In situ monitoring of pit gas composition during baking of anodes for aluminum electrolysis

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Abstract

Carbon anodes, which are consumed in aluminum electrolysis, are fabricated in separate anode plants where coke and pitch are mixed and vibrocompacted to green anode blocks before being baked in anode baking furnaces. The chemical environment inside an anode baking furnace is found to play an important role in the degradation of the furnace refractory lining. In this work, the pit gas composition was recorded during anode baking by an FTIR spectrometer and a gas chromatograph. The temperature dependence of the concentration of gas species during baking were obtained based on three measurement campaigns., The concentrations of CO and CO_2 were found to be very dependent on temperature, where the concentration of CO peaked around the maximum firing temperature. In addition to varying concentrations of CH_4 and HF, water was found in large amounts in the first part of the baking cycle. The water is to some extent originating from the cooling of the green anodes after vibrocompaction and is potentially important with respect to the chemical stability of the refractory lining. The variations in pit gas composition is related to operational parameters and discussed in relation to refractory degradation phenomena.

1. Introduction

The most used anode technology in state-of-the-art aluminum electrolysis cells is prebaked carbon anodes [1,2]. Anodes are manufactured in separate anode fabrication plants where the final step is the anode baking. The green anodes consists of petroleum coke, anode butts and coal tar pitch which are mixed and vibrocompacted to individual anode blocks prior to heat treatment (baking) in the anode baking furnace [3]. Over the course of the lifetime of the furnace, the refractory lining are exposed to both temperature cycling and gaseous reactions causing material changes in the refractory. Hence, the walls are subjected to stress of physical, thermal and chemical nature, reflected in observed degradation of the refractory walls [3–5]. Commonly, the walls are found to bend along the length of the pit walls, which, together with carbon deposition, is decreasing the pit width and the space in

which the anodes are placed during baking. At some point, the pits become too narrow and the walls must be replaced in order to fit the anodes into the pits [3–5].

Investigations of refractory degradation in anode baking furnaces have suggested several possible mechanism for the material degradation [6–9]. The most widely discussed cause of degradation is reactions with sodium and/or fluorine containing compounds. Investigations of spent lining from industrial furnaces have revealed significant levels of sodium in the regions close to the anode pit [4,5,9,10]. The level of amorphous phases is also found to be higher in these regions. Sodium, mostly introduced through frozen bath from the anode butts, forms volatile compounds during heat treatment. Both crystalline and amorphous sodium aluminosilicate phases have been observed in linings due to chemical reactions involving sodium during baking[4,5,9]. However, in later studies, the sodium level in the spent lining is not observed to be equally high, reducing the significance of sodium influence on the refractory stability in some furnaces [8]. In addition to the reactions with volatile sodium fluorides, the effect of reducing atmosphere on refractory stability has been discussed [9]. It is suggested that reducing gaseous compounds (H_2, CH_4, CO etc.) could affect the stability of the oxides at elevated temperatures, explaining some of the observations reported [9]. Detailed knowledge on pit gas composition therefore of high interest, and could improve the understanding of degradation mechanism of the lining. Investigations of pit gas atmosphere during anode baking has, to the best of the authors knowledge, not been reported by others, and the pit gas composition as a function of time and temperature during baking has been largely unknown. Preliminary studies conducted by the authors have shown that the concept of *in situ* measurements of pit gas is feasible, although challenging [11,12].

Here, we report on three measurement campaigns conducted in the same baking furnace. Based on the experience from the initial study[11], the sampling setup was adjusted and improved in order to expand the sampling period over the whole baking cycle. Pit gas composition as function of time and temperature was measured by a Fourier transformed infrared spectroscopy (FTIR) as described by Aarhaug *et al*. [11,12]. Composition of pit atmosphere, with especial focus on CO, CO_2, CH_4 and HF, were investigated and related to operational conditions of the furnace and the degradation of the refractory lining. Further modifications of the experimental setup were carried out before the last measurement campaign. The outcome obtained from the setup modifications is finally discussed.

2. Experimental

2.1 Experimental setup

The anode gas measurements were conducted through three experimental series in an open anode baking furnace. The initial experimental setup design consisted of a Kanthal (FeCrAl alloy) probe, inserted into the pit through the packing coke. The probe was made of two concentrically mounted Kanthal pipes with dimensions as shown in Figure 1. The double pipe construction was chosen for

increased mechanical support of the inner pipe in addition to reduce the risk of pipe blockage by packing coke. Above the packing coke, the two pipes were both mounted to a stainless steel (SS) connector, which on the top side where connected to the sampling line through a 1/4" SS connector. The first part of the sampling line consisted of a steel pipe (5 m, Ø 1/4"), before a 1/4" polytetrafluoreten (PTFE) tube surrounded by a heating tube (20 m, 180 °C) connected the probe to a cylindrical filter (Ø 10 cm, 30 cm length) filled with glass wool, and subsequently the FTIR in the end.

