

Types of greenhouse gas emissions in the production of cast iron and steel

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Abstract. Types of carbon dioxide emissions in iron and steel production are indicated. Production processes have been classified according to mechanisms of carbon dioxide formation. Mathematical models for calculation of carbon dioxide emissions for each type of process are found. Calculations results of carbon dioxide emissions of coke (BF + EAF) and cokeless processes (Corex, Midrex, HyL-3, Romelt) in combination with EAF are provided.

1. Introduction

Greenhouse gases (GHG) are responsible for temperature increase on earth. Ferrous metallurgy produces a lot of such greenhouse gas as carbon dioxide (CO₂). Methane, the other GHG, is a part of the secondary energy resources (SER) and is burnt to carbon dioxide in metallurgical units.

In addition to blast furnace (BF) process in iron and steel production Corex, Romelt, Midrex, HyL-3 processes are used currently. Pig iron or sponge iron with scrap iron addition are loaded into electric arc furnaces (EAF) for steelmaking [1-4].

There is a problem of comparative assessment of carbon dioxide through emission (carbon footprint) in the following metallurgical tandem processes: BF + EAF, Corex + EAF, Romelt + EAF, EAF + Midrex, HyL-3 + EAF. To solve it, we need to analyze the types of carbon dioxide emissions in metallurgical processes in terms of CO₂ formation, find formulae (mathematical models) for carbon dioxide emissions calculation in different types of metallurgical processes.

2. Classification of industrial emission of carbon dioxide in metallurgy

Let us reduce worldwide spread concept of carbon footprint in ferrous metals industry to M_{th} - integrated through emission of carbon dioxide, which is the sum of CO₂ emissions, consequently appearing in all processes of technological chain, starting with raw materials extraction and ending with the product for which emission is provided. In addition, we distinguish a process integrated emission M_p from a transit emission M_{tr} determined by share of total mass of carbon dioxide emission, generated in previous process, which has been transferred to the analyzed process. The through M_{th} obey the formula:

$$M_{th} = M_p + M_{tr}. \quad (1)$$

Blast furnace gas consists of the CO 25 – 27 % vol., and the CO₂ 16 – 23 % vol., depending on content of oxygen in blast [4]. We call this CO₂ direct gas or direct emission M_{dir} . Part of the CO is used directly in blast furnace process, it is oxidized in blast heaters to CO₂. But for the most part it is burnt in boilers of local power plants, and as the simplest CO is burnt in flares or completely burnt in



special units. We call the resulting CO₂ indirect gas or indirect emission M_{ind} . Fig. 1 shows CO and CO₂ gas flows in blast furnace operating on flux-bearing iron ore materials (no limestone in charge).

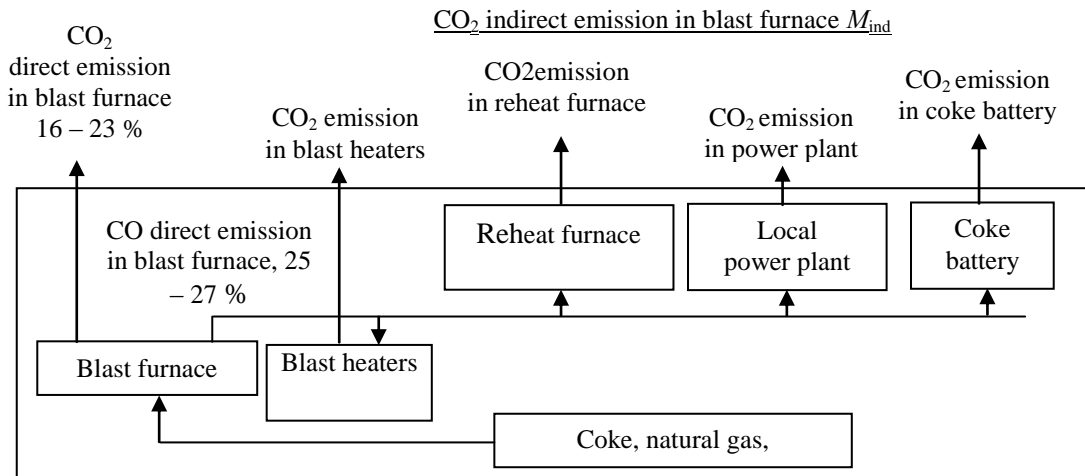


Figure 1. Gas flows during blast furnace operation.

