Influence of various sorts of coke breeze on the off-gas composition during iron ore sintering

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Summary

In the sintering of iron ores, the chemical composition and the physical properties of coke breeze has a significant effect on the sinter process and the sinter quality. This paper is focused on the influence of coke breeze from different deposits and coking plants respectively, in particular on the off-gas composition of the sinter process and the sinter quality. Laboratory-scale sinter feed mixtures with various sorts of coke breeze are produced, whereby the particle size distribution of the investigated coke breeze is constant as well as the individual coke breeze addition with respect to the fixed carbon content. The small scale sinter experiments are performed in cylindrical packings of sinter mix. During the sintering the emissions of CO, CO_2, NO and SO_2 in the off gas are monitored, as well as specific sintering parameters e.g. the sinter yield and strength. The results of the off-gas analysis are compared with the chemical elemental analysis of the coke breeze. The investigations demonstrate that a high carbon content of the coke breeze leads to a higher pressure loss across the sinter bed, thus to a shorter sintering time and correspondingly to higher productivity. Changes in the nitrogen concentration in the coke breeze cause significant NOx variations in the off-gas. As expected, the total sulfur in the off-gas cannot be entirely attributed to the coke breeze. The findings obtained on a laboratory scale enable a coke breeze characterization close to an industrial sinter belt, demonstrating the expected process parameters.

Key Words: carbon content, emissions, flame front speed, NOx, productivity

Introduction

Steel mills are confronted with different qualities of coke breeze in the sintering of iron ore. Varying chemical composition and physical properties of the coke breeze can affect the mode of operation of a sinter belt, the off-gas composition and the sinter quality. This work is focused on the influence of coke breeze from different deposits and coking plants respectively, on the sinter process in particular the off-gas composition, specific sintering parameters as well as the sinter quality.

The described sinter experiments were conducted with a miniaturized lab-scale small sinter test facility (SASITE). A schematic view of the SASITE can be found in

[1]. The test facility consists of a refractory ceramic tube (alumina) which can be filled with a cylindrical sinter packing of 80 mm diameter and a bed height of 400 mm on a carrier disk for the hearth layer at the bottom. Up to seven thermocouples (type N) can be positioned equally distributed over the height of the sinter packing. These measuring points can additionally be used for pressure loss measurements before (cold flow permeability) and after the sinter experiments. Another thermocouple (type K) is located directly under the carrier disk. Additional the setup comprised a methane/oxygen burner, an off-gas suction system (rotary vane vacuum pump) with integrated gas analysis (O_2, CO, CO_2, SO_2 and NO) as well as a control and data acquisition. The gas components CO, CO_2, SO_2 and NO are measured by a non-dispersive infrared sensor (NDIR), with a measuring range of 0-10 vol.% for CO, 0-100 vol.% for CO_2, 0-1 vol.% for SO_2 and 0-2500 ppm for NO. O_2 is measured electrochemically in a measuring range of 0-25 vol.%.

The sampling of the various sorts of coke breeze (A to G) was carried out in the as-delivered condition, in order to guarantee a pure grade. The coke breeze for the reference sinter series was taken after the ball milling process from the industrial project partner to ensure a standard operating particle size distribution, as presented in Table 1. Various sorts of coke breeze are classified in the initial state (without drying) to obtain the same particle size distribution of the reference coke breeze.

Table 1: Operating particle size distribution after the classification of various sorts of coke breeze

Particle size, mm	<0.1-1	1-2	2-3	3-4	4-5	5-6	6-10
Fraction, wt.%	40.90	21.45	21.81	10.65	4.31	0.67	0.22

The chemical analysis of the coke breeze samples are summarized in Table 2. The results show a wide variation even in the main composition parameters, which are discussed in more detail below.

Table 2: Chemical analysis of various sorts of coke breeze

	Moisture	Ash content (dry)	Volatile components (dry and ash-free)	Nitrogen (dry)	Carbon (dry)	Sulfur (dry)	Sulfur (burnable)	Hydrogen (dry)
	wt.%$_{moist}$	wt.%$_{dry}$	wt.%$_{dry,ash-free}$	wt.%$_{dry}$	wt.%$_{dry}$	wt.%$_{dry}$	wt.%$_{dry}$	wt.%$_{dry}$
Ref.	3.08	11.30	1.25	1.24	86.60	0.61	0.53	0.35
A	10.44	12.40	1.53	1.20	85.30	0.72	0.63	0.43
B	2.13	15.30	1.36	1.13	83.60	0.61	0.59	0.43
C	13.68	10.70	2.87	1.13	86.50	0.53	0.34	0.45
D	13.05	12.90	2.74	1.09	85.00	0.57	0.47	0.56
E	11.81	11.20	1.13	1.06	87.20	0.64	0.60	0.32
F	13.42	19.10	8.17	1.08	76.60	0.46	0.18	0.43

The raw materials for the granulated raw mixture (green mix) were directly obtained from the industrial project partner. Sampling of the individual raw materials took place at the respective conveyor belts following the bunker. When considering the results, it must be taken into account, that due to the long period of experimental time, for sinter series E and F separate iron ore samples had to be taken.

