demands more input, the gas valve must be opened first, which is then followed by the air valve.

Conversely, the air flow must be reduced first, followed by the gas flow. This is ensured by the Min/Max signal monitors, which block the corresponding demands for change until the respective other flow has followed (interlocked flow control). A special feature worth mentioning is, that in order to comply with environmental regulations, excess air must always be ensured during start-up, which means that the Min/Max monitoring function must be reversed during this phase.

When specifying the flow ranges for the stoichiometric ratio, all standardized signals of the flow control loops are in equilibrium; consequently, the air ratio factor $\lambda = 1$.

Feedstock charging may not begin before the working temperature required for the chemical reaction has been attained, so that the continuous reduction process can start. Simultaneously, the Min/Max monitoring functions become effective, as shown in Fig. 4, and ensure the required air deficiency in the process. Within the permitted actuator limits, the lambda controller intervenes

as necessary by shifting the air ratio for the required reduction potential.

Through changes in the process variables, other controller interventions may become necessary (not shown in Fig. 4). For example, it can be assumed that throughput, consistency, temperature, and spatial distribution of the feedstock in the reaction chamber will have an effect on the oxygen content and therefore on the reduction properties, if they are not constant or can be controlled. As the oxygen measurement also exhibits some sluggishness, changing process dynamics will have a corresponding influence on quality before one of the controllers is able to intervene. In most cases, it will be the temperature that responds first to changing influences. Therefore, it can be helpful to apply the temperature trend or a similar auxiliary variable to the air factor or load signal as a (disturbance) feedforward signal, enabling the control loop to react earlier.

The complex lambda calculation, the signal linking, and all control functions are implemented by a compact GSM multi-function unit (Fig. 5), which features a high-impedance O_2 sensor input in addition to the inputs for standardized signal and a direct temperature input. All important process and status signals are displayed and operated from the unit's front panel.

Conclusions

During implementation of the pilot plant, a central question involved evaluation of the reduction potential as a fundamental parameter. In terms of systematics, this question has been answered positively. Consequently, this immediately led to the wish for reproducible process conditions – which stands to reason, considering the more or less high fuel variations as a result of using chromium-containing waste. Thanks to the feedback of the measured oxygen partial pressure, and applying the resulting calculated lambda signal to the coupled fuel/air ratio controllers, it was also possible to meet this quality requirement.

Based on the positive experience with the pilot plant, a full-scale plant will be planned and built in a further step.

Literature

- [1] «Schutz- und Reaktionsgase» (Protective and reactive gases), published by LOI, 1978
- [2] «Metallurgical Thermochemistry» by Oswald Kubaschewski, published by Springer, 1951



Fig. 5: GSM multi-function unit