Blast furnace is the cause of total or process integrated emission of carbon dioxide

$$M_p = M_{dir} + M_{ind}. \quad (2)$$

Figure 2 shows CO₂ and CO gas flows for Corex process. It is obvious, that it would not be correct to compare blast furnace emission with Corex process units only by values of direct emissions, since their work causes formation of additional CO₂ mass during CO burning in the other technological units. Different processes should be compared by carbon dioxide emissions by total (2) of their direct and indirect CO₂ emissions, i.e., by values of CO₂ process integrated emissions M_p .

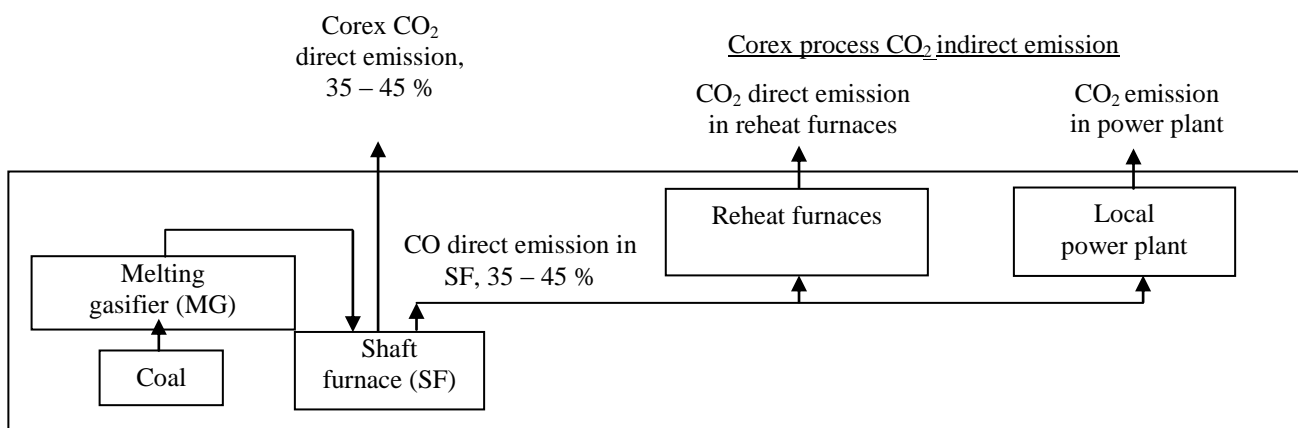


Figure 2. Gas flows in Corex process.

It is not possible to use formula from [5-8] to calculate the process direct and indirect emissions, as there is no data on SER consumption in reheat furnaces, boilers of local power plant, etc.

Thus, CO₂ mass produced in blast furnace, coke, electric arc and open-hearth processes will be determined by total carbon mass containing in raw fuels, taking into account CO reburning. In the

BOF process with reburning CO_2 mass [4] will be proportional to the mass of carbon burnt from charge.

It is interesting to estimate the so-called through emission of carbon dioxide throughout all the production chain to the final product. To calculate value of through emission we will present processes and their relations as a directed weighted graph with marked nodes - a sort of signal graph. In order to visualize formula derivation for through emissions calculation let us look at an example of general directed graph of emission (Figure 3).

