Continuous Off-gas Measurement and Energy Balance in Electric Arc Steelmaking

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A system has been developed for continuous determination of off-gas composition and off-gas volume rate during EAF steelmaking. It comprises devices for gas sampling and analysis of carbon monoxide, carbon dioxide, hydrogen, nitrogen, oxygen and argon, and of measurement of off-gas temperature. The data are processed by a computer to set up the differential heat balance which indicates the flow rates of chemical and sensible heat of the off-gas leaving the furnace at each moment. Several operations during the melting process were investigated with respect to energy utilization. For instance, the hydrogen content during injection of natural gas decreases strongly with increasing oxygen input. During coal injection there is high loss of chemical energy due to non-complete combustion. Also, the extent of combustion depends on the position of the coal lances. Injection of oxygen in the upper furnace part leads to lower loss of chemical but higher loss of sensible heat. The system is optimized at present to decrease the dead time between gas sampling and print out of the analysis.

KEY WORDS: EAF steelmaking; DC EAF; off-gas composition in EAF steelmaking; heat balance of EAF steelmaking; process control of EAF steelmaking.

1. Introduction

The energy consumption in EAF steelmaking has been investigated many times. It is well known, therefore, that a considerable amount of the energy input into the furnace is not utilized for making steel but leaves the furnace with the off-gas, in the form of sensible heat and chemical heat of non-combusted carbon monoxide and hydrogen.1–8) Most published energy balances represent averages over many heats. But the operational parameters in electric arc steelmaking vary considerably from heat to heat. Therefore, energy balances based on averages over a long period have little predictive capability for an individual heat. Another shortcoming in the procedure of establishing energy balances has been hitherto that composition, volume rate and temperature of the furnace gas were obtained by short time measurements which were generalized, or the enthalpy content of the off-gas was just taken to be the balance rest. Hence, continuous measurements of gas flow rate and gas composition are rather difficult. Several efforts have been described in the literature.3,5,6) In these works the off-gas sample was taken in the gap between elbow and fixed part of the gas duct, or close to the gap. There is the problem of air infiltration into the gas stream through the gap and there is the difficulty of keeping the sampling probe operational throughout the heats9) (see also next Section of this paper). So, the unobjectionable and functional method for sampling does not seem to be developed yet. Therefore, off-gas monitoring is not generally applied in EAF steelmaking.

In the present paper a novel system for continuous off-gas analysis of EAF off-gas will be described. The operational parameters in electric arc steelmaking vary considerably from heat to heat. Therefore, energy balances based on averages over a long period have little predictive capability for an individual heat. Another shortcoming in the procedure of establishing energy balances has been hitherto that composition, volume rate and temperature of the furnace gas were obtained by short time measurements which were generalized, or the enthalpy content of the off-gas was just taken to be the balance rest. Hence, continuous measurements of gas flow rate and gas composition are rather difficult. Several efforts have been described in the literature.3,5,6) In these works the off-gas sample was taken in the gap between elbow and fixed part of the gas duct, or close to the gap. There is the problem of air infiltration into the gas stream through the gap and there is the difficulty of keeping the sampling probe operational throughout the heats9) (see also next Section of this paper). So, the unobjectionable and functional method for sampling does not seem to be developed yet. Therefore, off-gas monitoring is not generally applied in EAF steelmaking.

In the present paper a novel system for continuous off-gas analysis of EAF off-gas will be described. The operational parameters in many heats that are necessary for making a complete energy balance were measured continuously including the off-gas parameters. The data were used for setting up the integral energy balance for individual heats and the differential energy balances in real time over a part or over the total duration of the heat. The method of differential energy balance is a powerful tool to clarify the effect of certain measures, for instance blowing of coal or injection of oxygen through the burners, and it can be used by the furnace crew for optimum process guidance.

2. Description of Furnace

The project was carried out in the steel melt shop of Georgsmarienhütte (GMH). The furnace is a DC furnace of 130t nominal tap weight/145 m³ volume with an installed power of 130 MVA. Its wall, roof and off-gas elbow are water cooled. The iron charge is exclusively scrap. At the time of the investigation, on average a heat of 127t was tapped every 70 min. The electric power is supplied via a 710 mm graphite cathode and a multi-pin bottom anode.
Fossil energy carriers, oxygen and other matter (e.g. dust) can be introduced via three natural gas-oxygen burners, a four-lances manipulator and six oxygen injectors, respectively. The addition of slag formers is carried out together with the scrap in one of the two baskets and, if desired, during melting, through a hole in the furnace roof. Tapping of the steel is performed through an eccentric bottom tap hole. The slag flows out of the furnace door on the side opposite to the tap hole. The furnace gas leaves the furnace via a direct withdrawal system. It is combusted, quenched and cleaned from dust with cloth filters. The furnace is operated with a hot heel to preserve a good electrical contact between charged scrap and bottom anode.

