Model predictions of PCDD and PCDF emissions on the iron ore sintering process based on alternative gaseous fuels

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A B S T R A C T
The technology of fuel gas utilization on the iron ore sintering process has been proposed as an alternative for reducing the environmental load and improvements on the sinter quality have been obtained with additional decrease on the return of fines (<5 mm). This paper deals with the numerical simulation of this innovative technology in order to evaluate the emissions of poly chlorinated di-benzene dioxin (PCDD) and Poly Chlorinated di-benzene furan (PCDF). The methodology is to partially replace solid fuel (coke breeze) by steelworks gaseous fuels; coke oven gas (COG), blast furnace gas (BFG) and mixture of these gases. A multiphase mathematical model based on transport equations of momentum, energy and chemical species coupled with chemical reaction rates and phase transformations is proposed to analyze the inner process parameters and the rates of PCDD and PCDF formations. A base case representing the actual industrial operation was used to validate the model and afterwards used as reference to predict four cases of fuel gas utilization: (a) 10% of the wind boxes inflow from N01 to N12 wind boxes with COG, (b) same condition with BFG, (c) same condition with 50% COG and 50% BFG and (d) mixture of 25% COG and 75% BFG. The model predictions indicated that for all cases, except only BFG, the sintering zone is enlarged and the solid fuel consumption is decreased. In order to maximize the steelworks gas utilization it is recommended the use of mixture of COG and BFG with optimum inner temperature distribution. It was found out that for all cases of gas utilization the PCDD and PCDF emissions could be decreased due to enlargement of the high temperature zone on the sintering bed and hence increasing the residence time of the reacting gas within the high temperature zone.

1. Introduction
The iron ore sintering process in the integrated steelworks is a well established technology and has been responsible to provide high quality of agglomerate raw materials for the blast furnace. However, further improvements regarding energy efficiency, flexibility of raw materials and environmental load have continuously been demanded.

The process is complex and involves various physical and chemical phenomena such as heat, mass and momentum transfer coupled with chemical reactions [1–4]. These
Fig. 1 – The sintering plant facilities for integrated steelworks.

phenomena take place simultaneously increasing considerably the complexity of process analysis. The raw materials used in the iron ore sintering process are obtained from several sources, like iron ore (mining sinter feed), dust recycling within the steelworks and addition of slag agents for blast furnace and enhance the sinter product quality, namely reactivity and mechanical strength, which plays crucial role on the blast furnace performance and reducing agent consumption.

In the conventional operation, the combustion of the solid fuels (coke breeze or anthracite) begins at the top layers, and as it moves, a relative narrow band of ignition zone moves downward through the bed, that can be strongly affected by the quality of the raw materials [5–9]. Several chemical reactions and phase transformations are affected not only by the heat front modifications but also due to changes in local gas composition and initial melting temperature of the mixture of raw materials. When local temperature and composition of the solid is reached, the phase transformations are driven by heat supply and diffusion that takes place within the sinter bed where the mechanism of liquid formation playing the major role. The materials partially melt down when the local temperature reaches the melting temperature and as it moves, the contact with cold gas promotes the re-solidification and thus, the particle agglomeration forms a continuous and porous sinter cake. The final sinter cake properties are strongly dependent upon the thermal cycle, initial raw material composition and thermophysical properties.

Fig. 1 shows a schematic view of the sintering facilities and peripheral system for gas treatment and sinter cooling and classification.

In this paper, the sintering process is analyzed, when fuel gases such as natural gas (NG), coke oven gas (COG) and blast furnace gas (BFG) are sucked through the sinter bed. It is expected that the fuel gas reaching the thermal front combust earlier leading to the result of enlargement of the sintering zone, which in turn, can increase the liquid formed (mushy) and residence time of the materials within the sintering temperature improving the amount of calcium ferrite and bonding phases. Several attempts have been made aiming at predicting the final properties of the sinter product.

