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GRAPH MODEL FOR CARBON DIOXIDE EMISSIONS FROM METALLURGICAL PLANTS

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Mathematical models are presented for estimating carbon dioxide emissions from metallurgical processes. The article also presents a new mathematical model in graph form to calculate transit and net emissions of carbon dioxide based on the estimates obtained for the individual processes. The graph model is used to compare the blast-furnace–converter process with the blast-furnace–EAF process.

Keywords: *integral emission of a process, transit emission, net emission of carbon dioxide, graph, carbon footprint.*

The emission of carbon dioxide – a greenhouse gas – is adversely affecting the environment regionally, nationally, and globally, and some scientists believe that it is changing the world's climate. Evaluating such emissions is an important part of the search that is going on to find the technologies which are the best from the standpoint of emitting the least amount of this gas. Evaluating carbon-dioxide emissions is also important for determining the penalties that factories should be assessed for exceeding established emission limits.

A carbon footprint is the analog of an emission of carbon dioxide. The carbon footprint is greater than this emission because it is determined with allowance for the effect of other greenhouse gases. However, metallurgical plants produce larger volumes of carbon dioxide than any other greenhouse gas – carbon dioxide is formed during the oxidation of the carbon in different types of fuel during a factory's operation. We will designate the total amount of carbon dioxide emitted in this manner as M_G and we will refer to it as the *integral emission* from the operation of the plant (it is being called "integral" because it characterizes the emission of the factory as a whole). For example [1], a blast furnace operated without the injection of natural gas forms blast-furnace gas having the following composition: 12–18% CO_2; 24–30% CO; 0.2–0.5 CH_4; 1.0–2.0% H_2; 55–59% N_2. The heat of combustion of blast-furnace gas is 3500–4000 kJ/m^3. Blast-furnace gas having the following composition is formed when the blast air is enriched with up to 30% oxygen and natural gas is also injected into the furnace: 15–22% CO_2; 22–27% CO; 0.2–0.5% CH_4; 8–11% H_2; 43–45% N_2. This blast-furnace gas has a heat of combustion of 4200–5000 kJ/m^3. Some of the gas is burned in the stoves of blast-furnaces, but most of it is burned in heating furnaces, municipal electric power plants, or flares. A similar pattern of use is seen in the case of residues of coke-oven gas that do not undergo combustion in coke-oven batteries.

Natural gas is currently being widely used in heating furnaces. In light of this, all of the carbon dioxide that is formed by the combustion of coke and injected gas in blast furnaces at a metallurgical plant is included in models of the smelting operation. A similar assumption is made for coke-oven batteries.

We further assume that the power plant of an integrated metallurgical plant supplies energy to all of the metallurgical plant's furnaces. It was reported in [2] that 90% of a metallurgical plant's energy needs are met by the output of its own power plant. Thus, in the graph models that have been constructed, electric power is obtained from outside networks only to make oxygen and operate the metallurgical plant's electric-arc furnaces.

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Since the models were developed to compare different processes, they do not account for the carbon dioxide lost with slag. Similar types of losses occur in all processes, but accurate data on them are difficult to find. The models also do not account for the losses from additions of coke or emissions of carbon dioxide in oxygen converters.

Mathematical models for calculating carbon-dioxide emissions M_{G} based on the mass of the burned fuel and oxidized carbon in a given process were proposed in [3]. The form of these models is different for different metallurgical conversions. They were developed to compare different combinations of metallurgical processes whose final product is steel. For example, they compare the combination of a blast furnace and an oxygen converter or a blast furnace and an electric-arc furnace.

Processes of type 1. These processes entail the combustion of a fuel (heating furnaces used in rolled-products manufacturing, kilns used to roast iron-ore pellets, heat-treatment processes, electric-power generation). The mass of the $\mathrm{CO_2}$ that is formed in a process of type 1 (M_{G1}) is determined by the mass of carbon that undergoes oxidation:

$$M_{G1} = 3.667 C^P M_F, \text{ tons/ton product,} \tag{1}$$

where 3.667 is a coefficient that indicates the fraction of gas which is formed per unit of oxidized carbon [4]; and C^P is the mass fraction (concentration) of carbon in the fuel – the ratio of the mass of carbon (M_{C}) in the fuel to the total mass of the fuel (M_F), tons/ton product.