The raw materials are weighed immediately before each sinter series according to a defined recipe (see Table 3). A sinter series consists of three individual sinter experiments. For each sinter experiment a separate refractory ceramic tube is used in order to exclude any influence from potential contamination during prior experiments. In addition, the moisture is adjusted to 3.75 ± 0.10 wt.% by adding water before mixing with a spiral stirrer for 45 s. For each sinter series, 16.5 kg green mix are produced once in order to exclude any influence of the mixing on the three single sinter experiments. Due to the different moisture and carbon content of the coke breeze samples (see Table 2), coke breeze is added in different proportions to the raw mixture to achieve a constant carbon content of 3.043 kg C per 100 kg raw mixture. The hydrogen content can be neglected in the energy balance of the flame front due to the fact, that it is already desorbed as part of the volatile species below approx. 600 °C and therefore does not contribute directly to the melting phase formation.

Table 3: Recipes and characteristics of the raw mixtures of the sinter series

	Ref.	A	B	C	D	E	F
Iron Ore, wt.%	60.6	60.4	60.4	60.6	60.4	60.4	60.0
Returns, wt.%	32.0	31.8	31.8	32.0	31.8	32.0	31.7
Limestone, wt.%	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Mill Scale, wt.%	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Coke breeze, wt.%	3.7	4.0	4.0	3.7	4.1	4.0	4.6
Bulk density[1], kg m^{-3}	1821 ± 11	1822 ±1 1	1808 ± 15	1830 ± 8	1817 ± 17	1811 ± 13	1800 ± 4

[1] … average bulk density of the three sinter experiments

Charging of the ceramic tube starts with a hearth layer of 250 g sintered material with particle sizes between 5 and 9 mm. The residual height of 386 ± 1 mm is successively charged with green mix. At selected measuring points, thermocouples are embedded carefully in the granular packing, protected in thin-walled alumina tubes. Prior to the sinter experiment the bulk density (see Table 2) and subsequently the green bed pressure loss (cold flow permeability) are measured (see Figure 4).

Ignition period of the burner lasts 90 s. After ignition, a constant superficial velocity of 0.83 ± 0.01 m s^{-1} is used until the temperature under the hearth layer begins to rise and the burn through point is reached. The burn through point (equating with the sinter time) is defined by the peak temperature under the hearth layer. When the temperature under the hearth layer has dropped below 100 °C, an additional permeability test for the sinter product is conducted. Afterwards the sintered material is dismounted and its strength measured with the shutter test (JIS-M 8711).

Figure 1 shows the temperature profile of the off-gas directly under the hearth layer and the trend of the off-gas components (SO_2, CO, CO_2, NO and residual-O_2) of the reference series. The temperature profiles show, that the adiabatic saturation temperature is reached after approx. 120 s, due to the formation of the condensation zone after the ignition. The peak of CO and CO_2 at the beginning of

the sintering experiments is due to the ignition caused by the influence of the burner on the off-gas composition. The SO_2 breakthrough starts after approx. 350 s due to saturation and drying of the condensation zone. For further result illustration, the values of the off-gas components (SO_2, CO, CO_2, NO) are summed over the test period time of 1200 s.
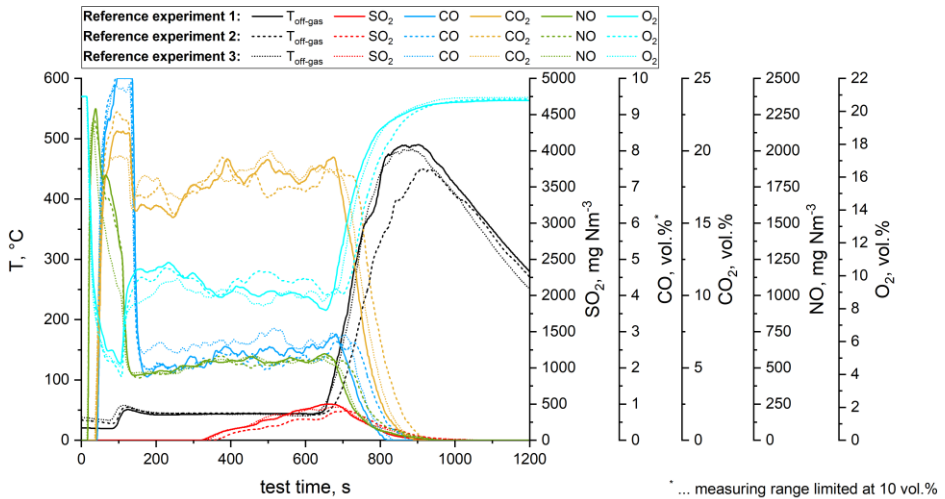