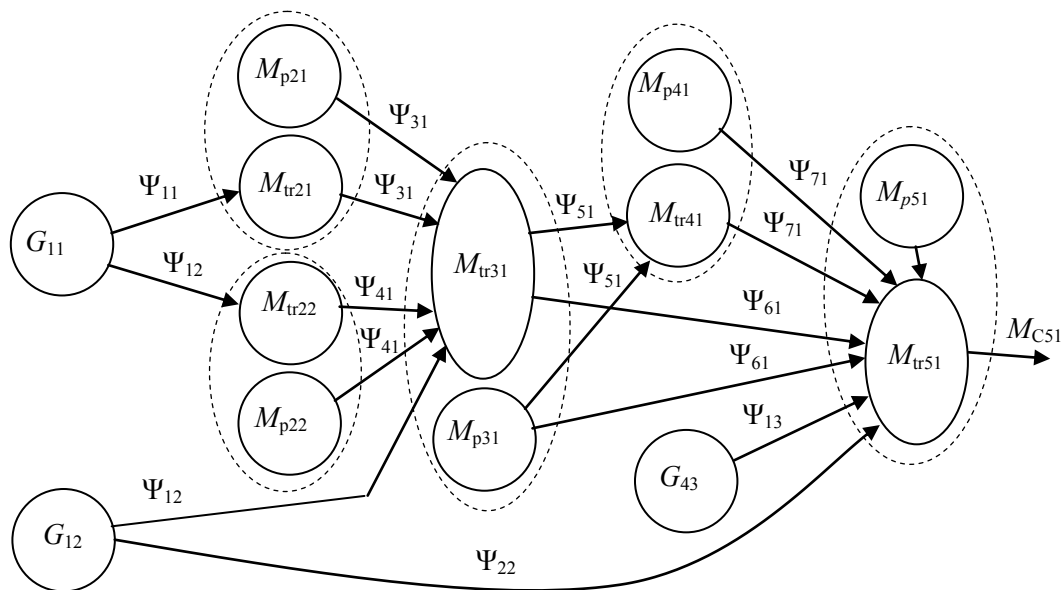


Figure 3. Graph of carbon dioxide emissions.

Weights of Ψ_{ik} directed lines, drawn from the node k to the node i , correspond to specific consumption of resources in tons or cubic meters, depending on emission dimension in the node, from which the line proceeds (kg/t of product or m^3/ton of product). Inside the twin nodes of complete graph (Fig. 3) values of transit emission M_{tr} and process emission M_p are indicated. The first index indicates the number of process stage, the second - number of process in the stage. Let us call sources the nodes from which arrows only proceed. Variety of processes correspond to these nodes (mining, transportation, crushing, screening, preparation, etc.), which are difficult to split. The value of their through emission we denote as G_{ik} , where the first index indicates the number of process stage, the second index – the source number.

For signal graphs signal value at the node totals to the sum of signals entering from the other nodes, taking into account the directed lines transmission factor. Then, through emission for the node 51 can be found by using the following calculations:

$$M_{th51} = M_{p51} + G_{43}\Psi_{13} + (M_{p31} + M_{tr31})\Psi_{61} + (M_{p41} + M_{tr41})\Psi_{71} + G_{12}\Psi_{22}.$$

After simple transformations we obtain a formula from which follows general formula for through emission calculation:

$$M_{Cik} = M_{Pik} + \sum_{i=1}^L (G_{ik} \cdot \sum_{j=1}^N P_{jk}) + \sum_{i=1}^M (M_{Pil} \cdot \sum_{j=1}^P P_{jl}), \quad (3)$$

where L – number of sources (graph nodes, from which lines only come out); N - number of paths from the source node to the analyzed node; P_{jk} - transmission of the appropriate way, the product of directed lines weights, for example, $\Psi_{11}\Psi_{31}\Psi_{51}\Psi_{71}$; M - number of nodes, relevant to processes that have not zero process emission; P - number of paths from such nodes to the analyzed node. The length of the paths is different. Here index i corresponds to the number of the process stage in technologic chain, and index k marks emission of carbon dioxide from the the k^{th} source in the i^{th} process stage, l - number of node in the i^{th} process stage, which has not zero process emissions.

For example, per 1t of agglomerate CO_2 emission is 319kg, per 1t of coke – CO_2 emission is 392kg, per 1t of pig iron CO_2 emission is 1.551kg. To produce 1t of pig iron 1.8t of agglomerate ($\Psi_1 = 1.8$, k index is not applied, as on each process stage one source of carbon dioxide is considered) and 0.6 t of coke ($\Psi_2 = 0.6$) should be used. Through emission per 1ton of pig iron $M_{th} = 1.8 \cdot 319 + 0.6 \cdot 392 + 1 \cdot 551 = 2 \, 360$ kg/t of pig iron. Considering injection of natural gas in blast furnace, CO_2 emission for blast furnace would have two components.

The integrated process emissions of carbon dioxide distinguish specific coefficient of carbon dioxide emission

$$\beta_{CD} = \frac{m_{CD}}{m_{prod}}, \quad (4)$$

which is produced by the resulting mass of carbon dioxide per 1t of product (sinter, coke, iron, steel, etc.). Value of this coefficient depends on many factors. For this reason, we can speak of the set of its values for variety of technological parameters. Average values of this coefficient are analyzed further on.