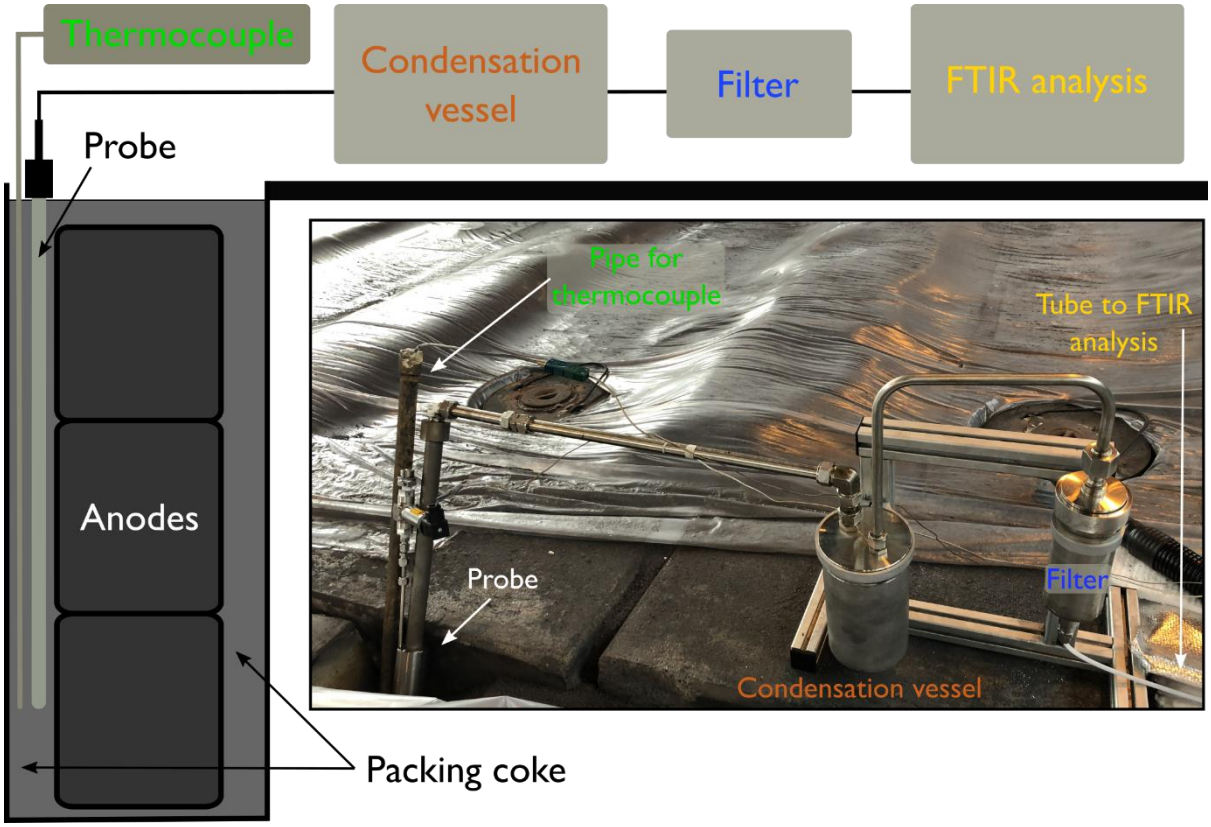

Figure 1: Overview of the experimental setup used in the second and third measurement campaigns. The Kanthal probe consists of two concentrically mounted pipes. The inner diameter, outer diameter and length are 20.9 mm, 36.7 mm and 4200 mm (inner pipe), and 34 mm, 40 mm and 4500 mm (outer pipe), respectively. The probe inlet is in the bottom of the pit, measuring the gas composition approximately 1 meter above the pit floor.

Several parts of the experimental setup design were improved prior to the second and third series. A cylindrical condensation unit with an approximate volume of 2 litres was constructed, with gas inlet and outlet mounted in the lid. The setup used for the second and third series is presented in Figure 1. The cylinder and lid were connected with threads allowing the cylinder to be disconnected from the lid and its content removed. To avoid problems with condensation in the piping between the probe and the condensation unit, the pipe diameter was increased from ¼" to ½" and ¾" in this part of the setup. After the condensation unit, a filter unit was mounted to remove potential volatile polyaromatic

hydrocarbons (PAHs) in the gas flow. The filter unit consisted of an outer shell, with an inner removable cylinder filled with XAD-2 adsorbent instead of the glass wool used as filter material in the first series. The gas exited the filter unit and reached the FTIR instrument the same way as in the first series. In the third series, the experiment was expanded to include a gas chromatograph connected in series after the FTIR instrument. The probe was inserted into the pit between the anodes and the flue wall prior to adding the packing coke, with the probe inlet positioned approximately in the middle between both side walls and 1 meter above the pit floor. For all three series, a thermocouple was inserted into the packing coke together with the Kanthal probe, measuring the temperature by the probe inlet.

2.2 Analysis

The FTIR analysis was carried out with a Protea LTD ProtIR 204M analyser. The equipment recorded data with a resolution of 1 cm^{-1}, averaging spectral data every 1-5 minutes. The instrument was heated to 180 °C, the same temperature as the Teflon tube leading the gas from the filter unit to the instrument. Library FTIR data of the expected gaseous species was used as basis for comparison during manual interpretation of the spectral data. Linear regression of peak height values was used to quantify the amount of each gas species. When spectral data form the experiments were outside the range of the library data, extrapolation of library data was performed. The instrument's built-in calibration model was in some cases applicable. An Agilent 490 Pro GC was calibrated for H_2, O_2, N_2 and CO_2 and was added to give information about the dilution of the air as well as oxygen concentration in the pit.

3. Results

Concentrations of CO and CO_2 from series 1 are presented in Figure 2. Here, concentrations are plotted as a function of time, i.e. days in the baking cycle. The figure shows a time span of 13 days, which is a typical length of a baking cycle. The measured temperature is also shown, linking the concentration of CO and CO_2 to the temperature and number of days into the baking cycle. The maximum temperature measured in the packing coke is almost 1200 °C. The measurements of series 1 was initiated ~5.5 days into the cycle, in a period where CO is dominating over CO_2 in the pit gas. As temperature decreases, the concentration of CO decreases while CO_2 increases. The data from series 1 was terminated at ~10.5 days, resulting in only partial coverage of the baking cycle.