One of the most important parameters is the size distribution which influences strongly the sinter performance within the blast furnace. Previous models addressed the sintering phenomena [1–3,10–15]. Kasai et al. [16] investigated the influence of sinter structure on the macroscopic sinter properties. A detailed explanation of the sintering mechanism and particle interaction was provided in order to clarify the bonding forces responsible for the sinter structure and strength. In the present days, the reduction of CO₂ emissions has become an urgent issue in the steel industry as counter-measure for greenhouse emissions [17,18]. It is estimated that nearly 60% of the steel industry emissions are attributed to the pig iron production unit operations, which includes sintering and blast furnace processes, and only the sintering process represents around 20% of this amount [18]. Therefore, sintering and blast furnace processes offer opportunities to decrease the CO₂ emissions in the whole steelmaking since small decrease in coke breeze consumption and bonding agent used in iron ore sintering process could decisively contribute to decrease the environmental load of the steelmaking industry. Therefore, alternative sources of energy with lower environmental impact or replacement of the coke breeze by in-house gaseous fuel are attractive technologies and could contribute to enhance the iron ore sintering process in the integrated steelworks [11,13,14,17].

The concept of gaseous injection into the sinter bed has been successfully applied and enhancement of the sinter properties related to reducibility and strength have been observed [11,17], in addition to drastically decrease the returned fines (<5 mm). In this perspective, the present work aims to apply a comprehensive multiphase multicomponent mathematical model to analyze the effect of gaseous fuels
such as natural gas, coke oven and blast furnace gases through the sinter bed of an industrial sintering machine and quantify the impact of this technology on the sintering process of iron ore with regard to the PCDD and PCDF emissions [18].

2. Methods

This paper proposes a model to evaluate the coupled phenomena of PCDD and PCDF formation in the sintering process of an industrial strand machine based on the multiphase and multicomponent concept [1–15]. The model is formulated using transport equations of mass, momentum and energy for gas, solid and liquid phases taking into account the local phenomena of porous sinter formation, as schematically shown in Fig. 2(a) and (b), while Fig. 2(c) shows an SEM image of dendrites structure. This model considers the initial quasi-particle already formed and as the reactions take place, multiphase phenomena occur. Therefore, a model based on multiphase transport phenomena is expected to be suitable for modeling the mass, momentum and energy transfer within the sintering bed. The chemical species are individually taken into account by solving the transport equation of each chemical species of the gas and solid phases.

The solid phase includes the mixture of iron ore sinter feed, fine sinter (returned fine sinter), coke breeze (or other solid fuel), scales (fines from steel plant), fluxes and limestone. The liquid phase is composed of melted and formed components in the liquid phase [3–6,18–23]. The re-solidified phase comprises the liquids re-solidified and phases formed during the re-solidification process. Eqs. (1)–(4) describe the conservation equations for momentum, energy and chemical species of each phase considered in the model [7–15,19,20].

\[
\begin{align*}
\frac{\partial (\rho_i \varepsilon_i u_{ij})}{\partial t} + \frac{\partial (\rho_i \varepsilon_i u_{i,k} u_{kj})}{\partial x_k} &= \frac{\partial}{\partial x_k} \left( \mu_i \frac{\partial u_{ij}}{\partial x_k} \right) - \frac{\partial P_i}{\partial x_j} - F_{i,j}^l \quad (1) \\
\text{Continuity:} \\
\frac{\partial (\rho_i \phi_i)}{\partial t} + \frac{\partial (\rho_i \varepsilon_i u_{i,k} \phi_i)}{\partial x_k} &= \sum_{m=1}^{N_{reacts}} M_n r_m \quad (2) \\
\text{Enthalpy balance:} \\
\frac{\partial (\rho_i \varepsilon_i H_i)}{\partial t} + \frac{\partial (\rho_i \varepsilon_i u_{i,k} H_i)}{\partial x_k} &= \frac{\partial}{\partial x_k} \left( \kappa_i \frac{\partial H_i}{\partial x_k} \right) + E^{f,l} + \sum_{m=1}^{N_{reacts}} \Delta H_m r_m \quad (3)
\end{align*}
\]

The chemical species are individually considered within the gas, or components of the solid or liquid phases, as presented in Eq. (4).