3. Development of Continuous Off-gas Analysis

Experiments had been carried out at GMH for some time to conduct the continuous analysis with a mass spectrometer. A large problem was the sampling procedure. It was attempted to draw the gas sample continuously with a lance introduced, through a small opening, into the movable off-gas elbow which connects the off-gas channel with the furnace, or into the gap between elbow and fixed off-gas channel. But in this manner the gas sample was falsified by the uncontrolled infiltration of air. Placement of the sampling location closer to the furnace introduced the problem that the lance opening became clogged by slag and metal droplets. Also dust formed, together with condensed water, a tight plug closing the lance. A detailed description of the encountered difficulties is given elsewhere.9) Finally, a sampling system was developed which is rather sophisticated but works very satisfactorily. The sampling port is directly attached to the furnace and has a design that makes it less sensitive for build up of deposits of slag and dust. There are several cleaning openings in the port and in the adjacent pipe through which mechanical cleaning is possible in a few minutes, if necessary. Normally, however, it suffices to clean the system with a counter pulse of pressurized air. This is performed during the charging of the furnace. All the filter dust is returned into the furnace in this manner. The optimized system for the gas analysis is explained in Fig. 1. There are three filters in the line before the gas enters the mass spectrometer. The flow time of the gas from its entry into the port to its arrival at the mass spectrometer is about 40 s and the time for the analysis 10 s. Hence, the time lapse between sampling and provision of the analysis is just below 1 min.

The off-gas composition depends on the gas production in the furnace and on the volume of air that enters into the furnace through the slag door, the slit of the furnace roof, the electrode opening and other leaks. Since the pressure in the interior of the furnace varies the volume rate of the entering air is fluctuating considerably. No effect is exerted on the measured off-gas composition by the air sucked into the off-stream through both gaps of the movable off-gas elbow. The momentary volume rates of the total off-gas and of the infiltrated air are determined from the analyzed nitrogen and argon contents of the off-gas, the nitrogen contents of air and of oxygen, the argon contents of air and of oxygen, and the known flow rate of oxygen, via the molar balances for nitrogen and argon.

The following species are analyzed: CO₂, CO, H₂, CH₄, O₂, N₂, Ar. The determination of carbon dioxide, carbon monoxide, hydrogen and methane serves to judge the combustion reactions. It was found, however, that methane combusts (or decomposes) almost quantitatively in all cases so that its content is very small and can be neglected. The analysis of water vapor (H₂O) is important but could not be performed because a heated gas line is needed to prevent condensation which was not available at the time of the investigation. The oxygen content of the off-gas should be very low as long as there are contents of carbon monoxide and hydrogen in the gas. If this is not the case there is a leak in the sampling system. Also, a high rate of oxygen injection into the furnace causes an increase of oxygen content. Hence, the analysis of the oxygen content of the off-gas has two purposes: control of tightness of the system for the gas analysis and provision of a warning if the oxygen supply into the furnace is too high. The contents of nitrogen and argon are needed for the computation of the volume rates of off-gas and infiltrated air, as has been mentioned.

Figure 2 gives an example of the measurement during a typical heat. The times in which the power was on are indicated by the bars at the top section of the figure. The zero of time is the end of tapping of the preceding heat. From the many heats investigated it became evident that the course of gas development can differ considerably from heat to heat. Therefore, it is necessary to operate the system...
for each heat if a permanent energy minimization of the total production is to be achieved.

4. Differential Heat Balance

The contents of carbon monoxide and hydrogen in the off-gas already indicate "loss" of energy. Moreover, there are energy losses of sensible heat of the off-gas. A particularly conspicuous demonstration of energy losses can be performed by setting up the differential heat balance which gives the energy fluxes at each moment during the course of a heat. So, from the differential heat balance, the furnace operator can see, at each moment, how much and in which manner he is loosing energy.

