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PRODUCTIVITY AND DIOXINS REDUCTION ANALYSIS DURING SINTERING ORE OPERATIONS[1]

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Abstract

Sintering is a fundamental process for ironmaking operations, it represents one of the main sources of production of PCDD (polychlorinated dibenzo-p-dioxins), PCDF (polychlorinated -dibenzo-furans), NOx and SOx. In the present study the optimal operating conditions, through which a reduction of dangerous emissions can be achieved, are underlined through numerical analysis. By employing a multi-objective optimization tool, a deep analyses capable of representing the process behavior leading to the optimal operating conditions was developed. Through such analysis, a broad range of processing parameters affecting the development of PCDD/Fs in the sintering process has been evaluated. The first aim was the possible reduction of dangerous emissions through numerical and experimental analysis allowing the definition of the optimal conditions for the minimization of the pollutants. Although the resultant optimal combination of input parameters able to reduce the dangerous emissions from the plant, it was largely examined the impact of the chosen input parameters on the sinter productivity. In such a way it was possible to reduce the emissions close to the legal limits with an high to with an high level of productivity and efficiency of the plant.

Keywords: Iron ore sintering; Dioxin emission; Numerical analysis; Productivity.

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1 INTRODUCTION

1.1 Process Description

Ironmaking and steelmaking are a highly material and energy intensive industrial operations. More than half of the mass input becomes outputs in the form of off-gases and solid products. The most dangerous emissions are those to air.

The sintering of raw material is certainly one of the top steps in the ironmaking processes, the process was largely described by the authors in[1, 2]. Iron ore fines, other iron-bearing wastes and coke dust are blended and combusted[3-7]. The agglomeration process gives rise to many different physical and chemical phenomena. During heating, the following main steps can be distinguished:

• around 100 °C, drying of the mixture; at higher temperatures the water of crystallization is removed;

• between 600 and 800 °C the first agglomeration of fine particles into a porous material takes place and the swelling grains adhere weakly to each other;

• more than 1000 °C, the grains soften and we can see the same physical and chemical conditions that lead to the completion of the agglomeration process.

At the end of the grate a sinter breaker is placed. It reduces the sintered material to the desired size[8]. Here PCDD/Fs form in the presence of carbon-containing materials[9, 10] the process is favored by the presence of specific organic compounds or a carbonaceous matrix-sand sources of chlorine and oxygen. The temperature increase favors the PCDD/Fs formation in the range 200-800 °C, at higher temperatures they rapidly decompose. It was observed that the presence of catalytic metals (Cu) can be essential at modest temperatures[11,12].

1.2 Emissions Formation

The gas temperature inside the wind boxes and wind legs is lower (100-500 °C) with respect to the sintering grate; such conditions lead to the optimal physical and chemical conditions for the formation of pollutants such as PCDD/Fs, NOx and SOx[13]. Polychlorinated dibenzo-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) are persistent stable organic pollutants formed in all those high temperature processes with abundance of organic material in presence of chlorine and copper. Dioxins and furans are chlorinated tricyclic organic compounds resulting from the combination of organic compounds impregnated with halogens (i.e. fluorine, chlorine, bromine or iodine) with a specific molecular heterocyclic structure. A deep and complete thermodynamic description of the PCDD/Fs formation has been presented in literature by Tan et al.[14]. Among the 200 types of known dioxins, the most famous are certainly the PCDD, they are characterized by the presence of chlorine atoms that will complement the aromatic rings. The most dangerous of dioxins, for serious problems of bioaccumulation and environmental contamination, is certainly TCDD[15].