\[
\frac{\partial (\rho_i \varepsilon_i \phi_0)}{\partial t} + \frac{\partial (\rho_i \varepsilon_i u_{i,k} \phi_0)}{\partial x_k} = \frac{\partial}{\partial x_k} \left( P^n \frac{\partial \phi_0}{\partial x_k} \right) + \sum_{m=1}^{N_{reacts}} M_n r_m \quad (4)
\]

The indexes i and l represent the phases, j and k are the indexes for coordinates, component direction n is chemical species and m the indicator of the reactions, M is the molecular weight of the chemical species, P is phase pressure, F is component of momentum interactions among the phases and r is the rate of chemical reactions. \( \rho, \varepsilon, C_p, k \) and \( \Delta H \) are density, volume fractions, heat capacity, heat conductivity and heat generated/consumption due to chemical reactions (endothermic or exothermic), respectively.
The quantity \( F^{1-1} \) is the heat transfer among the phases and accounts for convective and radiation intra bed heat transfer, since conductive heat transfer is include in Eq. (3). The gas–solids momentum interactions are represented by \( F^{1-1} \). The model equations are completed with suitable correlations for the thermophysical properties of the phases, rate equations for the source terms and the initial and boundary conditions representing the sintering process. The chemical species considered in this model are presented in Table 1.

The source terms are modeled based on semi-empirical correlations taking into account the intra bed phenomena. The momentum transfer between the solid and gas are modeled based on the modified Ergun’s equation, which takes into account the local soft-melting behavior of the raw materials with the volume fraction and effective diameters modified by the soft-melting data, as follows [1–15,20],

\[
E_g = \left[1.75 \rho_g + \frac{150 \mu_g}{U_g - U_s} \left( \frac{\varepsilon_g}{d_g^{3/2}} \right) \left( \frac{\varepsilon_g}{1 - \varepsilon_g} \right) d_g^{3/2} \right] \times \left[ U_g - U_s \right] (u_{g,j} - u_{s,j}) \tag{5}
\]

The overall heat transfer coefficient between the gas and the packed bed [20] is given by Eq. (6).

\[
E^{3-5} = \frac{6 \varepsilon_g}{d_g^{3/2}} \frac{k_g}{d_g^{3/2}} \left[ 2 + 0.39 (Re_{g,j})^{1/2} (Pr_{g,j})^{1/3} \right] (T_g - T_s) \tag{6}
\]

In Eq. (6), the gas–solid interface heat transfer is given by the product of the overall effective heat transfer coefficient, the interfacial area and the average temperature differences of the bed and gas phase. The parameters of the sinter bed \( \varepsilon_g \), \( d_g \), and \( v_g \) are temperature dependent and account for the effective volume fraction, particle diameter and shape factor, respectively, which strongly affect the momentum and energy transfer on the soft-melting zone. The solid diameters and shape factors are given as raw materials properties from the harmonic average of the particle size distributions. In the present model these parameters are calculated by using soft-melting experimental data for the raw materials used [5,20], as presented in Eqs. (7)–(9).

\[
\varepsilon_I = 1 - (0.403(100d_j)^{0.14}) \times \left( 1 - \text{MAX} \left( 0, \text{MIN} \left( 1, \left( \frac{T_g - T_{im}}{\Delta T_{im}} \right) \right) \right) \right) \frac{S_m}{100} \tag{7}
\]

\[
\varepsilon_S = \sum \varepsilon_i + \varepsilon_L + \varepsilon_S \tag{8}
\]

\[
d_s = d_{\text{initial}} + (d_{\text{final}} - d_{\text{initial}}) \left( \frac{\varepsilon_I + \varepsilon_L + \varepsilon_S}{\varepsilon_S} \right)^3 \tag{9}
\]

In Eqs. (5)–(9), the indexes \( i \) stands for iron ore sinter feed, returned sinter, solid fuels, fluxes and mill scales on the sintering mixture charged on the sinter bed, \( l \) and \( l_r \) are the liquid and solid bridges volume fractions formed during sintering phenomena. The average size of the sintering structure are given by Eq. (9) with the parameters \( d_{\text{initial}} \) and \( d_{\text{final}} \) representing the average particle size of the quasi particles charged in the bed and the particle size for complete sintering product [15,20].