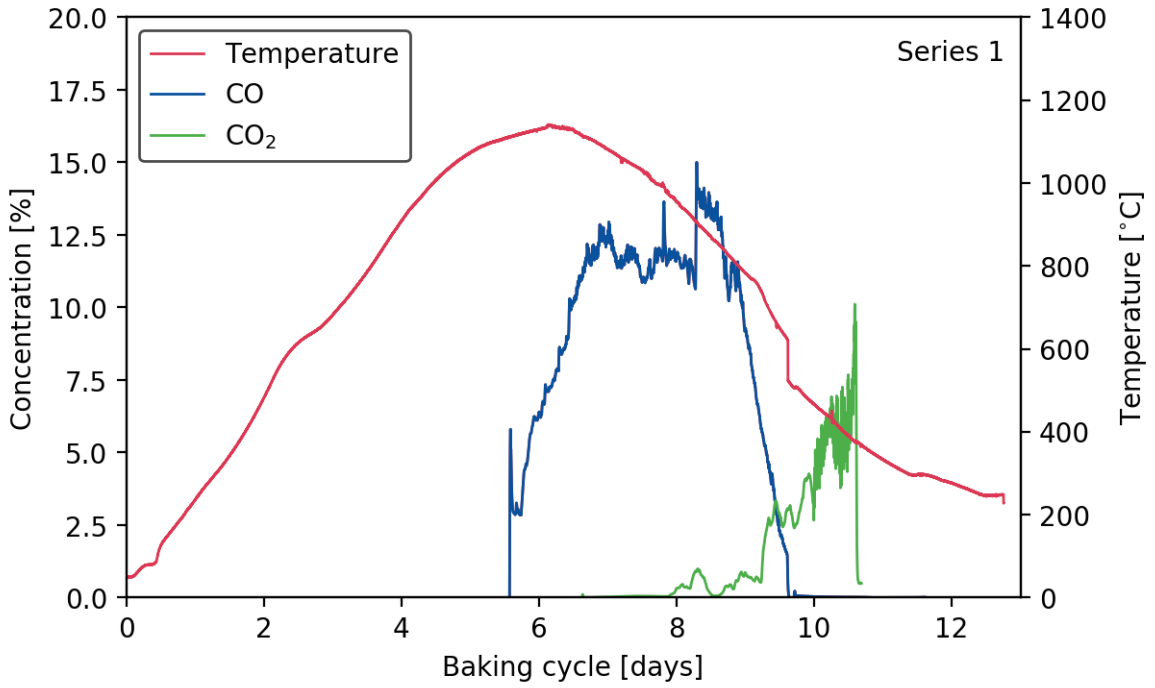

Figure 2: Concentration of CO and CO_2 from series 1 during the baking cycle. The corresponding temperature is also shown.

Concentrations of CO and CO_2 from all three series are presented in Figure 3. The figure gives an overview of the development of CO and CO_2 concentration during a baking cycle. Here, the aspects addressed in series 1 are emphasized by the results from series 2 and 3. The temperature cycle is fairly similar for all series, and the temperature curve from series 1 is used for all three data sets. During heating of the anodes, the FTIR data shows that the pit atmosphere is to a large extent dominated by CO_2, peaking at 12 - 13 %. As the temperature increases, the CO_2 concentration is reduced while CO increases to 15 % at the most. The measured levels are a clear indication that much of the CO and CO_2 origins from packing coke reacting with oxygen in the air. During the highest baking temperature, CO remains the dominating specie, before CO_2 again starts to appear at ~800 °C during cooling. In the last part of the baking cycle, it is clear that CO concentration goes down as CO_2 becomes the dominating reaction product in the pit, peaking at 15-16 %. The ratio between CO and CO_2 concentration is shown in the lower part of Figure 3, emphasizing the abovementioned shifts in concentrations. In addition to FTIR measurements, some regions of series 3 were also covered by the gas chromatography (GC) measurements. At ~930 °C during the heating cycle, hydrogen was estimated to near 80 %, while N_2 and O_2 were estimated to 16 % and 3 %, respectively. The instrument was calibrated to measure H_2 up to 20 %, and a linear extrapolation was used outside this range. The estimation demonstrates that the H_2 level was significantly higher than 20 %, but it was difficult to determine the exact level. A longer period was sampled during the cooling period of series 3. Between ~890 °C and ~850 °C, the H_2 estimate declined from 7500 ppm to 5800 ppm, CO_2 increased from 7.5 % to 9.5 %, O_2 was stable at 3.1 % and N_2 increased from 78 % to 80 %.

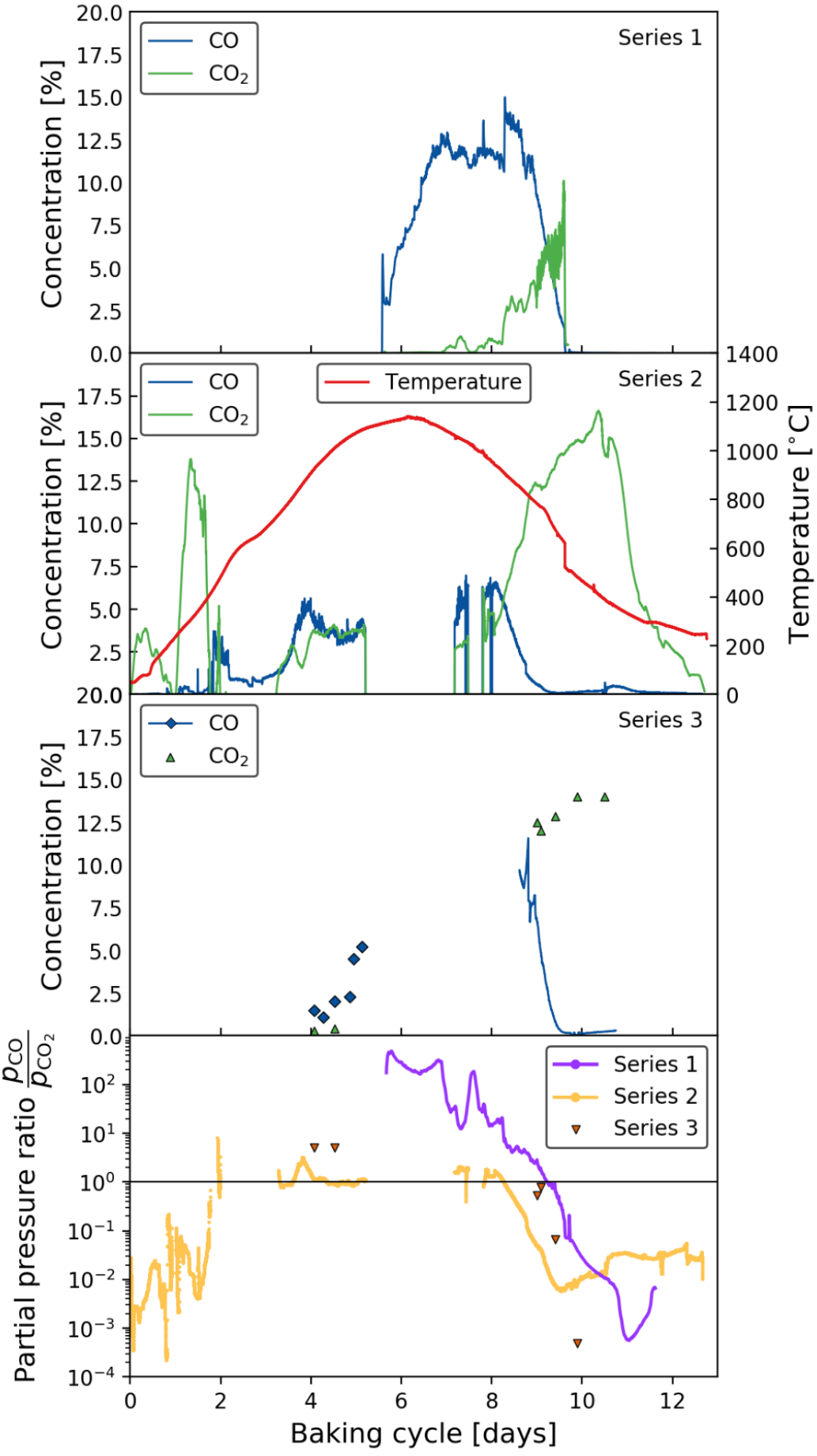
Series 1
CO
CO_2
Concentration [%]
Series 2
Temperature
Temperature [°C]
Series 3
Partial pressure ratio $\frac{p_{CO}}{p_{CO_2}}$
Baking cycle [days]