The energy input and output into the electric arc furnace can be subdivided into continuous and discontinuous parts. The continuous parts which are (or can be) measured are electrical power, heat of combustion of fine coal added via lances, heat of combustion of natural gas added via burners, losses of chemical heat and sensible heat of the off-gas, heat loss by water cooling of the furnace walls, heat loss by evaporation of the electrode spray cooling water, heat loss through the furnace walls. Other energies are added discontinuously, or continuously but their time function is not measured. Such additions (or losses) are treated in the heat balance as instantaneous events. The discontinuous energy additions (or losses) are the enthalpy in the scrap batches continuously, or continuously but their time function is not measured. The mass of calcium oxide decreases during the melting phase (melting of first scrap basket) through the heat, and the lime and dolomite added during the first lance is added at via lance, of oxygen via lance, of oxygen via lance and via injectors and of natural gas. The oxygen input with the burners is not shown because it is coupled to the input of natural gas by constant ratios of 2/1 in the starting phase and 9/2 in the main (over-stoichiometric) phase. The oxygen injectors are turned on together with two of the three burners at t=10 min. Oxygen via lance is added at t=13 min till t=30 min. The charging of the second basket (scrap, lime) is carried out at t=31 min. Fine coal injection is started at t=38 min. This causes a light increase of carbon mass in the furnace, Fig. 3(a), that is during a certain period the carbon input is larger than the output. At t=47 min and t=60 min samples of steel and of slag are taken, and the temperature is measured. At t=64 min the charge is deslagged and then tapped. The iron mass decreases by the amounts filled into the ladle and contained in the slag and in the dust. In this heat the sump was decreased by 8 388 kg (corresponding to 8 333 kg Fe). Therefore, the curve for the mass of Fe ends in the negative. The mass of calcium oxide decreases during deslagging by the amount of calcium oxide in the slag.

\[
\begin{align*}
\frac{d(m_aH_a + m_bH_b + m_cH_c + m_dH_d + m_eH_e + m_fH_f)}{dt} + \frac{\dot{V}}{V_m} \sum n_i \Delta H_i(T) & = - \dot{V} \left( x_{CO} \Delta H_{CO}^{f}(298) - \Delta H_{CO}^{f}(298) \right) + x_{H_2} \Delta H_{H_2O}^{f}(298) \\
& - \dot{m}_{cal,fc} \Delta H_{cal,fc}^{f}(298) - \dot{V}_{ng} \Delta H_{cal,ng}^{f}(298) \\
& = \dot{m}_{H_2O,k} \Delta H_{H_2O}^{f}(298) \\
& = h(T_s - T_a) \\
& = \dot{V}_{W,C} \Delta H_{W,C}(373)
\end{align*}
\]

The symbols are explained at the end of the paper.

5. Example for Typical EAF Heat

Figures 3 to 6 give the time traces of the relevant process parameters and terms of the differential heat balance equations derived from them, for a typical heat. The initial contents of iron, lime and carbon are taken to be zero. At t=4 min the first basket (scrap, coal) is charged giving an increase of the iron and carbon contents, Fig. 3(a). Also, the electrode consumption which occurs during the course of the heat, and the lime and dolomite added during the first melting phase (melting of first scrap basket) through the hole in the furnace roof is included in the first increases of carbon and lime. Figure 3(b) indicates the input rates of fine coal via lance, of oxygen via lance and via injectors and of natural gas. The oxygen input with the burners is not shown because it is coupled to the input of natural gas by constant ratios of 2/1 in the starting phase and 9/2 in the main (over-stoichiometric) phase. The oxygen injectors are turned on together with two of the three burners at t=10 min. Oxygen via lance is added at t=13 min till t=30 min. The charging of the second basket (scrap, lime) is carried out at t=31 min. Fine coal injection is started at t=38 min. This causes a light increase of carbon mass in the furnace, Fig. 3(a), that is during a certain period the carbon input is larger than the output. At t=47 min and t=60 min samples of steel and of slag are taken, and the temperature is measured. At t=64 min the charge is deslagged and then tapped. The iron mass decreases by the amounts filled into the ladle and contained in the slag and in the dust. In this heat the sump was decreased by 8 388 kg (corresponding to 8 333 kg Fe). Therefore, the curve for the mass of Fe ends in the negative. The mass of calcium oxide decreases during deslagging by the amount of calcium oxide in the slag.
The amount of slag in the sump decreases slightly, by 128 kg in this heat. The small step on the curve for the mass of carbon is the output of carbon with the tapped steel.