3. Classification of metallurgical processes

In this paper, for the purpose of deriving formulas for calculation of integrated emission of carbon dioxide in production of pig iron and steel these processes have been analyzed in terms of distribution of carbon between gases and products, as well as carbonates content in charge. Here are the types of processes division into types that are different by ways of carbon dioxide formation that defines the methods of generated carbon dioxide weight or volume calculation. Division is performed by the product (columns) and mechanism of carbon dioxide formation (lines). Types of processes are sequentially numbered in all columns in order to eliminate unnecessary complexity in their listing.

Type 1. Processes in which volatilization of volatile fractions occurs, which are used as fuel in the same processes (coking).

Type 2. In processes of this type carbon dioxide is emitted due to oxidation of carbon fuel and decomposition of charge components (limestone, dolomite) under affect of high temperature (sintering machines and fluxed iron ore pellets firing machines).

Type 3. Processes, in which fuel is burnt, part of carbon transfers to the final product and flux carbonates decompose (blast furnace process, Romelt, Corex).

Type 4. Processes in which charge metal carbon is burnt, but fuel is not used (oxygen converter production).

Type 5. The processes in which carbon from metal charge is burnt and fuel is burnt (electric furnace production).

Type 6. The process type in which fuel is burnt (HyL-3, Midrex).

4. Mathematical models of the carbon dioxide emissions in metallurgy

There is specific mathematical model (MM) for calculation of carbon dioxide emissions corresponding to each process type.

4.1. MM of the type 1 technological process

Processes in which volatilization of volatile fractions from charging feed without access of air occurs and combustion of the purified of these fractions for the purpose of these processes (coking) takes place. During all produced coke oven gas combustion the whole carbon is oxidized in a way of direct and indirect emissions to CO₂. Carbon mass in coke oven gas is calculated based on data on mass or volume of coke oven gas outlet, its composition, its density.

$$w_c = M_c / M_{cc} = (0,65 - 0,75); w_{cog} = M_{cog} / M_{cc} = (0,12 - 0,15),$$

where M_{cc} - mass of coking coal; M_c - mass of coke produced from this coal; M_{cog} - mass of dry or reverse coke oven gas; w_{cog} - reverse coke gas yield coefficient of coal; w_c - coke yield coefficient of coal. CO₂ mass produced in combustion of $M_F = M_{cog}$ mass of fuel gas mixture - coke oven gas, is determined by formula:

$$M_{G5} = 3,667 \cdot w_c \cdot M_F = 3,667 \cdot w_c \frac{w_{cog}}{w_c} M_{cog}. \quad (5)$$

Per 1,000kg of coke oven gas the amount of CO₂ is produced, mass of which is determined by formula

$$\beta_{DC5} = 3667 \cdot w_c \frac{w_{cog}}{w_c}, \text{ kg of CO}_2/\text{t of coke} \quad (6)$$

4.2. MM of the type 2 technological process

Specific weight of CO₂ produced in type 2 technologic process is determined by mass of carbon completely oxidized during use of N types of fuel and masses of carbonates:

$$M_{G1} = 3,667 \sum_1^N C_I^P M_{FI} + 0,44 \cdot m_L + 0,47 \cdot m_D \quad (7)$$

where M_{G1} - mass of gas formed during total fuel combustion of the, t; $3,667 \approx 44/12$ - coefficient that determines amount of mass of generated gas per unit of combusted carbon (at CO combustion, this coefficient is 1.571); C_I^P - mass volume of carbon content (concentration) in the I^{th} fuel - ratio of carbon mass M_{CI} to M_{FI} ; M_{FI} - mass of burnt I^{th} fuel, t; M_L - limestone mass, t; M_D - dolomite mass, t.

4.3. MM of the type 3 technological process

Representatives of this process type are blast furnace, Corex, Romelt processes. Formula for calculation of carbon dioxide mass formed in the type 3 process is as follows:

$$M_{G1} = 3,667 (C_{F1} M_{F1} + C_{F2} M_{F2} + 0,44 \cdot m_L + 0,47 \cdot m_D - C_1 m_1) \quad (8)$$

where C_{F1} - mass fraction of carbon in coke; M_{F1} - mass of burnt coke; C_{F2} - mass fraction of carbon in injection fuel; M_{F2} - mass of burnt injection fuel; C_1 - mass fraction of carbon in cast iron; m_1 - mass of cast iron; m_L - limestone mass, t; m_D - dolomite mass, t.