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Figure 3: Concentration of CO and CO_2 from series 1, 2 and 3. The lower part of the figure shows the ratio between CO and CO_2, illustrating the shift in the dominating specie from CO (high temperature) to CO_2 (low temperature). The temperature profile plotted for series 2 applies for all series.

In addition to the shifts in CO and CO_2 concentrations during the cycle, the pit gas atmosphere at three stages in the cycle is presented in Table 1, illustrating the variation in pit gas composition. Other observed gaseous compounds are included to give a broader overview of the gas composition. At 700 °C during heating, the CH_4 level is measured to 29 % in series 1 and 7 % in series 2. The top part of Figure 4 summarizes the overall development of CH_4 based on the available data. A peak in CH_4 concentration is present in the range of 400 to 850 °C, which diminishes during further heating. The height of the peak is varying between the series. HF was measured in significant concentrations at ~1100 °C in series 3, presented in the lower part of Figure 4. When comparing the concentrations in Table 1 at 700 °C during heating and cooling, there are some notable differences. Firstly, the high concentration of CH_4 measured during heating is not present towards the end of the cycle. Secondly, the level of CO_2 is much higher and more stable in the last part of the cycle, while varying more during heating. At 700 °C during heating, the CO_2 concentration in series 1 and 2 is measured to 0.15 % and 2 %, as shown in Table 1. At the same temperature during cooling, the CO_2 level is measured in the range from 8 % to 12.9 %.

