

PRIMARY MEASURES FOR THE REDUCTION OF NO_x EMISSIONS FROM IRON ORE SINTERING - A REVIEW

Christof LANZERSTORFER, Andreas GAHLEITNER

University of Applied Sciences Upper Austria, Wels, Austria, EU, c.lanzerstorfer@fh-wels.at

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Abstract

During the sintering of iron ore in the sintering process, nitrogen oxides (NO_x) are produced and discharged with the process off-gas. The reported concentrations of nitrogen oxides expressed as NO₂ in sintering off-gas are typically in the range of 300-500 mg/Nm³. However, also concentrations up to 1000 mg/Nm³ have been reported. NO_x emissions from combustion can originate from three different formation mechanisms: thermal NO_x, prompt NO_x and fuel NO_x. It has been established that in the sintering process the most significant source of NO_x emissions is the fuel NO_x. According to literature, only a few iron ore sinter plants operate a DeNO_x system for the reduction of the NO_x emissions (Secondary measures). However, there is plenty of ongoing research in primary measures for the reduction of the NO_x emissions from the sintering process. These measures include the recirculation of the process off-gas, pre-treatment of the coke breeze used as fuel, replacement of the coke breeze by other fuels and the addition of various compounds to the sinter feed for the reduction of the NO_x formation. In this study, the data available in the literature about the primary measures for the reduction of the NO_x emissions from iron ore sinter plants are summarized, compared and discussed.

Keywords: Sintering process, NO_x emission, primary measures, emission reduction

1. INTRODUCTION

In the sintering process the feed material - a mixture of fine grained iron ore, flux, recycled fines and a solid fuel, usually coke breeze - is granulated and subsequently placed on a continuous traveling grate, the sinter strand. A burner at the beginning of the strand ignites the fuel contained in the mixture, after which the combustion is self-supporting. Beneath the grate there are several windboxes to draw air and combustion gases through the sintering bed. The combustion of the coke which accounts for approximately 4-6 % of the charge generates sufficient heat (1300-1480 °C) to sinter the fine particles into a porous sinter. The off-gas from the sinter strand which is typically in the range of 1500-2500 Nm³ per tonne of sinter produced contains considerable quantities of entrained particles and various gaseous pollutants. Therefore, it has to be cleaned before it is released into the atmosphere via the main stack [1].

In the combustion zone nitrogen oxides (NO_x) are produced and discharged with the process off-gas. The reported concentrations of NO_x expressed as NO₂ in sintering off-gas are typically in the range of 300-500 mg/Nm³, but also concentrations up to 1000 mg/Nm³ have been reported. The NO_x emitted consists mainly of NO and only a small fraction is present as NO₂. The dominating source for NO_x is the nitrogen contained in the coke breeze [1,3]. Since the NO_x emissions from sinter plants account for approximately half of the total NO_x emissions from the iron and steel industry reduction of the emissions from sinter plants is of great importance [2].

In general, the emissions limits for sinter plants have been tightened in recent years. For Europe the Best Available Technique Associated Emission Levels (BAT-AELs) for air emissions from sinter plants are defined in the commission implementing decision of 28 February 2012 [4], which establishes the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions for the iron and steel production [5]. The defined BAT-AELs depend on the BAT technology

applied for emission reduction, while in contrast, fixed emission limits are valid in China [6]. **Table 1** shows the current NO_x emission limits for sinter plants in Europe and China [4-6].

Table 1 Emission limits for NO_x for iron ore sinter plants

	Europe [4,5] *	China [6]
Off-gas recirculation, Low NO _x burner for ignition	500 mg/Nm ³ dry	300 mg/Nm ³ dry
Regenerative activated carbon process	250 mg/Nm ³ dry	
Selective catalytic reduction (SCR)	120 mg/Nm ³ dry	

* daily mean value related to an oxygen content of 15 %

2. OFF-GAS RECIRCULATION

The partial recirculation of off-gas is an efficient technique for reducing the amount of exhaust gas from a sinter plant discharged through the main stack [1,7]. Such recirculation is possible because of the high oxygen content of off-gas from conventional sintering of about 15 %, while the minimum oxygen content for sintering is in the range of 9-13 % [1,8]. Therefore, the maximum possible degree of recirculation depends on the oxygen content of the off-gas when no off-gas is recirculated. The published results show that the increase in the NO_x concentration of the off-gas is small compared to the reduction of the off-gas volume, which leads to a net reduction of the NO_x emissions [9-11]. Additionally, the sinter off-gas contains about 1 % CO, which is oxidized when the recirculated gas passes through the flame front in the sinter bed. Thus, off-gas recirculation also reduces the fuel consumption in the sinter process, which further reduces the NO_x emissions.

There are several process designs in use for off-gas recirculation in sinter plants at industrial scale. In the EOS system, part of the exhaust gas collected in the windboxes is returned after dedusting to a hood covering the entire sinter strand [9]. In other designs (NSC system [10], LEEP system [11] and Eposint system [12]) selective off-gas recirculation is applied, where the off-gas from selected windboxes is returned to hoods, which are located over certain parts of the sinter strand. **Table 2** shows the published NO_x reduction data for the different systems.