1.3 Multi-objective Analysis

In the present study, a broad range of processing parameters affecting the development of PCDD/Fs in the sintering process has been evaluated. The main aim

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was the possible reduction of dangerous emissions through numerical and experimental analysis allowing the definition of the optimal conditions for the minimization of the pollutants. The employed multi-objective optimization software is modeFRONTIER® (ESTECO), through which a set of input parameters, governing the plant and the production process, was defined. They were evaluated on the basis of an optimization algorithm, chosen for the multi-objective analysis. Starting from a database, built by employing experimental and literature data, a computational model (n-dimensional virtual surfaces), capable of reproducing at best the actual process, was developed. The analysis performed led to the minimization of the output variables (PCDD/F, NOx and SOx). For PCDD/F, it was necessary to apply a filtering system in order to obtain quantities of emissions below the legal limit of 0.4 ng I-TEQ/Nm3 as actually required by legislation. The main objectives of sintering ore plant operations include maximizing grate productivity (expressed in tons per square meter of grate area of sintering machine per day), minimizing fuel consumption, maintaining fired pellet quality within limits specified by blast furnace or reduction furnace requirements and to minimize greenhouse gas and sulfur emissions to the environment. Some interesting results are available in literature belonging to studies performed to reach an optimization of sintering operations coupled with a reduction in dangerous emissions[16-18]. In the present study a coupled analysis of input parameters leading to a reduction of dangerous emissions and an acceptable productivity of the plant was carried out by employing a multi objective optimization strategy.

2 MATERIALS AND METHODS

2.1 Workflow Definition

In order to obtain a strong optimization and control of the industrial operations in sintering ore plants different models were proposed and are available in literature, many of those models refers to experiments performed on laboratory scale[19-21]. In the present study a model belonging to a multi-objective optimization analysis have been carried out from data belonging to a real industrial plant. The recorded compositional values of the employed coals (wt%) is shown in table 1. The sintering process is outlined in the Workflow through the analysis carried out by modeFRONTIER, as shown in figure 1.

Table 1. Composition ranges of the used coals

Volatiles	1.8-4.7
Carbon fix	74.8-84.8
Sulphur	0.52-2.3
Hydrogen	4.5-4.9
Nitrogen	1.7-1.9
Chlorine	0-0.35
Oxygen	7-8.8

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The workflow is divided into data flow (solid line) and logic flow (dotted line) which have a common node, the calculator node in which mathematical functions and chemical reactions representative of the process are introduced. In the data flow, all the input parameters are grouped; such input parameters should be optimized during numerical simulations as a function of the multi-objectives (in the present case the reduction of emissions). The analysis of the sintering process were performed on a sintering plant belonging to an italian steel company (Dwight-Lloyd sinter). For the development of such analysis, the emissions levels of the last 6 years and the corresponding inputs have been recorded to define the starting point of the problem. The corresponding productivity of the plant and the quality of the sintered material have been taken into account for comparison. The main goal is the reduction of dangerous emissions coupled with acceptable levels of productivity and quality of the material. Each windbox was equipped with thermocouples (k-type) in order to monitor the off-gas temperature during sintering. The flue gases composition was monitored, according to EN1948 parts 2 and 3, EN-1948SS (sampling standards, Wellington Laboratories EN-1948ES (extraction standards, Wellington Laboratories) and EN-1948IS (injection standards, Wellington Laboratories), by employing an high resolution gas chromatograph and an high resolution selective mass detector.

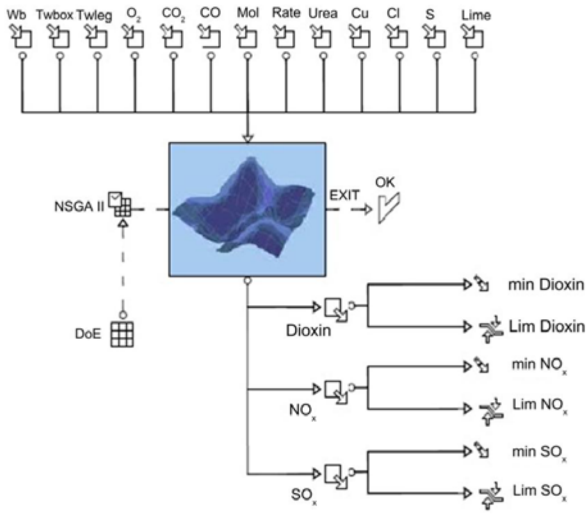

Figure 1. Workflow of analysis.