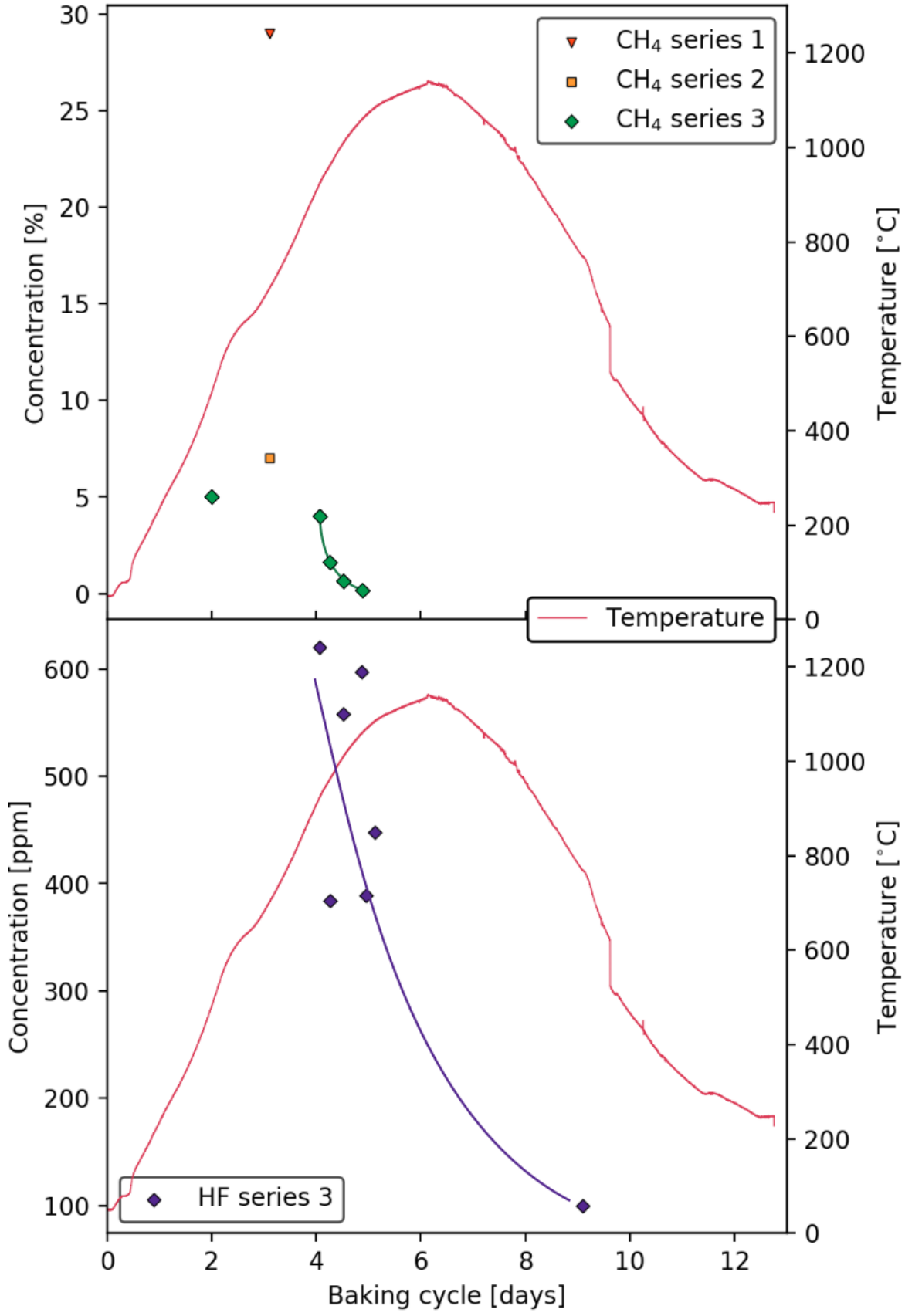

Figure 4: Concentrations data of CH_4 and HF. Both compounds are mostly present during the first part of the baking cycle.

Table 1: Concentration data from series 1, 2 and 3, covering three periods of the baking cycle. For NH_3 linear extrapolation from 0.1 % was performed. The spectral line for C_6H_6 was compared to a 0.1 % library spectrum, which indicated a concentration higher than 0.1 %. Exact quantification was however difficult due to overlapping signals from other species present in the gas.

	~700 °C (heating)		~1150 °C (max temp)			~700 °C (cooling)		
	S1	S2	S1	S2	S3	S1	S2	S3
CO [%]	1.5	1.1	2.9	5	5.3	1.5	0.18	1.1
CO_2 [%]	0.15	2	175 ppm	0.6	0.1	8	12.5	12.9
H_2O [%]	2.2	1	2.0	6.1	0.5	0.6	6.3	0.7
CH_4 [%]	29	7	0.1		285 ppm			
NH_3 [%]	~ 1	~ 0.1						
C_6H_6 [%]	> 0.1							
HF [ppm]					400-597			

During the first 24 hours of the baking cycle, water was extracted from the condensation vessel. The average condensation rate of water was measured to 0.19 kg water per hour. Based on the pressure difference over the FTIR nozzle during the 24 hours of water condensation, the average gas flow was estimated to 0.5 – 1.0 L per minute. With the estimated gas flow, the average water content of the pit gas was 3.2-6.5 g per L gas. The pit temperature increased from 75 °C to 330 °C over the sampling period, and the condensation rate was fairly constant over that temperature range.

In the temperature range from 400 to 800 °C during heating, pitch residues were observed to accumulate in the condensation vessel. A brown/yellow, sticky condensate was found in the bottom of the vessel, illustrating the good control of condensation. If similar compounds had accumulated in the narrow parts of the piping or in the filter, the experiment would suffer greatly from reduced flow through the equipment. Some lighter volatiles escaped the vessel and were captured in the filter material instead, discoloring the filter material. As the temperature increased beyond 800 °C, the level of condensation diminished and the gas became cleaner with respect to pitch residues.

In addition to the data presented above, several other compounds were also detected during the experiments. During the heating period of series 1 and 2, NH_3 was measured to 0.1 - 1 %. In the same period of the baking cycle, ~200 ppm HCN was detected in series 3. Details concerning the hydrocarbons showed that both ethane and propane were present, but methane being the dominating specie of the three. 300 ppm of HF was detected in series 2 at 400 °C during temperature decrease. Finally, sulfur compounds were detected in the last part of the baking cycle in series 3. At 625 °C, a distinct shift from COS to SO_2 was measured. Extrapolation of library data from 200 ppm indicated a COS concentration of ~700 ppm. SO_2 was measured to maximum 2500 ppm.

4. Discussion

4.1 The pit environment

The gas composition in the anode baking furnace, measured in this study, varied greatly during the course of a baking cycle. This expected variation is mainly affected by two factors; the temperature cycle and the baking processes going on in the anodes. The gas composition at 700 °C during heating and cooling, presented in Table 1, shows a high level of CH_4 during heating, while CO_2 is dominating during cooling. The temperature in the packing coke is measured to 700 °C in both cases, but the different gas atmospheres demonstrate that the chemical and overall thermal conditions are far from being equal during heating and cooling. During heating, the coal tar pitch in the anodes are decomposing, creating an atmosphere of volatile hydrocarbons, including CH_4. As the temperature increases, and the pitch decomposition process ceases and the concentration of CH_4 diminishes, as presented in Figure 4. This is also in accordance with the low thermodynamic stability of CH_4 at elevated temperatures[13]. At 700 °C during cooling, the pitch decomposition is no longer a dominating factor. The gas composition mainly consists of CO_2 at this stage, after a dramatic decrease in CO during cooling from maximum baking temperature. This is in accordance with the expected thermodynamic behavior. Due to the lower pressure inside the pit compared to the outside, air is entering the furnace through the packing coke. Oxygen is thus reacting with the packing coke producing CO or CO_2. The overall thermodynamic equilibrium between CO and CO_2, with solid carbon present, is assumed to be governed by the Boudouard reaction (Reaction 1):

$$C\,(s) + CO_2\,(g) = 2CO\,(g) \qquad (1)$$

This reaction becomes spontaneous above 700 °C. Figure 3 show the time series of all three series, where the reduction in CO upon cooling is clearly present. With solid carbon present, Equation 1 will be the governing reaction between CO and CO_2 at equilibrium, and the ratio $(p_{CO})^2/p_{CO_2}$ describes the relation between the equilibrium partial pressures of CO and CO_2.