Table 2 Reported emission reduction achieved with various off-gas recirculation systems

		EOS [9]	NSC [10]	LEEP [11]	Eposint [12]
Off-gas volume	m ³ /h	-47 %	-28 %	-45 %	-40 %
NO _x emission	kg/h	-39 %	-31 %	-49 %	-24 %

3. SUBSTITUTION OF COKE BREEZE OR PRETREATMENT

3.1. Substitution of coke breeze

Since most of the emitted NO_x originates from fuel nitrogen the substitution of coke breeze by a fuel with a low nitrogen content can reduce the NO_x emissions.

In a study using charcoal at different rates in sinter pot tests for the substitution of coke the equivalent fixed carbon substitution method was applied [16]. Because of the higher content of volatiles in the charcoal the energy input was increased using the substitution method. Up to a substitution rate of 60 % the sintering process parameters were not deteriorated, while according to the diagrams the NO_x emissions decreased almost linear with increasing coke substitution. However, no detailed data for the NO_x reduction were reported.

In another study, the use of charcoal, charred-straw and molded-sawdust was investigated in sinter pot tests [17]. The substitution was performed on an equivalent heat basis. The process parameters and the quality of

the sinter produced were nearly unchanged up to coke substitution rates of 40 %, 20 % and 15 % for charcoal, charred-straw and molded-sawdust. The respective reductions of NO_x emissions were 26.8 %, 18.3 % and 15.5 %.

In an investigation about straw-based fuels in sintering the limits for the use of straw char and preformed straw char resulting from process and sinter quality parameters were 20 % and 40 % substitution on an equivalent heat basis, respectively [18]. The corresponding reductions of NO_x emissions were 16.9 % and 28.2 %.

3.2. Pretreatment of the coke breeze

The NO_x emissions from the sintering process can be reduced by pretreatment of the coke breeze. In a study, sinter pot tests were performed where the coke was modified with CeO₂ prior to its use. Fine grained CeO₂ powder in the range of 28-150 μm was added into water to make a suspension with a certain concentration. The coke was impregnated in the CeO₂ suspension and subsequently dried. The CeO₂ content of the coke was up to 2.0 %. At the highest CeO₂ content an emission reduction for NO_x of 18.8 % was observed [13].

In another study, the preparation of the coke breeze was performed with a solution of urea [14]. The highest NO_x reduction (16.2 %) was achieved at 1.0 % urea content of the coke, while at higher urea concentrations of the coke the NO_x emissions were increased.

The combination of off-gas recirculation and use of impregnated coke for the reduction of NO_x emissions was investigated in sinter pot tests [15]. Thereby, the coke was modified with CeO₂, K₂CO₃ or CaO prior to its use. The reduction of NO_x emissions using coke loaded with CeO₂, K₂CO₃ or CaO was in the range of 34-38 %, which was approximately 10 % higher than in the reference test with off-gas recirculation only.

3.3. Pretreatment of the sinter feed

The NO_x emissions can be influenced by the distribution of the fuel in the sinter feed. During preparation of the sinter feed the blended fine materials including iron ores, fluxes, return fine and coke breeze are granulated at suitable moisture to improve the permeability of the sinter mixture. In a laboratory study double-layered granules were produced by pre-granulation of all the coke breeze, part of the iron ores and fluxes in a first step. The rest of the iron ores and fluxes as well as the return fines were added in the second granulation step [2]. Thus, the structure of the granules was divided into two layers: the inner layer containing the all the coke breeze and the outer layer consisting of iron ores and fluxes. Since the fuel was wrapped inside the granules it was not directly exposed to air and, therefore, needed more time to burn out. The O₂ concentration in the atmosphere of the inner layer is comparatively low, which reduces the conversion of fuel nitrogen to NO_x. As a result, the NO_x emissions were reduced. In the study a 25 % reduction of NO_x emission was reported [2].

4. ADDITION OF NOX-REDUCING AGENTS

The addition of calcium ferrite into the sinter feed mixture is proposed to reduce NO_x emissions since calcium ferrite enhances the catalytic reaction of CO with NO in the sintering bed [19]. Additionally, the strength of the sinter will be improved with the help of calcium ferrite because of its low melting point. The results of sinter pot tests showed a reduction of NO_x emissions of 26.8 % compared to conventional sintering at 8 % addition of calcium ferrite, which was the optimum rate. At higher calcium ferrite addition the permeability of sintering bed was significantly reduced.

The addition of 1.0 % rice husk, flour, saw dust or cane slag to the sinter feed mixture showed little potential for NO_x emission reduction and eventually decreased the productivity [20]. In contrast, the addition of 1.0 % sugar led to a reduction of NO_x emissions of 28 %. Additionally, the productivity was somewhat increased.

5. CONCLUSION

Primary reduction of NO_x emissions from iron ore sintering can be achieved by various methods: off-gas recirculation, substitution or pretreatment of coke as fuel or addition of NO_x-reducing agents. However, only off-gas recirculation is applied on an industrial scale. The performance of the other primary reduction methods was reported only for pilot scale tests. Future efforts would be required to demonstrate the performance of these methods on full-scale plants.

The highest reduction rates for NO_x emissions are reported for off-gas recirculation (24-49 %), followed by substitution of coke by charcoal or straw char (16.9 up to approximately 40 %). The addition of NO_x-reducing agents (26.8-28 %), the substitution of coke by other organic material (15.5-18.3 %) and pretreatment (16.6-25 %) shows less NO_x reduction potential.

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