Processes of type 2 are processes in which carbon in the metal of the charge undergoes combustion but no fuel is used (this group includes all conversion-type processes, including the operation of basic oxygen converters). In processes in which secondary combustion occurs, carbon monoxide is either burned near the mouth of the converter with the release of additional heat or leaves the furnace along with the flue gases and enters a system in which the gases are cleaned and final combustion takes place. All the carbon burned from the initial charge is in the form of $\mathrm{CO_2}$. The mass of $\mathrm{CO_2}$ which is formed in a type-2 process, represented by M_{G2}, is determined by the mass of the carbon that undergoes oxidation:

$$M_{G2} = 3.667 \Delta m_{\mathrm{C}}, \text{ tons/ton product,} \tag{2}$$

where Δm_{C} is the amount of carbon that is burned.

For converter steelmaking involving the use of a cold charge composed of scrap and pig iron, the value of Δm_{C} can be found from the formula

$$\Delta m_{\mathrm{C}} = \mathrm{C_P} m_{\mathrm{P}} + \mathrm{C_S} m_{\mathrm{S}} - \mathrm{C_{ST}} m_{\mathrm{ST}} = \mathrm{C_P} D_{\mathrm{P}} m_{\mathrm{CH}} + \mathrm{C_S} D_{\mathrm{S}} m_{\mathrm{CH}} - \mathrm{C_{ST}} m_{\mathrm{CH}}, \tag{3}$$

where $\mathrm{C_P}$ and $\mathrm{C_S}$ are the mass contents of carbon in the pig iron and the scrap; m_{P} and m_{S} are the masses of the pig iron and scrap in the charge; $\mathrm{C_{ST}}$ is the mass content of carbon in the finished steel; m_{ST} is the weight of the steel, tons; D_{P} and D_{S} are the mass contents of pig iron and scrap in the charge; $m_{\mathrm{CH}} = m_{\mathrm{P}} + m_{\mathrm{S}}$ is the weight of the metallic part of the charge, tons. The following was obtained with allowance for the coefficient $K_{\mathrm{L}} = m_{\mathrm{ST}}/m_{\mathrm{CH}}$ – which expresses the amount of mass lost from the charge due to the combustion of carbon, iron, and the charge's other components:

$$\Delta m_{\mathrm{C}} = m_{\mathrm{CH}}(C_{\mathrm{P}} D_{\mathrm{P}} + C_{\mathrm{S}} D_{\mathrm{S}}) - C_{\mathrm{ST}} m_{\mathrm{ST}} = m_{\mathrm{ST}} \left(\frac{C_{\mathrm{P}} D_{\mathrm{P}} + C_{\mathrm{S}} D_{\mathrm{S}}}{K_{\mathrm{L}}} - C_{\mathrm{ST}} \right). \tag{4}$$

The coefficient K_{L} is determined from the formula [1]

$$\begin{aligned} K_{\mathrm{L}} &= K_{\mathrm{B}} \frac{D_{\mathrm{P}}(1 - \mathrm{C_P} - \mathrm{Si_P} - \mathrm{Mn_P} - \mathrm{P_P} - \mathrm{S_P}) + D_{\mathrm{S}}(1 - \mathrm{C_S} - \mathrm{Si_S} - \mathrm{Mn_S} - \mathrm{P_S} - \mathrm{S_S})}{1 - \mathrm{C_{ST}} - \mathrm{Si_{ST}} - \mathrm{Mn_{ST}} - \mathrm{P_{ST}} - \mathrm{S_{ST}}} = \\ &= \frac{K_{\mathrm{B}} \sum D_i (1 - \mathrm{C}_i - \mathrm{Si}_i - \mathrm{Mn}_i - \mathrm{P}_i - \mathrm{S}_i)}{1 - \mathrm{C_{ST}} - \mathrm{Si_{ST}} - \mathrm{Mn_{ST}} - \mathrm{P_{ST}} - \mathrm{S_{ST}}}, \end{aligned} \tag{5}$$

where D_i, C_i, Si_i, Mn_i, P_i, and S_i represent the mass content of the *i*th component of the charge and the mass contents of carbon, silicon, manganese, phosphorus, and sulfur in that component, respectively; and K_{B} is a coefficient that expresses the combustion of carbon from the charge.