Figure 4 presents the contents of carbon monoxide, hydrogen, carbon dioxide and oxygen in the off-gas. The traces start at about $t=5$ min. Before this time the elbow of the gas duct is moved to the side and gas samples are not taken. It is evident from the trace for oxygen that indeed the oxygen content decreases to almost zero if there is carbon monoxide in the gas. Only at the very beginning of melting oxygen and carbon monoxide are present simultaneously over a short time. In the first minutes after charging and turning on the power the off-gas consists mainly of carbon monoxide and hydrogen. Then the carbon monoxide and hydrogen contents first decrease. Subsequently they increase again during the melt down period, and the carbon dioxide content decreases. After charging the second basket there is complete combustion of the carbon to carbon dioxide at first. Afterwards, the contents of carbon monoxide and carbon dioxide are about 30% and 20%, respectively, both fluctuating considerably.

Figure 5 gives the supplementary data necessary to set up the differential heat balance. The volume rates of the off-gas and of air are presented in Fig. 5(a). Between $t=10$ and 12 min the furnace door is closed and there is no lance operation. Consequently, the volume rates of the off-gas and air are small. (The strong fluctuations at $t<11$ min (and $t=33$ and 48 min) occur because oxygen input has just started and the determination of the volume rates with the tracer method are still inaccurate).

Throughout the rest of the heat, the off-gas volume increases whenever the carbon monoxide content increases in
Table 1. Energy quantities for complete duration of the heat No. 622053 obtained by integration of the continuously added (and lost) energies. The quantity of tapped steel before additions was 122.9 t.

<table>
<thead>
<tr>
<th>Energy Type</th>
<th>Quantity (MWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrical energy</td>
<td>56.30</td>
</tr>
<tr>
<td>heat of combustion of fine coal</td>
<td>15.69</td>
</tr>
<tr>
<td>heat of combustion of natural gas</td>
<td>1.01</td>
</tr>
<tr>
<td>energy loss by water cooling</td>
<td>-17.76</td>
</tr>
<tr>
<td>sensible heat of off-gas</td>
<td>-6.96</td>
</tr>
<tr>
<td>chemical heat of off-gas</td>
<td>-10.93</td>
</tr>
<tr>
<td>heat losses by heat transfer and electrode cooling</td>
<td>-0.45</td>
</tr>
</tbody>
</table>

Table 2. Energy quantities (and lost) discontinuously (or taken to be added discontinuously in the balance) for the considered heat No. 622053. The quantity of tapped steel before additions was 122.9 t.

<table>
<thead>
<tr>
<th>Energy Type</th>
<th>Quantity (MWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat of combustion of lump coal</td>
<td>10.99</td>
</tr>
<tr>
<td>heat of combustion of electrode graphite</td>
<td>1.62</td>
</tr>
<tr>
<td>heat of combustion of carbon in scrap</td>
<td>1.65</td>
</tr>
<tr>
<td>heat of oxidation of metals in scrap (slag formation)</td>
<td>12.51</td>
</tr>
<tr>
<td>sensible heat of tapped steel</td>
<td>-45.78</td>
</tr>
<tr>
<td>chemical heat in carbon of liquid steel</td>
<td>-1.12</td>
</tr>
<tr>
<td>sensible heat of slag</td>
<td>-8.14</td>
</tr>
<tr>
<td>sensible heat of dust</td>
<td>-1.23</td>
</tr>
<tr>
<td>radiation loss and off-gas loss during opening of the furnace roof</td>
<td>-2.47</td>
</tr>
</tbody>
</table>

6. Special Observations and Influence of Certain Parameters

Only little changes of the melting routine could be made during the measuring program because disturbances of production had to be avoided. Since in the normal procedure several measures are often performed simultaneously, e.g. oxygen input through lances, burners and injectors, or input of fossils by scrap (oil), natural gas and coal, the effects of the individual activities superpose each other. Also, there is an inherent fluctuation of the off-gas parameters with time due to the non-uniformity of the phenomena in the furnace, due to discontinuous input of materials and other reasons. It is difficult, therefore, to elucidate the effects of distinct measures. Nevertheless, despite these difficulties some observations were made which seem to be of general validity and interest.

6.1. Combustion of Natural Gas

There are three gas-oxygen burners installed in the furnace, two of them in the wall and one in the slag door. The natural gas is normally injected in the beginning of the...
melting phases (after charging the first and second basket) to increase the heat up rate. In general the hydrogen content of the off-gas is high during these periods. In the main period with overstoichiometric oxygen/gas ratio of 9/2 the hydrogen and carbon monoxide contents are low, and the carbon dioxide (and H₂O) content high. Data for the first melting period of an experimental heat in which the natural gas burners were operated almost over the entire melting period of the first scrap batch (the door was closed and the lances were not operated) are given in Fig. 7.