The output variables (PCDD/F, NOX and SOX) define a multi goal analysis and have been minimized taking into account some constraints or limitations typical of the actual process of sintering. At this stage the nodes that make up the logic flow of numerical analysis are defined. The first node is the DoE, which is the set of different designs reproducing different possible working conditions, among which the most affective ones are highlighted. Therefore it means creating a set number of designs that will be used by the scheduler (the node where the best algorithm is introduced) for the optimization. Depending on how this space is filled, the designs, defined by the scheduler, are more or less truthful. The second node filters the input experimental data; the filtering is possible by employing three types of different algorithm. Such algorithms are MOGA II,

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MOGT and NSGA II. The description of the algorithms properties is largely described in Cavalieri et al.[1] and Cavalieri.[2]

2.2 Multi-objective analysis

By continuing the analysis, the core work flow is defined, which in the present case is a specific RS, which proves to be the only node in common between the Logical flow and data flow. Generally, in this kind of analysis, the heart of the optimization is represented by a series of equations of chemical and physical nature of a given resolution to get the desired output. Optimization software allows the following of different kind of RS. For each output variable to be minimized it is necessary to create a response surface. The analysis starts from a database built with data of operating conditions of the sintering plants obtained from experimental measurements and other related values found in the literature.

2.3 Database Construction

The database is built by introducing the input parameters, the corresponding output for each working condition experimentally analyzed and the physical correlations between the different conditions. Of the 578 starting designs, 572 were used to generate meta-models, while 6 designs were employed as designs of control to verify the affordability of the response surfaces. In the validation phase, they were included in the RSM "trained" only the input remaining conditions and they were compared the numerical calculated output with the experimental output, measuring the Δ error. The phase of the training and validation are the Design of Experiment (DOE). The choice of these 6 was taken in order to get the right information on the entire range of existence of the output variables.

2.4 Optimization Procedure

At the beginning of the analysis, modeFRONTIER generates the space of DoE, following the Reduced Factorial method. Then these designs are transformed by NSGA II algorithm. New designs created by mF fill all the range of analysis. These designs are introduced in the response surface that has been set in the first step of study. In this way mF generates a determined number of working parameters which lead to a particular emission value. At this point the user has to choose the set of input that produces the lower emission value for each output, considering the physical constraints and the legal limit.

3 RESULTS AND DISCUSSION

Concerning the gas temperature in windbox and windleg it must be noted that their trends are very similar and differ only from 30 to 50 °C; the last box can reach even higher temperatures, up to 500-550 °C. From deep numerical analysis belonging to experimental set-up of the plant many fundamental results have been obtained in terms of input parameters (in a broad range of existence) influencing the dioxin, NOx and SOx emissions. Dioxin emission shows a maximum in the windbox 19, in the temperature range 350-480 °C (Figure 2a), it increases also with increasing O2 content up to very

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high levels (Figure 2b), from the graph it is clear how the emissions are very sensitive to such parameters. Dioxin reaches highest values for high temperature and high moisture presence. In such conditions also the CO2 formation reaches its maximum values. Dioxin emissions reach high values for high levels of flow rate in the windboxes, high values of dioxin correspond to low values of carbon monoxide. Many elements and compounds are very active in dioxins formation, Cu and Cl lead to a strong increase in the levels of dioxins emissions.