Figure 1: Temperature profile of the off-gas directly under the hearth layer and trend of the off-gas components (SO_2, CO, CO_2, NO and residual-O_2) of the reference sinter experiments 1-3

At the beginning, the ignition caused data acquisition failures in individual experiments, so that not for all parameters three values were available for averaging, this particularly concerns CO, CO_2 and NO. The results for CO and CO_2 provide a consistent amount, with minor variations for CO_2 from 941 ± 26 to 1014 ± 69 g, as shown in Figure 2. The amount for CO is almost constant between 109 ± 3 and 116 ± 8 g CO due to the interplay of the Boudouard and the water-gas shift reaction [2]. Since a constant carbon content of 3.043 kg C per 100 kg raw mixture was set in all sinter series, the fluctuations in CO_2 are probably due to calcination.

Regarding the average results of SO_2 in Figure 2, experiments E and F stand out with significantly low values of 377 ± 40 and 437 ± 36 mg SO_2. For all other series, the SO_2 amount is in the range between 507 ± 57 and 572 ± 55 mg SO_2. The results of the chemical analysis of the coke breeze, as presented in Table 2, do not follow this trend, possibly due to the separate iron ore sampling for these two sinter series. In addition, Table 4 compares the possible sulfur load from the coke breeze with the measured amount of sulfur in the off-gas. As expected, the total sulfur from the coke breeze cannot be completely recovered in the off-gas. This means that a significant portion of the desorbed sulfur is re-embedded into the sinter due to the desulfurization capability of the free basicity provided with the green mix.
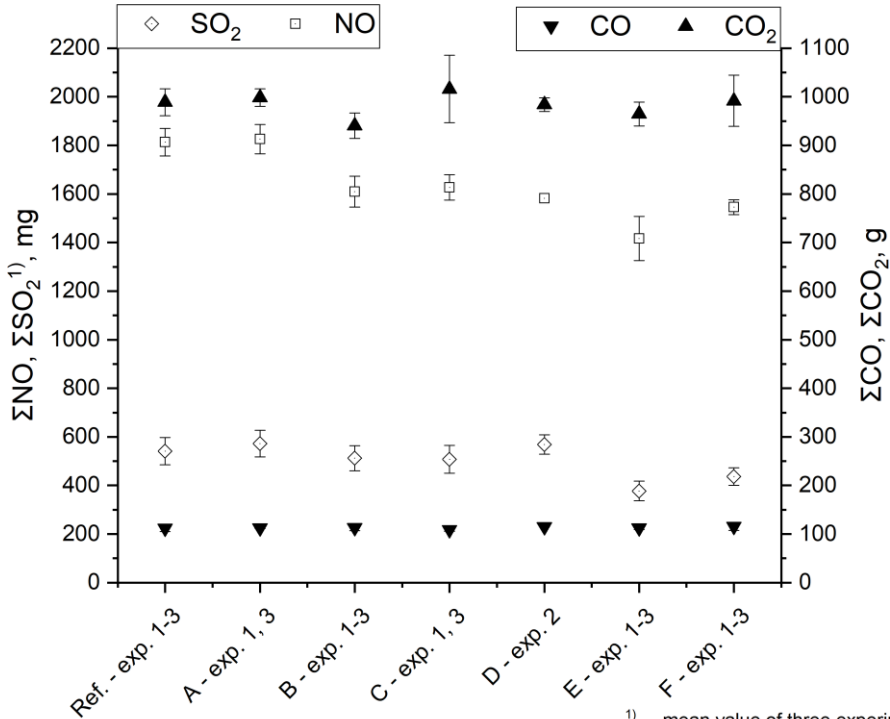
Figure 2: Summed averaged values of the off-gas components NO, SO$_2$, CO und CO$_2$ over the test period (0 - 1200 s) of the sinter experiments