It is evident that the oxygen supply is very important. At first, till about \( t = 14 \) min, there was not sufficient oxygen for the high rate of natural gas. The carbon monoxide and hydrogen contents were high and so was the loss of chemical energy. Then, the gas rate was decreased at the same oxygen rate resulting in practically zero content of carbon monoxide and high content of carbon dioxide. Thus, in this overstoichiometric period, the energy loss in form of chemical energy of the off-gas was low. At about \( t = 16 \) min the additional oxygen injection (via injectors) was discontinued. Consequently, the content of carbon monoxide and the associated loss of chemical energy increased again.

### 6.2. Coal Injection

Coal blowing has a strong effect on the off-gas composition. That is, the carbon monoxide content increases during coal blowing and decreases when the coal rate decreases. This is demonstrated in Fig. 8. Note again that the peaks on the curves for the gas composition occur about 1 min later than peaks on the curve for the coal rate. This delay is due to the time lapse between gas sampling and print out of the analysis.

There is also considerable influence of how the coal and oxygen lances are positioned. Figure 9 gives the results of a charge in which two different lance positions were applied. In position “a” the coal and oxygen lances are immersed, with their openings closely together, into the slag, Fig. 10. In position “b” the oxygen lance is positioned at the left side of the furnace door whereas the coal lance is positioned at the right side, steeply inclined so that the coal stream penetrates into the metal melt. Coal and oxygen rates are almost the same during the two periods (43 to 48 and 50 to 55 min, respectively). Also the electrical power is almost the same. But the gas composition differs markedly being about 51\% carbon monoxide and 15\% carbon dioxide for position “a” and 23\% carbon monoxide and 28\% carbon dioxide for position “b”. Hence, position “b” is much more favorable from the point of view of energy utilization.

There is a characteristic flow pattern in the bath due to the electromagnetic forces, Fig. 10. With position “b” the coal is carried away from the lance towards the center of the furnace and there is sufficient time for carburization of the melt. On the other hand, if the tips of the coal and oxygen lances are directed to the same point as in position “a” a large fraction of the coal is combusted immediately to carbon monoxide. It seems that the complete combustion of the coal to carbon dioxide (position “b”) is enhanced if the coal first carburizes the metal bath. An explanation may be that in this case the formation of carbon monoxide occurs with low rate over a comparatively large area of the bath/slag interface, and that therefore the conditions for postcombustion of the carbon monoxide to carbon dioxide are favorable. On the other hand, the combustion in position “a” is so fast, yielding a high local flux of carbon monoxide, that the carbon monoxide cannot be postcombusted.
The conclusion is that also by proper control of the position of the oxygen and coal lances the utilization of fossil fuels can be improved markedly.

### 6.3. Oxygen Injection

There are six oxygen injectors installed in the upper part of the furnace. Before the use of the system for gas analysis the input of oxygen via the injectors was coupled to the input of electrical energy. Now the injectors can be controlled according to the gas analysis. That is, the oxygen rates can be varied in steps according to the carbon monoxide level. If the content of carbon monoxide is below a certain level the lowest oxygen rate is turned on (16 Nm³ min⁻¹). Figure 11 shows that a strong decrease of carbon monoxide and hydrogen content occurs when the injectors operate at their maximum rate. If the low step is used they increase again.

It is of interest, of course, to find out whether the additional heat of oxidation serves to heat up the scrap, or the cooling water or the off-gas. Figure 11 shows that indeed the temperature of the off-gas increases somewhat. But the losses of sensible and chemical heat do not have opposing tendencies as they should have if the gas is heated up by the combustion. Hence, it appears that the postcombustion has a beneficial effect on the energy consumption of the process.

The automatic control system does not function so well yet because the dead time is too long and the controller too simple (simple two point controller). Ideally, the oxygen input should be metered so that the carbon monoxide content is about constant on a low level (and the oxygen content zero). Hence, the real benefit of the postcombustion can only be assessed if a better controller and a gas analyses system with shorter dead time become available.

### 7. Summary and Conclusions

In the present paper a system is described for gas sampling out of the interior of an electric arc furnace and chemical analysis. The species determined are CO₂, CO, H₂, O₂, N₂, Ar. The volume rates of the off-gas and of the infiltrated air are obtained from the contents of nitrogen and argon. A problem in the development of the system was the sampling procedure. It was solved finally by building the sampling port directly into the furnace and giving it a special design for minimizing buildup of deposits and facilitating easy cleaning. The system can be used to make energy balances that are based only on measured data.