In the present model these parameters are given for each sintering mixture with their own softening-melting data, where the model uses the parameters \( T_{im} \), \( \Delta T_{im} \) and \( S_m \) representing the initial melting temperature, meting temperature interval and percentage of volume shrinkage. This parameters are obtained from the pressure vs. temperature curve obtained from the softening-melting experiment [5,6]. The model formulation is completed assuming initial and boundary conditions for momentum, energy and chemical species of each phase.

The computational domain is defined by the region of the sinter strand for the industrial scale process simulation and the equations are solved considering steady state conditions, therefore the first terms on the left of the equations are set to zero and the initial conditions are regarded as guess values for the numerical iterations. The boundary conditions is assumed for the solid phase at the charging position of the strand the composition, particle diameters and volume
fraction distribution and moisture content. The outlet boundary condition for the solid phase is assumed to be fully developed flow and no slip condition is assumed at the sinter strand. The other boundaries such as lateral and bed surface are assumed zero velocity gradient.

For the energy balance equations convective and radiation coefficients are assumed for each of these surfaces. The gas inlet and outlet flow rates are determined by the pressure drop specified for each wind box and it is calculated iteratively by considering simultaneously the momentum balance and pressure drop of each wind box. The gas inlet temperature is specified at the surface of the bed and the outlet temperature is calculated by assuming fully developed flow. As for the chemical species of the gas phase, specified values on the surface of the sinter bed are assumed and similarly to the solid phase, the gas velocity is calculated at the outlet by using fully developed flow conditions at the bottom of the bed with the integral mass balance restriction for each wind box volume. The solution of the differential equations representing the model of this complex process is solved numerically.

This multiphase multicomponent model is composed of a set of partial differential equations that can only be solved by numerical method due to their nonlinearities on the boundary conditions and source terms.

Fig. 3 – Model validation using intra bed temperature data.

Fig. 4 – Temperature patterns for the cases of alternative gaseous fuels considered in this study.

Fig. 5 – The gas and solid temperature intra bed distributions for the mixing of blast furnace and coke oven gas (BFG-COG). (a) PCDD for the base scenario; (b) PCDD for the scenario mixing BFG and COG.
Fig. 6 – Comparison of PCDD emissions for the proposed operation of combining BFG and COG fuels. (a) PCDF concentration for the base scenario; (b) PCDF concentration for the combined BFG-COG scenario.

In this work, the set of differential equations is discretized by using the finite volume method (FVM) and the resulting set of algebraic equations are solved by the iterative procedure using the line by line method combined with the tri-diagonal matrix solver algorithm [24]. It has been developed a computational code implemented in Fortran 90/2000 language with the executable compatible with all Windows versions using single or parallel processing using MPI routines.

A typical run takes about 8 h in an i7 8 cores multiprocess computer.

In this paper, the numerical grid used to simulate the industrial strand of the sinter machine was discretized based on the Cartesian coordinate system with $22 \times 180 \times 18$ control volumes, assumed suitable for the calculations after continuous grid refinement to assure solutions independent of the control volume size. The numerical convergence was accepted...
for tolerance of the order of $10^{-6}$ for the velocity and temperature fields, meanwhile, for the chemical species the overall mass balance was accepted less than 1% for all chemical species calculated.

3. **Results and discussions**

In this section the model was applied to simulate the industrial operation of the sintering process currently used in the large facilities. A base case which corresponds to an actual sinter plant operation was used to demonstrate the model accuracy and validate the model predictions. Afterwards, in order to analyze the effect of the partial substitution of the solid fuel by gaseous fuel on the PCDD and PCDF emissions in the sintering process, three cases were simulated to verify the feasibility of the new technology proposed based on partial substitution of the coke breeze by gaseous fuel available at the steelworks. The model validation was carried out by monitoring the sinter bed temperature into three distinct heights of the bed by

**Fig. 7** Model predictions of PCDF concentrations for the proposed scenario compared with actual operation.
inserting encapsulated thermocouples and recording the temperature measurements along the moving bed. The data used in these calculations were the averaged values of 1 h of uninterrupted operation. In this interval, three measurement runs were obtained and the averaged values of the temperatures were used to compare with the numerical predictions. Fig. 3 presents the comparison of temperature predictions by the model and measured data obtained in the industrial sintering machine for the actual operation conditions.