Table 4: Theoretical amount of SO$_2$ produced from stoichiometric conversion of sulfur load in the coke breeze compared to measured amount of SO$_2$ in the off-gas (all values normalized by the specific amount of sinter produced during each experiment)

	Summed averaged SO$_2$ measured via off-gas analysis	Stoichiometric converted SO$_2$ from coke breeze (burnable sulfur[1])
	mg kg^{-1}$_{Sinter}$	mg kg^{-1}$_{Sinter}$
Reference	288 ± 26	672
A	303 ± 36	806
B	280 ± 35	832
C	278 ± 21	402
D	307 ± 21	601
E	205 ± 21	760
F	249 ± 23	270

[1] … data shown in Table 2

The results of NO in Figure 2 show a significant variation, which cannot be attributed to different proportions of thermal NO$_x$, since the temperature profiles in the sinter packing for the individual sinter series show a similar profile and approximately the same peak temperatures. The peak temperatures in the flame front of all experiments lay well below the formation limit for thermal NO$_x$, which will become significant at gas temperature levels not lower than 1400 °C. For closer analysis, the NO results of the gas analysis are additionally presented with the

nitrogen content of the coke breeze samples in Figure 3. This data suggest a correlation between the nitrogen content in the coke breeze and the NO concentration in the off-gas.
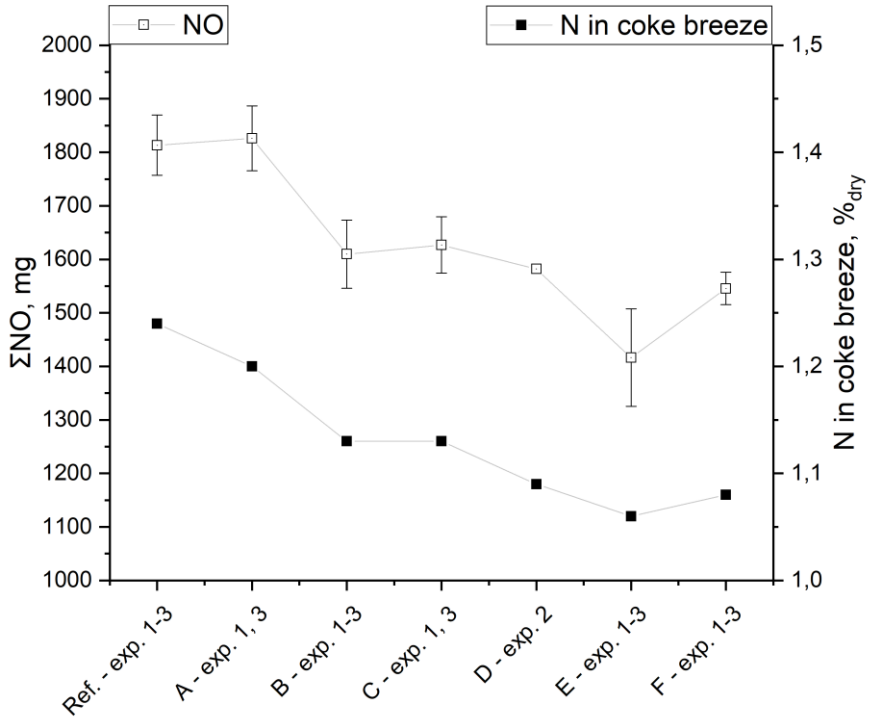

Figure 3: Summed averaged values of the off-gas component NO over the test period (0 - 1200 s) of the sinter experiments plotted together with the nitrogen content of the coke breeze samples.

Sintering leads to a typical decrease of the bed height, whereby no perceptible difference could be observed between the sinter series. It must also be noted that the thermocouples in the sinter packing have a certain support function of the sintered package and therefore only the upper 100 mm (height from the top of the ceramic tube to the first positioned thermocouple) are taken into account of the shrinking analysis. The results of the loss of mass in Figure 4 are in the range of 19.7 ± 0.3 and 20.8 ± 1.7 wt.% and confirm the observation of the similarly height decreases, which mainly follows the evaporation of moisture and carbon burnout including the calcination. The yield shows minor differences and is in the range of 52.2 ± 1.4 to 55.2 ± 1.2 wt.%. Accordingly, the differences can also be observed in the returns and range from 24.8 ± 0.7 to 27.1 ± 1.3 wt.%.