A large number of heats has been studied during their entire melting time. A characteristic feature of the gas development in the furnace is its fluctuation of composition and volume rate which was expected but not to such a strong extent. So it is indeed impossible to deduce average gas composition values for a particular heat from the analysis of a single gas sample or from short time measurement which has been done so in previous investigations. Only continuous measurement over the whole melting time can...
serve to deduce meaningful averages.

It is difficult to elucidate clear effects of distinct operational activities because of these fluctuations and because different measures are often taken simultaneously. But, nevertheless, some could be determined. For instance, coal injection produces high contents of carbon monoxide. Gas injection on the other hand is accompanied by low contents of carbon monoxide and hydrogen. Injection of oxygen in the upper furnace room makes high contents of carbon dioxide as expected.

Thus, the gas control system is a helpful tool to assess the melting process, particularly also if new measures are introduced, e.g. use of other materials. The furnace crews are learning at present to operate the system, and further work is going on to confirm effects of process steps that have been found and to elucidate effects that are not known yet or unclear. The final objective is to use the system for direct process control. This is possible to some extent already at present. The limitation is given by the dead time (lapse between times when the gas enters the sampling port and when its analysis becomes available) which is about 50 s at present. This is much too long in view of the fast changes occurring in the furnace. So the dead time must be decreased. If the dead time would be only a few seconds (≤ 10 s) the operator could see immediately the consequences of what he is doing or of the phenomena he is seeing in the furnace, and he could react by changing input rates, position of lances etc. Work is underway to develop a control system with the required short dead time.

Nomenclature

- \( h \): Heat transfer coefficient
- \( f_k \): Mass fraction of \( k \) in fine coal
- \( m_k \): Mass of \( k \)
- \( \dot{m}_k \): Mass flow rate of \( k \) (kg per s)
- \( n_k \): Moles of \( k \) in 1 kg fine coal or in 1 Nm\(^2\) natural gas, respectively
- \( \dot{n}_k \): Molar flow rate of \( k \) (mol per s)
- \( t \): Time
- \( x_k \): Mol fraction of \( k \) in gas phase
- \( H_k \): Enthalpy of \( k \) per kg
- \( \Delta H_k^{r}(298) \): Enthalpy of formation of compound \( k \) from elements at 298 K per kg
- \( H_{\text{cal}} \): Calorific value (heat of combustion of 1 kg coal or 1 Nm\(^2\) gas at 298 K)
- \( \bar{H}_k \): Enthalpy of \( k \) per mol at \( T \)
- \( \Delta \bar{H}_k(T) \): Enthalpy difference of \( k \) between \( T \) and 298 K per mol (content of sensible heat)
- \( \Delta \bar{H}_k^{r}(298) \): Enthalpy of formation of compound \( k \) from elements at 298 K per mol
- \( \Delta H_{\text{w}}(373) \): Enthalpy difference between steam at 373 K and water at 298 K per kg
- \( \dot{Q}_{\text{el}} \): Flow rate of electrical energy into furnace, electrical power
- \( V \): Volume rate of off-gas at standard conditions (Nm\(^3\) per s)
- \( V_m \): Molar volume of gas at standard conditions
- \( T \): Temperature

Subscripts

- \( \text{st, sl,lc, re, el} \): Steel, slag, lump coal charged in the basket, refractory, electrode
- \( \text{fc} \): Fine coal charged by injection
- \( \text{cw} \): Cooling water of furnace vessel
- \( \text{cwe} \): Cooling water of electrode
- \( \text{w} \): Water
- \( \text{ng} \): Natural gas
- \( \text{og} \): Off-gas
- \( \text{org} \): Organic matter in fine coal

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Appendix. Derivation of Eq. (2) of the Preceding Paper

The first term of expression (1) is given as

\[ \Delta m_0 H_0 + \Delta m_H H + \Delta m_C H_C + \Delta m_W H_W + \Delta m_H H_H \] ..........................(A1)

The enthalpy of the gas phase is small compared with that of the condensed matter and can be neglected.

The terms of main interest are the second and third terms of expression (1), and it is convenient to treat them together. Output of enthalpy out of the furnace (second term) is by the off-gas and input (third term) by the fine coal (injected via lance), natural gas, oxygen, and air. The temperature of the input materials is taken to be 298 K.