The ratio between $(p_{CO})^2$ and p_{CO_2} of the experimental data from series 1, 2 and 3 are presented in Figure 5, comparing the experimental data to the same ratio based on equilibrium data. The ratios are plotted as a function of measured temperature in order to more easily follow the evolution during cooling in the last part of the baking cycle. When comparing the experimental data to the equilibrium data, it is possible to evaluate the degree of equilibrium in the pit gas in each series. In general, the experimental data is in good accordance with the equilibrium ratio, both with respect to the level and the temperature dependence. The data from series 1 is following the equilibrium ratio especially well, and the gas composition in series 1 during cooling can thus be assumed to roughly be in equilibrium. The results from series 2 and 3 also indicate a good correspondence with the equilibrium ratio, but not to the same degree as for series 1. The Boudouard reaction can thus be regarded as a good model for describing the pit atmosphere in this part of the cycle.

The pit gas composition is in general showing similar trends in all three series, where the same main gas components are observed, and their concentration profile through the baking cycle are

comparable. There are however some quantitative discrepancies from series to series. These variations are mostly related to the amount of gas measured in various parts of the baking cycle, and could be due to both experimental challenges and real variations from one baking cycle to another. The absolute value of CH_4 during the heating period (presented in Figure 4) is for example varying from one series to the next. Based on this work, it is therefore difficult to determine the accurate concentration of the various gas components throughout the baking cycle. However, based on this study we have been able to establish the gas component present in the baking furnace and how the concentration of these species vary qualitatively through the baking cycle.

The temperature probe is positioned in the packing coke between the anodes and flue wall. The actual temperature in the flue wall and inside the anodes are hence not necessarily the same as the temperature measured in these experiments. A study modelling the flow of gas in the flue walls report on potential thermal gradients across the flue walls in the range of 50 - 100 °C [14]. In addition, the heating rate of the anodes is assumed to create a thermal gradient from the center of the anode and outwards during heating, with the opposite direction during cooling. The temperature in the center of the anode is thus not the same as the temperature measured by the thermocouple in the packing coke. During heating, most of the processes occurring within the anodes (evaporation and cracking of pitch) are occurring at a lower temperature than measured by the probe. Due to the delay in heat transport from the surface to the center of the anode, the actual anode temperature will always be lower than measured in the packing coke during heating. Similarly, as the furnace is cooled in the last part of the baking cycle, the anode temperature will be higher compared to the measured temperature in the packing coke. The measured pit gas composition is also very dependent on reaction kinetics, especially in the first part of the cycle when the pitch is evaporating and cracking. The thermal gradients and reaction kinetics do therefore result in variation in the evolution of the pit atmosphere from one backing cycle to another, particularly during heating. We therefore expect some variation in the pit atmosphere during heating and a different atmosphere during cooling compared to heating. The GC data from series 3 complements the overall FTIR measurements. At 930 °C during heating, the H_2 level was estimated to ~80 %. This estimate is based on a linear extrapolation from the upper limit of the calibration range at 20 %. The H_2 concentration is therefore not accurately determined, and should not be used for quantitative evaluation. There is however no doubt that the H_2 concentration is very high in this part of the cycle. The N_2 estimate (16 %) and O_2 estimate (3 %) demonstrate a significant dilution of incoming air, most likely originating from the formation of H_2. The nitrogen to oxygen ratio in the pit (5.3) is higher compared to air (~4), resulting from oxygen consumption by reaction with the packing coke. The reaction between O_2 and the packing coke, forming CO and/or CO_2, will also contribute to dilution of nitrogen and oxygen. Between ~890 °C and ~850 °C during cooling, the GC measurements showed a distinct different pit gas concentration. The nitrogen level is now approximately the same as in air, while the oxygen concentration is estimated to 3.1 %. The high

nitrogen level demonstrate that the dilution of incoming air by formation of gases in the pit is low. The low oxygen level is reflecting the reaction of oxygen with carbon. The draft in the furnace, i.e. the reduced pressure in the flue gas, causing air to flow into the furnace, is lower towards the end of the baking cycle. This results in less air flow and more time for the oxygen to react in this part of the cycle. An oxygen concentration of 3.1 % is, however, higher than expected from the reaction kinetics (air burn) at these temperatures. The GC coverage of these experiments are low compared to the FTIR measurements, and some caution is therefore advised when interpreting the GC results.

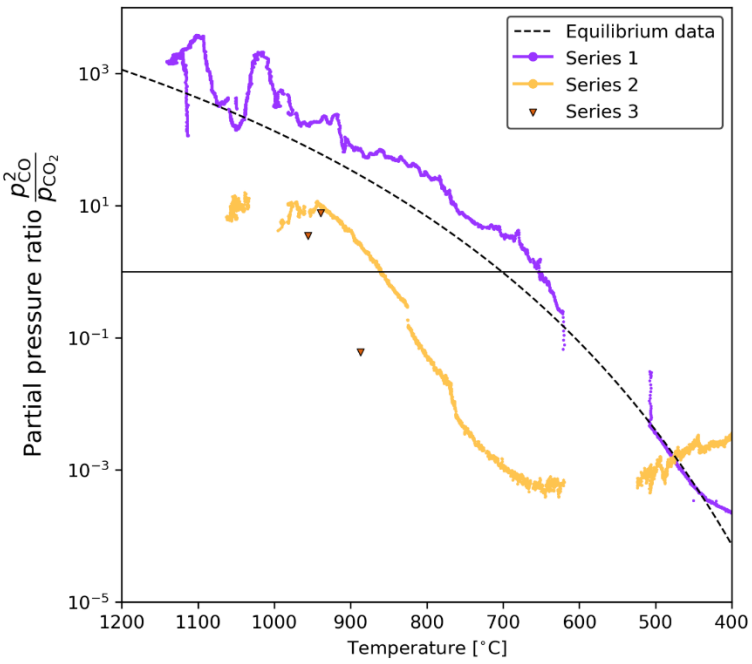

Figure 5: The ratio between $(p_{CO})^2$ and p_{CO_2} for series 1, 2 and 3, in addition to equilibrium data, plotted as a function of temperature. The experimental data is in good accordance with the equilibrium data.