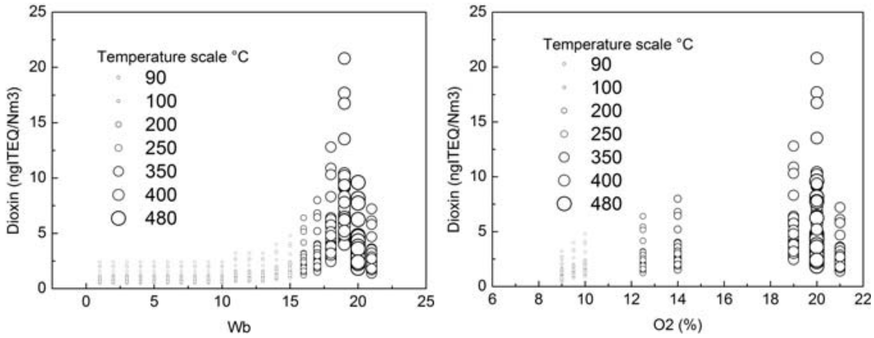

Figure 2. Dioxin emission in the sintering plant monitored in the present study as a function of windbox number and temperature a), and as a function of oxygen and temperature b).

On the contrary, the addition of urea and CaCO3 leads to a strong efficiency in dioxins emission reduction (Figure 3).

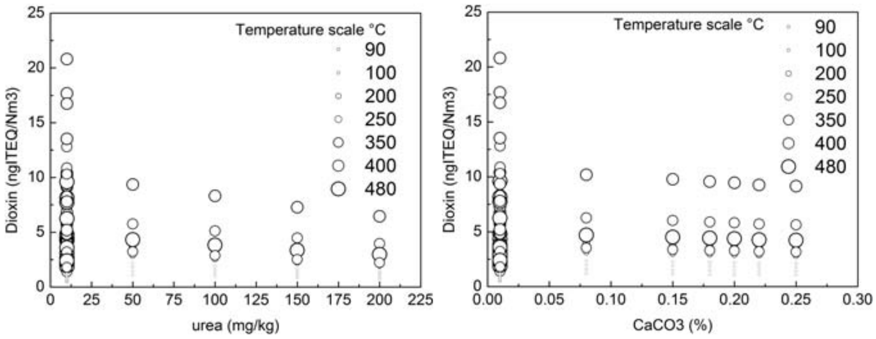

Figure 3. Dioxin emission in the sintering plant monitored in the present study as a function of urea and temperature a), and as a function of CaCO3 and temperature b).

The emissions levels are reduced as the lime quantity in the raw materials increases. The lime also brings to a strong reduction of SOx and a moderate reduction of NOx. Although the resultant optimal combination of input parameters able to reduce the dangerous emissions from the plant, it is very important to examine the impact of the chosen input parameters on the sinter productivity. As a matter of fact, many different studies were performed on the productivity measurements for selected designs with controlled levels of dioxin, NOx and SOx emissions. As shown in Figure 4, high levels of dioxin emissions are found in correspondence of very low levels of productivity, then productivity increases with increasing dioxins and then increases with decreasing dioxin emissions (Figure 4a). By analyzing also the oxygen addition it can be concluded that a decrease in O2 shifts the same productivity to lower dioxin emissions (Figure 4b).

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Actually, temperature and oxygen flow influences moisture behavior in the sinter bed and it is strongly related to the quality of the sinter, all the input parameters ranges were set in order to fix the quality of the pallets at a well known level.

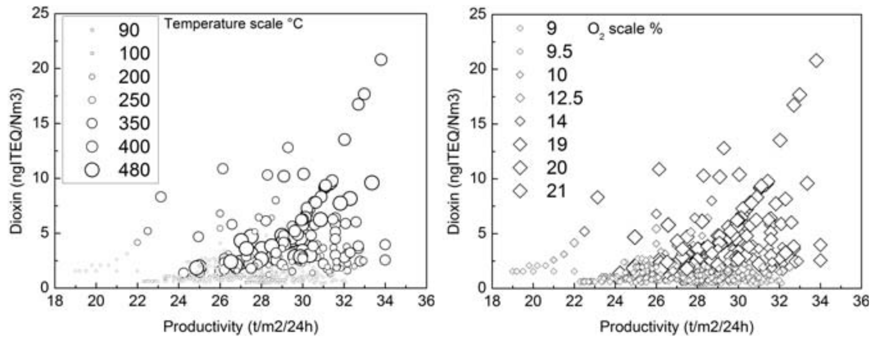

Figure 4. Dioxin emission in the sintering plant monitored in the present study as a function of productivity and temperature a), and as a function of productivity and O2 b).