The calculated results were compared with the measured data obtained by thermocouples inserted within the sinter bed in fixed positions of 75 mm, 355 mm and 725 mm from top of the bed and the temperatures were recorded at intervals of 10 m along the strand. Excellent concordance of the operational measurements and model predictions were observed, as shown in Fig. 3.

In the scenarios proposed in this study the gaseous fuels available in a steelmaking plant were taken into account. The scenarios analyzed consider injections from the positions of the wind boxes N01 until N15 of a total of 23 wind boxes. These positions were selected to guarantee the gaseous fuel to be consumed within the bed.

Four fuel injection scenarios were selected: (a) 2% fuel gas through the wind boxes from N01 to N15 where replaced by dry blast furnace gas (BFG); (b) same condition with natural gas (NG); (c) same condition with coke oven gas (COG) and (d) a mixture of 50% of COG and BFG. Fig. 4 shows the comparison for the temperature pattern within the sinter bed for a vertical slice located at middle position of the bed width of the four scenarios considered.

As can be observed, the sintering zone was gradually enlarged for BFG, NG and COG injection scenarios. This expected behavior can be explained due to the amount of heat released when the gaseous fuel was burned out. The results indicated that the sintering zone was gradually enlarged from BFG to COG gaseous fuel when compared with the base case of actual operation.

The results indicated that the coke oven gas was the most effective fuel to enlarge the sintering zone while the blast furnace gas showed lower effect. Thus, a combined scenario of blast furnace gas and coke oven gas is proposed to utilize both the abundant steelmaking gases, as shown in Fig. 5. The combined scenario of BFG-COG shows intermediate temperature pattern, as expected, and indicated feasible operation practice since the temperature distributions are compatible with actual operation practice. Fig. 6(a) and (b) combined with Fig. 7(a) and (b) shows predicted PCDD and PCDF emissions of the industrial sintering process compared with the actual operation used as base scenario for analyzing the emissions.

As could be observed, the combined utilization of auxiliary gaseous fuel replacing coke breeze decreased the total emissions and concentrated the emissions around the wind box N18, which can be used to improve the effectiveness of the countermeasures to avoid the gas emissions by using high temperature burners only in this wind box.

4. Conclusions

In this paper the innovative technology of gaseous fuel injection in the iron ore sinter bed was simulated based on a multiphase mathematical model able to predict the process phenomena within the sinter bed taking into account the coupled phenomena of momentum, heat and mass transfer to analyze the possible emissions of PCDD (Poly Chlorinated Di-benzene Dioxin) and PCDF (Poly Chlorinated Di-benzene Furan) on the gas flue. The model was validated by sinter bed temperature measurements obtained by inserting thermocouples into the sinter bed of the industrial sinter machine.

The model was used to analyze cases of gaseous utilization in the sinter bed and partially replace the solid fuel. Simulation results indicated that gaseous injection enlarges the sintering zone and enhance the sintering phenomena, which confirmed previous predictions based on model and experimental procedures reported in the literature [11,13,14,17]. The calculated results indicated that solid fuel can be decreased for the gaseous fuel scenarios (2.3 kg for BFG, 5.8 kg for NG, 6.5 kg for COG and 5.8 kg for COG-BFG per ton of sinter product) which also confirmed similar trends previously presented by the authors [11,14].

This study confirmed that this technology is attractive for steel plants which have excess of process gas such as COG and BFG and can represent considerable decrease in the solid fuel used for the sintering process and can contribute to make this process more environmentally cleaner. For these new operational conditions, regarding to the PCDD/F emissions, this study indicated that based on calculated results the gaseous injections can contribute to reduce the PCDD and PCDF emissions and clarify that when the sintering zone is enlarged the dioxin (PCDD) and furans (PCDF) can be decomposed within the bed and the adsorption on the sinter porous structure can be decreased.

Based on the simulations results, for the scenarios considering the mixture of COG (50) and BFG (50%) the amount about of 20% for PCDD and 25% of PCDF decrease compared with the actual operation practice can be expected.

Conflicts of Interest

The authors declare no conflicts of interest.

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