The hydrogen balance is set up correspondingly:

\[ \Delta(n_{C,fc} + n_{C,ng} - n_{C,fc}) = 0 \] ..........................(A5)

Eliminating \( \dot{n}_{CO} \) and \( \dot{n}_{H2} \) in Eq. (A3) by application of Eqs. (A5) and (A6), respectively, yields

\[ \Delta(\Delta H_{CO,ng}(T)) + [x_{CH4,ng} + x_{CO2,ng}] \Delta H_{CO,ng}(298) \] ..........................(A7)

In Eq. (A3) \( \dot{n}_{C,fc}, \dot{n}_{C,ng}, \dot{n}_{H2,fc}, \dot{n}_{H2,ng} \) are the molar rates of the species in the off-gas. The term \( \Sigma \dot{n}_{H2}(T) \Delta t \) with the sum taken over all the species (elements and compounds) is the sensible heat of the off-gas. The mass rates \( \dot{n}_{H2,fc} \) and \( \dot{n}_{H2,ng} \) refer to the injected fine coal and natural gas, respectively. The heat of formation of the organic matter in fine coal \( \Delta H_{C,org}(298) \) is defined as the enthalpy for making 1 kg organic matter from its elements. The heat of formation of ash is taken to be the same as that of the minerals in the coal.

The molar flow rates of \( CO_2, CO, H_2, O_2, H_2O \) in the off-gas are related to the molar rates of \( C, H_2, CH_4, H_2O, CO_2 \) injected with the fine coal and natural gas via the molar balances for carbon and hydrogen.

Carbon balance:

\[ \text{change of mols of carbon in furnace} \quad \text{in time} \ \Delta t \quad + \quad \text{output of mols of carbon out of furnace with off-gas in time} \ \Delta t \]

\[ - \text{input of mols of carbon into furnace with fine coal and natural gas in time} \ \Delta t \]

\[ = 0 \] ..........................(A4)

The change of mols of carbon in the furnace refers to the metal phase, the lump coal (batch coal) and the electrode. The lump coal is made up, similarly as the fine coal, from organic matter, ash and water. The electrode is taken to consist of pure graphite.

\[ \Delta(n_{C,at} + n_{C,le} + n_{C,ng}) = (\dot{n}_{C,at} + \dot{n}_{C,ng}) \Delta t \]

\[ - (\dot{n}_{C,le} + \dot{n}_{C,ng}) \Delta t = 0 \] ..........................(A5)

Eliminating \( \dot{n}_{CO} \) and \( \dot{n}_{H2} \) in Eq. (A3) by application of Eqs. (A5) and (A6), respectively, yields

\[ \Delta(\Delta H_{CO,ng}(T)) + [x_{CH4,ng} + x_{CO2,ng}] \Delta H_{CO,ng}(298) \] ..........................(A7)

The term \( \dot{n}_{CO,ng} \Delta H_{CO,ng}(298) \) cancels with \( \dot{n}_{H2,ng} \Delta H_{CO,ng}(298) \times \Delta H_{CO,ng}(298) \), and the term \( \dot{n}_{H2,ng} \Delta H_{CO,ng}(298) \) with \( \dot{n}_{H2,ng} \Delta H_{CO,ng}(298) \). The chemical energy in the injected fine coal and natural gas is expressed in terms of their calorific values which are the heats of combustion of 1 kg fine coal or 1 Nm\(^3\) natural gas respectively, at 298 K:

\[ H_{cal,fc} = - [f_{CH4,ng} \Delta H_{CH4,ng}(298) + f_{H2,ng} \Delta H_{H2,ng}(298)] \] ..........................(A8)

\[ H_{cal,ng} = - [n_{NG} \Delta H_{NG}(298) + 2 \Delta H_{H2,ng}(298)] \] ..........................(A9)

Calorific values are taken as positive numbers despite the exothermic (negative) formation enthalpies, therefore the negative signs before the brackets in Eqs. (A8) and (A9). The quantities \( n_{CH4,ng} \) and \( n_{H2,ng} \) are the mols of carbon and hydrogen in 1 kg fine coal and natural gas, respectively.
are the moles of gas in 1 Nm$^3$ natural gas. Hence, $\dot{n}_{\text{C,fc}} = m_{\text{fc}}\Delta H_{\text{CO}_2}(298)$, $\dot{n}_{\text{H}_2,\text{fc}} = m_{\text{fc}}\Delta H_{\text{H}_2O}(298)$ and $\dot{n}_\text{ng} = V_{\text{ng}}/V_m$. Replacing $\dot{n}_{\text{C,fc}}\Delta H_{\text{CO}_2}(298)$, $\dot{n}_{\text{H}_2,\text{fc}}\Delta H_{\text{H}_2O}(298)$, $\dot{n}_{\text{ng}}\Delta H_{\text{ng}}(298)$, and $\dot{V}_{\text{ng}}\Delta H_{\text{ng}}(298)$ in Eq. (A7) by $-m_{\text{fc}}\Delta H_{\text{cal,fc}}$, and $\dot{n}_{\text{ng}}\Delta H_{\text{ng}}(298)$ in Eq. (A8) by $-V_{\text{ng}}\Delta H_{\text{cal,ng}}$, and setting $\dot{n}_k = (V/V_m)\dot{x}_k$ yields