4.4. MM of the type 4 technological process

In addition to carbon dioxide in BOF carbon monoxide - combustion gas is formed due to oxygen blowing. Carbon monoxide goes with flue gases to purification and post-combustion system. In this respect, assume that the entire carbon of initial charge being burnt forms carbon dioxide. Integrated CO₂ emissions in type 4 process is determined by the following formulas

$$M_{G2} = 3,667 \Delta m_C, \quad (9)$$

$$\Delta m_C = m_{ch}(C_i D_i + C_s D_s) - C_{st} m_{st} = m_{st} \left(\frac{C_i D_i + C_s D_s}{K_{loss}} - C_{st} \right), \quad (10)$$

$$K_{loss} = \frac{K_B [D_i (1 - C_i - Si_i - Mn_i - P_i - S_i) + D_s (1 - C_s - Si_s - Mn_s - P_s - S_s)]}{1 - C_{st} - Si_{st} - Mn_{st} - P_{st} - S_{st}}$$

$$= \frac{K_{Tr} \sum D_l (1 - C_l - Si_l - Mn_l - P_l - S_l)}{1 - C_{st} - Si_{st} - Mn_{st} - P_{st} - S_{st}} \quad (11)$$

where M_{G2} - mass of CO₂ formed at carbon burning, t; Δm_C - amount of carbon burnt, t; C_l - mass fraction of carbon in cast iron; m_l - mass of iron in metallic charge, t; C_s - mass fraction of carbon in scrap; m_s - weight of scrap in metal charge, t; C_{st} - mass fraction of carbon in produced steel; m_{st} - mass of produced steel, t; D_l - mass fraction of iron in metal charge; D_s - mass fraction of scrap in metal charge; $m_{Ch}=m_l+m_s$ - mass of metal charge, t. $K_{loss}=m_s m_{Ch}$ - the loss factor, which accounts to the loss of initial mass of charge due to carbon, iron and other charge raw components burnout; K_{Tr} - coefficient of charge pure iron transition into steel; $D_l, C_l, Si_l, Mn_l, P_l, S_l$ - mass fractions of charge, carbon, silicon, manganese, phosphorus, sulfur in the l^{th} component.

4.5. MM of the type 5 technological process

In this process, carbon dioxide is produced in fuel carbon oxidation M_{G1} (7) and in burning of initial materials carbon (9) M_{G2} :

$$M_{G3} = M_{G1} + M_{G2}. \quad (12)$$

This type includes melting in electric arc furnaces. Carbon in charge is in metal scrap and cast iron.

4.6. MM of the type 6 technological process

Specific gravity of CO₂ formed in the type 6 process, M_{G1} , is determined by the mass of completely oxidized carbon during using N types of fuel (7).

5. Results and discussions

Based on the above noted calculations are performed, the results of which are presented in Tables 1 and 2.

Table 1. Values of carbon dioxide emissions in various metallurgical processes.

| Process stages | Through emission, kg per 1 t of product | Process emission to through emission ratio | Process range by CO ₂ emission |
|----------------|---|--|---|
| EAF on scrap | 1021 | 0.087 | 1 |
| HyL-3 | 1044 | 0.593 | 2 |
| Midrex | 1211 | 0.524 | 3 |
| EAF with iron | 1434 | 0.062 | 4 |
| BOF | 2147 | 0.067 | 5 |
| Blast furnace | 2148 | 0.655 | 6 |
| Corex | 3475 | 0.768 | 7 |
| Romelt | 3925 | 0.954 | 8 |

Table 2. Values of carbon dioxide emissions in different metallurgical tandem processes of steel production.

| Process stages | Through emission per 1 t of product | | Process range by emission |
|----------------|-------------------------------------|------------------------|---------------------------|
| | Mass, kg | Volume, m ³ | |
| EAF on scrap | 988 | 500 | 1 |
| HyL-3 + EAF | 1171 | 592 | 2 |
| Midrex + EAF | 1226 | 620 | 3 |
| BF + EAF | 1401 | 709 | 4 |
| Corex + EAF | 1832 | 926 | 5 |
| Romelt + EAF | 1980 | 1001 | 6 |

6. Conclusions

1. Processes at EAF scrap, HyL-3, Midrex and HyL-3+EAF, Midrex+EAF tandems have the lowest through emission (carbon footprint).
2. Corex, Romelt processes and Corex+EAF, Romelt+ EAF tandems have the highest carbon footprint.
3. BF + EAF tandem by its carbon footprint is at intermediate position.

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