High levels of productivity and low levels of dioxins can be reached with high level of moisture (Figure 5a), high levels of gas flow rate leads to an increase of productivity but unfortunately to an increase in dioxin emissions (Figure 5b). Such parameter results very important because it is strongly linked to the sinter permeability which can be directly related to the ore quality in terms of granule size and distribution, such parameter was taken strongly into account during the definition of the parameters ranges in order to set an acceptable pellets quality for all the analyzed input conditions. Also moisture strongly influences the sinter quality because it is strongly related to voidance, also the range of such parameter was set to fix a given range of the product quality. Generally, low levels of moisture lead to a decrease in the spread of granule size distribution and to an increase in the spherical aspect of the product, such behavior leads to a material with improved voidance and consequently to good levels of productivity. In the conditions of higher levels of moisture, normally the sinter thickness decreases and this leads to a tendency for voidance to decrease, in this way the productivity tends to decrease. For all the productivity levels shown by the plant, the SOx and NOx levels can be reduced by reducing the oxygen flux. In each case, from the previous analysis it can be concluded that the effect of such input parameters leads to an effect on NOx and SOx emissions in a different way, if they leads to a decrease in NOx they produce an increase in SOx and vice versa, so the control of input parameters should be tuned in order to reach an optimum point of acceptable dioxins NOx and SOx levels coupled with input and operative conditions maintaining good levels of productivity. The increase of gas flow rate leads to an increase in SOx levels while it leads to a decrease in NOx levels for all the values of productivity measured in the present study. By increasing the lime content it is possible to reach good values of productivity and, at the same time, to reduce the dioxin emissions. Lime is very effective in improving productivity with contemporary reduction of SOx emissions, the addition of lime leads to a moderate reduction of NOx for a given value of productivity. With the numerical simulation by mF software, a series of operating conditions for the sintering process has been defined. But not all the numeric strings have produced low amounts of emissions. In some cases the value is low for PCDD/F, but very high for the other

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output, NOx and SOx. It's very important to consider all the aspects of the physical process.

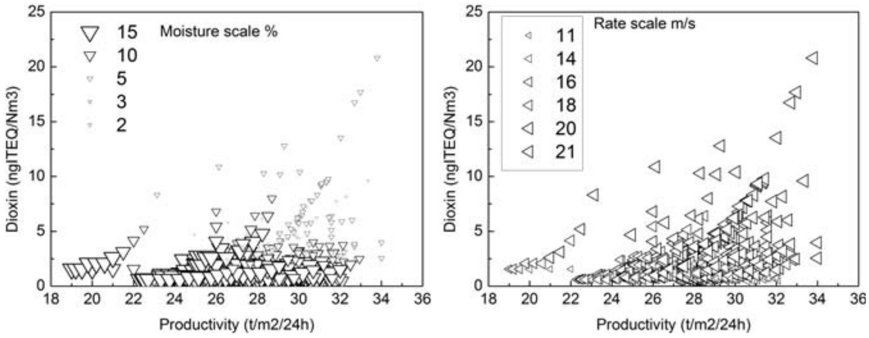

Figure 5. Dioxin emission in the sintering plant monitored in the present study as a function of productivity and moisture a), and as a function of productivity and gas flow rate b).