The results in Figure 4 also demonstrate a high carbon content of the coke breeze to lead to a higher pressure loss across the sinter bed, and thus to a shorter sintering time and correspondingly to higher productivity. Series C to E stand out with rather high productivities of 33.2 ± 2.7 to 34.0 ± 0.9 t m^{-2} day^{-1} and series F

with a particularly low productivity of $28.3 \pm 0.9\ \text{t m}^{-2}\ \text{day}^{-1}$. Furthermore, the productivity correlates with yield and bulk density (see Table 3). Therefore, the green bed pressure loss is proportional to the bulk density, although the correlation is not as strong. The results of the permeability test for the sinter product are almost exactly 31 mbar below those of the green bed pressure loss for all sinter series, showing the same trend as the latter.

The results of the illustrated sinter experiments do not correlate with the definition for the heat transfer front speed (HTF) described by Cheng et al [3]:

$$v_{HTF} = u_g \rho_g c_g / \left[\varepsilon \rho_g c_g + (1 - \varepsilon) \rho_s c_s \right] \tag{1}$$

Accordingly, a higher bulk density would result in a lower heat transfer front speed, or a longer sinter time. Probably the carbon content of the coke breeze overrides this basic effect and has a greater influence on the heat transfer front speed in our experiments. Generally, a lower carbon content in the coke breeze is accompanied by a higher content of inert substances (see ash content in Table 2), which in turn may lead to a lower accessibility of reactive surface for oxidation and thus to a lower heat transfer front speed.
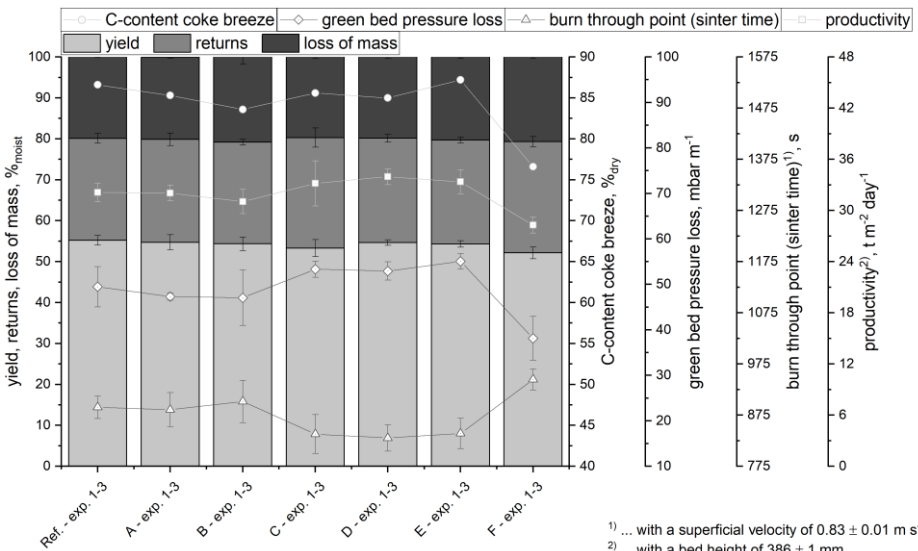

Figure 4: Yield, returns and loss of mass of the sinter experiments including the carbon content of the coke breeze samples, the green bed pressure loss, the burn through point and the productivity

Sinter strength of the samples was measured by the shutter test. The strength tests were carried out within 24 h after sintering in order to avoid possible aging effects from storage of the sinter samples under atmospheric contact. The results show consistent sinter strength values, with no significant outliers up or down. An influence of the moisture of the coke breeze samples on the sinter process could not be observed.

Conclusion

The influence of various sorts of coke breeze on the sinter process and in particular the off-gas composition during iron ore sintering was investigated by miniaturized lab-scale sinter experiments. Laboratory-scale sinter feed mixtures with various sorts of coke breeze were produced, whereby the particle size distribution of the investigated coke breeze was constant as well as the coke breeze content with respect to the fixed carbon content. The investigations demonstrate a significant influence of the coke breeze composition on the sinter process. This affects in particular the off-gas composition, especially the NO concentration, as well as the heat transfer front speed and thus considerably the productivity. The results suggest that a coke breeze with high carbon content combined with a low nitrogen content will increase the productivity and allow for low NO emissions at the same time. Even if implementation of the process optimization potentials identified might be challenging due to the operative difficulty of a selective coke breeze sourcing, at least a deeper understanding of the influence of different coke breeze on the sinter process could be created in this study. In summary, small scale sinter experiments could demonstrate relevant process influences of different coke breeze qualities on the industrial sinter production.

References

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