\[
\dot{V}/V_m \left[ \sum x_k \Delta H_{c,k}(T) - \dot{V}/V_m (x_{\text{CO}}\Delta H_{\text{CO}_2}(298) - \Delta H_{\text{CO}_2}(298)) + x_{\text{H}_2}\Delta H_{\text{H}_2O}(298) - m_{\text{fc}}\Delta H_{\text{cal,fc}} + V_{\text{ng}}\Delta H_{\text{cal,ng}} \right] \Delta t
\]

\[
-\Delta(n_{\text{C,fc}} + n_{\text{H}_2,\text{fc}} + n_{\text{ng}})\Delta H_{\text{ng}}(298)
\]

\[
-\Delta(n_{\text{H}_2,\text{fc}})\Delta H_{\text{H}_2O}(298)
\]

..........................(A10)

Inserting the obtained analytical expressions for [first term] and [second term]–[third term] (Eqs. (A1) and (A10)) into Eq. (1), using $\Delta Q_{\text{el}}$ as the fourth and the appropriate formulae for the fifth term, dividing by $\Delta t$ and taking the limit $\Delta t \to dt$ yields the differential Eq. (2) given in the main text.

\[
d(m_{\text{FC}}H_{\text{FC}} + m_{\text{HC}}H_{\text{HC}} + m_{\text{LC}}H_{\text{LC}} + m_{\text{RE}}H_{\text{RE}} + m_{\text{EL}}H_{\text{EL}})
\]

\[
\frac{dt}{\text{change of enthalpy of matter in furnace}}
\]

\[
\dot{V}/V_m \sum x_k \Delta H_{c,k}(T)
\]

\[
\text{sensible heat of off-gas}
\]

\[
\frac{\dot{V}}{V_m} \left\{ x_{\text{CO}}[\Delta H_{\text{CO}_2}(298) - \Delta H_{\text{CO}_2}(298)] + x_{\text{H}_2}\Delta H_{\text{H}_2O}(298) \right\}
\]

\[
\text{chemical heat of off-gas}
\]

\[
\frac{-m_{\text{fc}}\Delta H_{\text{cal,fc}}}{\text{chemical heat in fine coal}}
\]

\[
\frac{-V_{\text{ng}}\Delta H_{\text{cal,ng}}}{\text{chemical heat in natural gas}}
\]

\[
\frac{-d(n_{\text{C,fc}} + n_{\text{H}_2,\text{fc}} + n_{\text{ng}})}{dt} \Delta H_{\text{ng}}(298)
\]

\[
\text{heat loss to surrounding air}
\]

\[
\frac{-d(n_{\text{H}_2,\text{fc}})}{dt} \Delta H_{\text{H}_2O}(298)
\]

\[
\text{heat loss by cooling water}
\]

\[
\dot{Q}_{\text{el}} - \frac{-V_{\text{cw}}\rho c_w(T_{\text{w,out}} - T_{\text{w,in}})}{hA(T_e - T_s)}
\]

\[
\text{heat loss by water cooling of electrode}
\]

Here, the terms representing the output of sensible and chemical heat of the off-gas and the continuous input of chemical heat with the injected fine coal and natural gas as well as the electrical power and the heat loss by cooling water are obtained from continuous measurement. The rate of change of enthalpy of the material in the furnace (terms with differential quotients $d/dt$) can not be evaluated accurately because their time functions are unknown. But on their integration over melting time they yield the enthalpies added and withdrawn from the furnace by the discontinuous inputs and outputs of matter. So they are part of the integral heat balance. The ash of the injected fine coal enters into the slag phase and, consequently the term $-m_{\text{fc}}\Delta H_{\text{ash}}(298)$ in (A11) is combined with $d(m_{\text{FC}}H_{\text{FC}})/dt$ on integration and cancels.