The user has to analyze the different set of parameters and the output values reached and he has to choose the best operating conditions. From the list offered by the first step of analysis, with numerical simulations, the three most suitable designs have been proposed because these lead to the minimum value of PCDD/F, Nox and SOx. Such optimum designs are summarized in table 2.

Table 2. Windbox optimum design N° 19

WbN°	O_2	CO_2	CO	Moi	Twb	Twleg	Rate	Cu	Urea	Cl	S	Lime	SOx	Nox	PCDD/F
19	21	3	0,5	7	502	463	21	80	400	110	0,8	0,25	**371**	**106**	**0,56**
19	21	5	0,6	6	498	422	21	80	400	150	0,6	0,15	**351**	**101**	**0,58**
19	20	3	0,2	5	503	663	19	90	350	120	0,8	0,2	**276**	**115**	**0,59**

It should be put in evidence that in all these cases there are high values of oxygen, while those of monoxide and carbon dioxide are relatively low, as well as the level of moisture. The gas temperatures in the windbox turn out high; the Chlorine and Copper value is low, while the levels of additives cover upper-middle values. Maximum emissions of SOx and Nox are found respectively in windbox 17 and 7. When sulfur rises, the level of SOx emissions increases, while the increasing of the lime addition leads to a reduction in the levels of Nox and PCDD/F emissions. At this point the best operating conditions of all the 21 windboxes of the system were fixed and the medium value, weighed in the three different cases, was estimated. At least it is possible to describe the optimal design deriving from the present study in which it is put in evidence the productivity deriving by the underlined choices. In all the optimized cases, the medium values of emissions of SOx and NOx are largely below the legal limit. Unfortunately, with such operating conditions the PCDD/F levels exceed the value limit of 0,4 ng I-TEQ/Nm3. Besides offering the minimal value in the optimization regarding windbox 19, Design 1 proposes

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valid operating conditions for the whole system and the lowest values of pollutants. In order to define the optimization strategy reference to design 1 was chosen.

Table 3. Parameters fixed for all the windboxes a), Temperature fixed in windboxes and windlegs b), Emission values c)

Cu mg/kg	Urea mg/kg	Cl mg/kg	S %	Lime %
80	400	110	0,8	0,25

Windbox / Windleg	T windbox (°C)	T windleg (°C)
1 - 15	115	95
16	220	190
17 - 21	500	460

	SOx	NOx	PCDD/F	Productivity
New Design	297	201	0,45	29.8
Design 1	291	177	0,43	29.0
Legal limit	400	400	0,4	

The process parameters, that result independent from the position on the belt conveyor, were fixed. They are shown in the table 3a. At last, the temperatures of the windboxes and windlegs for the New Design were chosen and shown in the table 3b. With these values attributed to the input variables, the minimum value of emissions obtained can be discovered. In table 3c the results of the different designs are compared. Some of the optimal operating conditions were removed in favour of profiles easier to apply to the system. in addition it was possible to obtain a value of productivity close to 30 in agreement with the industrial desires. With the exception of the latter, the PCDD/F still exceeded the legal limits. Despite an increase of emissions, the application of the set of parameters of the New Design was chosen because technologically simpler to realize. A further possible improvement was studied, that consists in the application of a determined filtered device that can carry to a further reduction of pollutants[1].

4 CONCLUSIONS

The aim of this study was to analyze some crucial aspects of the iron ore sintering process. The study outlines the influence of different parameters affecting it in order to establish a set of operating conditions capable of reducing the dangerous emissions. The way to tackle the problem consists in using numerical multi-objective


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optimization software with which to define optimal operating conditions. The analysis led to the definition of a series of best design practices that lead to lower emissions. A large attention was put on the analysis of the reduction of dangerous emissions coupled with an acceptable level for productivity. All the input parameters, before the optimization, were chosen in order to fall in a range guaranteeing an acceptable quality of the sintered material in terms of dimension, sphericity and voidance. The results confirmed the applicability of the obtained optimal conditions for the ordinary industrial production.

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