4.2 Implications of water condensation

Water was measured in significant quantities during the first part of the baking period. The average condensation rate of water during the first 24 hours was 0.19 kg/hour, corresponding to a pit gas humidity of 3.2 – 6.5 g/L. The high level of water in the pit causes dramatic changes to the chemical environment in the pit, especially affecting the volatility of traces of fluorides from recycled anode butts. Thermodynamic calculations carried out on cryolite, representing the electrolyte, and water, show an onset of fluoride volatility at a lower temperature compared to a system with dry cryolite[15]. With no water present, cryolite decomposes into NaF and $NaAlF_4$ above 1000 °C[7,15]. When cryolite is heated in an atmosphere containing water, HF volatility is becoming significant above 800 °C, following Equation 2.

$$9Na_3AlF_6\ (s) + 14H_2O\ (g) = 28HF\ (g) + 26NaF\ (liq) + NaAl_9O_{14}\ (s) \qquad (2)$$

The presence of water in the pit is thus lowering the onset temperature for fluoride volatility, in addition to favor the formation of HF over $NaF/NaAlF_4$[15]. The measured level of HF in series 3 is presented in the lower part of Figure 4. Between 900 and 1100 °C during heating, HF was measured to 400 – 600 ppm. These values are given by the instrument built-in model and are most likely an underestimate the actual HF concentration. A manual evaluation of the HF signal was attempted, where the experimental signal was compared to calibration data for various concentrations. Due to the complexness of the experimental signal and the lack of easily interpreted data, it was found difficult to give accurate values for the HF concentration. The data from the instrument built-in model was therefore decided to be used. However, based on overall signal from the FTIR, the true HF concentration is proposed up to 1500 – 2000 ppm. Regardless of the actual HF level, the important observation is that HF is present in the furnace in significant amounts. A thermodynamic assessment has addressed the effect of HF on aluminosilicate refractories during a baking cycle[15]. Mullite ($Al_6Si_2O_{13}$), a major phase in many aluminosilicate materials, reacts with HF to form $SiAl_2F_2O_4$ at moderate temperatures in accordance to Equation 3:

$$Al_6Si_2O_{13}\ (s) + 4HF\ (g) = 2SiAl_2F_2O_4\ (s) + Al_2O_3\ (s) + 2H_2O\ (g) \qquad (3)$$

$SiAl_2F_2O_4$ is however not thermally stable and will decompose above ~1100 °C as described in Equation 4.

$$4SiAl_2F_2O_4\ (s) = 2SiF_4\ (g) + Al_2O_3\ (s) + Al_6Si_2O_{13}\ (s) \qquad (4)$$

Through the reaction path described here, fluorine ends up as gaseous SiF_4 leaving the furnace through the off-gas. Based on these considerations, it is thus not expected to find fluorides in autopsy samples of refractory linings. The calculations are also addressing the tendency for traces of the electrolyte in the green anode to react with water before decomposing into NaF and $NaAlF_4$ [15]. Water is thus "cleaning" the green anodes for electrolyte. A recent study of spent refractory lining has reported very low levels of sodium in the samples, and related this to low levels of electrolyte in the green anodes [8]. However, with the current observations of water and HF in the pit, some electrolyte must be present in the green anodes, reacting with water before reaching its decomposition temperature. Several studies on spent refractory lining reports regions or layers of SiO_2 depletion [8–10,16]. As described in Equations 3 and 4, HF reacts with the lining to form a condensed fluoride phase, which, when heated above 1100 °C, forms gaseous SiF_4 and depletes the lining of silicon. This reaction path could explain the SiO_2 depletion observed in the spent lining in other studies [8–10,16].

During production of the green anodes, extensive use of water cooling is applied after forming in order to regain mechanical stability prior to storage. The anodes are immersed into a water basin and kept there for ~2 hours, while the anodes are cooled and water is absorbed into the open porosity. The Mettler softening point of pitch is usually 110 – 120 °C[17], and the anodes must be cooled below this temperature to avoid creep during storage. To reduce the amount of water in the green anodes, it could

therefore be interesting to investigate the water content in relation to soaking time. If the anodes are removed from the water basin at e.g. 80 °C, there is still enough residual heat in the anodes to increase the evaporation of water during storage.

4.3 Evaluation of the experimental method

In situ measurements of pit gas composition has proven to be a challenging, but rewarding exercise. Especially with respect to the setup design and the obstacles with measuring pit gas continuously during the whole cycle. The degree of pitch residue condensation was much higher than first expected, and the construction of a condensation vessel and increase in pipe diameters were direct consequences of that observation. With the condensation vessel in place for series 2, it became possible to run the experiment during the heating period, which resulted in large amounts of water in the condensation vessel. The high condensation rate measured during the first 24 hours of the baking cycle was not expected, but seen in light of the extensive use of water cooling, not surprising. The pressure drop over the filter cylinder increased when the XAD-2 was wetted, and the filter material had to be changed regularly during the humid period of the cycle. Series 2 was carried out in the middle of December with an outside temperature below -20 °C. This caused the outlet tube from the FTIR to freeze due to humidity in the gas, and several discontinuities occurring in the measurements. Given these challenges, combined with the long duration of the baking cycle, measurements of pit gas during anode baking has not been a trivial experimental exercise. The results have, on the other hand, given valuable insight in the development of the pit gas atmosphere during the anode baking process.

Spectral analysis from the experiments have in some cases been challenging. Especially in the first part of the baking cycle, where the level of pitch residues high and the raw spectra were a mixture of partly overlapping signals. The setup was not designed for controlled dilution prior to the FTIR analysis, resulting in the signal exceeding the detection limit of the instrument. The main peak of CO_2 (~2350 cm^{-1}) is reaching the detector limit at ~1 %, hence secondary peaks had to be used in the analysis. The secondary peaks are however interfering with the IR response from water, making accurate quantitative analysis above moderate concentrations in humid atmospheres difficult. The same was experienced with HF in series 3, where the underestimated values from the model were used due to difficulties finding frequencies without interference for manual evaluations. That being said, the overall experimental results give a good indications of the dominating compounds and the trends in gas compositions over the course of a baking cycle.

The data presented in this study is based on three experimental series of pit atmosphere, conducted over the course of 15 months. The measurement were carried out in different sections of the baking furnace, in pits of varying age. The three series cover various parts of the baking cycle, with varying degree of overlap. The spread in sampling periods is due to the experimental design and unexpected difficulties during the measurements. Most of the pitch components are found to vaporize during the

first part of the heating cycle (from 400 ℃ to 800 ℃), constituting a critical period in terms of potential pipe or filter blockage. This period was thus omitted in some of the series in order to maintain an open system for the rest of the experiment. HF was measured in considerable concentration during the third series, constituting a significant threat to the silica-based optics in the FTIR instrument. Some parts of the third series are therefore shorter measurements spread out instead of continuous measurements.

5. Conclusion

In situ measurements of pit gas atmosphere during anode baking were successfully performed by FTIR spectroscopy. The experiments resulted in valuable insight in the development of pit atmosphere as a function of baking time and temperature. Time series of CO and CO_2 showed that CO_2 is the dominating specie at moderate temperatures, while CO takes over above ~700 ℃. Condensation of water at an average rate of 0.19 L/hour was measured the first 24 hours of the baking cycle. Between 400 ℃ and 800 ℃ during heating, large concentrations of CH_4 was present, originating from the decomposition of pitch in the anodes. At ~1100 ℃ during heating, significant levels of HF was detected, expected to come from the reaction between cryolite in the anodes and water. HF have a destabilizing effect on the refractory oxides, and could serve as an explanation for the earlier reported SiO_2 depletion.

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References

1 E.H.M. Moors: *J. Clean. Prod.*, 2006, vol. 14, pp. 1121–38.

2 H.-G. Schwarz, S. Briem, and P. Zapp: *Energy*, 2001, vol. 26, pp. 775–95.

3 F. Becker and F. Goede: *Alum. Int. J.*, 2006, pp. 1–15.

4 P. Prigent and M.L. Bouchetou: *Interceram*, 2009, vol. 58, pp. 202–9.

5 P. Prigent and M.L. Bouchetou: *Interceram*, 2009, vol. 58, pp. 121–6.

6 T. Brandvik, A.P. Ratvik, Z. Wang, and T. Grande: *Light Met.*, 2017, pp. 1281–8.

7 T. Brandvik, A.P. Ratvik, and T. Grande: Proceedings of the 34th International ICSOBA

Conference *2016*.

8 T. Brandvik, Z. Wang, A.P. Ratvik, and T. Grande: *Int. J. Appl. Ceram. Technol.*, DOI:https://doi.org/10.1111/ijac.13108.

9 F. Brunk: *Light Met.*, 1995, pp. 641–6.

10 N. Oumarou, D. Kocaefe, and Y. Kocaefe: *Ceram. Int.*, DOI:10.1016/j.ceramint.2016.08.178.

11 T.A. Aarhaug, T. Brandvik, O.S. Kjos, H. Gaertner, and A.P. Ratvik: in *Light Metals*, 2018, pp. 1379–85.

12 T.A. Aarhaug, T. Brandvik, H. Gaertner, A.P. Ratvik, and O.S. Kjos: in *AASTC*, 2018.

13 D. Trommer, D. Hirsch, and A. Steinfeld: *Int. J. Hydrogen Energy*, 2004, vol. 29, pp. 627–33.

14 F. Grégoire and L. Gosselin: *Int. J. Therm. Sci.*, 2018, vol. 129, pp. 532–44.

15 T. Brandvik, A.P. Ratvik, and T. Grande: Travaux 47, Proceedings of the 36th International ICSOBA Conference, *2018*, pp. 555-562.

16 Z. Wang, S. Rørvik, A.P. Ratvik, and T. Grande: *Light Met.*, 2017, pp. 1265–74.

17 C. Sommerseth, R. Thorne, A. Ratvik, E. Sandnes, H. Linga, L. Lossius, and A. Svensson: *Metals (Basel).*, 2017, vol. 7, p. 74.

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Figure 1: Overview of the experimental setup used in the second and third measurement campaigns. The Kanthal probe consists of two concentrically mounted pipes. The inner diameter, outer diameter and length are 20.9 mm, 36.7 mm and 4200 mm (inner pipe), and 34 mm, 40 mm and 4500 mm (outer pipe), respectively.

Figure 2: Concentration of CO and CO_2 from series 1 during the baking cycle. The corresponding temperature is also shown.

Figure 3: Concentration of CO and CO_2 from series 1, 2 and 3. The lower part of the figure shows the ratio between CO and CO_2, illustrating the shift in the dominating specie from CO (high temperature) to CO_2 (low temperature). The temperature profile plotted for series 2 applies for all series.

Figure 4: Concentrations data of CH_4 and HF. Both compounds are mostly present during the first part of the baking cycle.

Figure 5: The ratio between ratio $(p_{CO})^2$ and p_{CO_2} for series 1, 2 and 3, in addition to equilibrium data, plotted as a function of temperature. The experimental data is in good accordance with the equilibrium data.

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Table 1: Concentration data from series 1, 2 and 3, covering three periods of the baking cycle. For NH_3 linear extrapolation from 0.1 % was performed. The spectral line for C_6H_6 was compared to a 0.1 % library spectrum, which indicated a concentration higher than 0.1 %. Exact quantification was however difficult due to overlapping signals from other species present in the gas.

	~700 °C (heating)		~1150 °C (max temp)			~700 °C (cooling)		
	S1	S2	S1	S2	S3	S1	S2	S3
CO [%]	1.5	1.1	2.9	5	5.3	1.5	0.18	1.1
CO_2 [%]	0.15	2	175 ppm	0.6	0.1	8	12.5	12.9
H_2O [%]	2.2	1	2.0	6.1	0.5	0.6	6.3	0.7
CH_4 [%]	29	7	0.1		285 ppm			
NH_3 [%]	~ 1	~ 0.1						
C_6H_6 [%]	> 0.1							
HF [ppm]					400-597			