Processes of type 3 burn carbon from the metal in the charge and also burn fuel (this group includes open-hearth steelmaking, electric steelmaking, and agglomeration processes). In these processes, CO_2 is formed by oxidation of the carbon of the fuel (2) and the combustion of the carbon in the initial materials (3):

$$M_{G3} = M_{G1} + M_{G2}. \tag{6}$$

Processes of type 4 are processes in which a fuel is burned and some of the carbon in the fuel ends up in the finished product. Blast-furnace smelting is a typical example. Coke is the main fuel in blast furnaces, and nearly all of it is burned and forms carbon dioxide or carbon monoxide. The CO is subsequently burned to CO_2 in coke-oven batteries or blast-furnace stoves. Some of the carbon ends up in the pig iron. The following formula is used to calculate the mass of CO_2 that is formed:

$$M_{G1} = 3.667(\mathrm{C}_F M_F - \mathrm{C_P} m_\mathrm{P}), \tag{7}$$

where C_F is the mass content of carbon in the coke; M_F is the mass of the burned coke; $\mathrm{C_P}$ is the mass content of carbon in the pig iron; and m_P is the mass of the pig iron that is obtained.

In modern blast furnaces, the blast air is injected with fuel in the form of natural gas, fuel oil, pulverized coal, etc. When allowance is made for this practice, Eq. (7) takes the more complicated form:

$$M_{G1} = 3.667(\mathrm{C}_{F1} M_{F1} + \mathrm{C}_{F2} M_{F2} - \mathrm{C_P} m_\mathrm{P}), \tag{8}$$

where C_{F1} is the mass content of carbon in the coke; M_{F1} is the mass of the burned coke; C_{F2} is the mass content of carbon in the injected fuel; and M_{F2} is the mass of the injected fuel that is burned.

It is also interesting to estimate the net emission of carbon dioxide (the amount emitted throughout the manufacture of the finished product). The net emission is uniquely analogous to the energy content and environmental-energy characteristic of a production process [5]. A net energy-greenhouse analysis is based on allowance for the emissions of carbon dioxide that occur during all of the stages in a series of interrelated production processes (such emissions are analogous to the carbon footprint). The net emission (M_C) is determined as

$$M_\mathrm{C} = M_\mathrm{G} + M_\mathrm{T}, \tag{9}$$

where M_T represents the transit emissions (the percentage of carbon dioxide emitted in previous conversions, which is included as part of the net emission of the conversion being analyzed).

The parameters of a complete series of production processes are usually represented in tabular form [5]. We believe that these parameters can be most clearly represented in graphical form. To calculate the net emission of CO_2 in this case, we represent the production processes in the form of a weighted directed graph with designated vertices – a type of signal graph [6]. We will examine an approximate emissions graph in general form (Fig. 1) in order to obtain a formula for calculating net emissions.

The unit weights of the arcs Ψ_{ik} correspond to the unit consumptions of resources in tons or cubic meters. The specific units used in a given problem depend on the dimensions associated with an emission at a vertex where an arc originates (kg/ton product or m^3/ton product).

The values for the transit emissions or the emissions due to the production process being analyzed are indicated inside the vertices of the complete graph, while in the simplified graph the vertices indicate the net emissions (9) (see Fig. 1). The first subscript in the graph denotes the number of the conversion and the second subscript corresponds to the number of the production process in the given conversion. We will use the term "sources" to refer to the vertices from which arrows only emanate. We designate the net emission for these vertices as G_{ik}, the first subscript denoting the number of the conversion and the second representing the number of the source. We propose to determine the values of G_{ik} based on the value of the technological fuel number (TFN) [7].

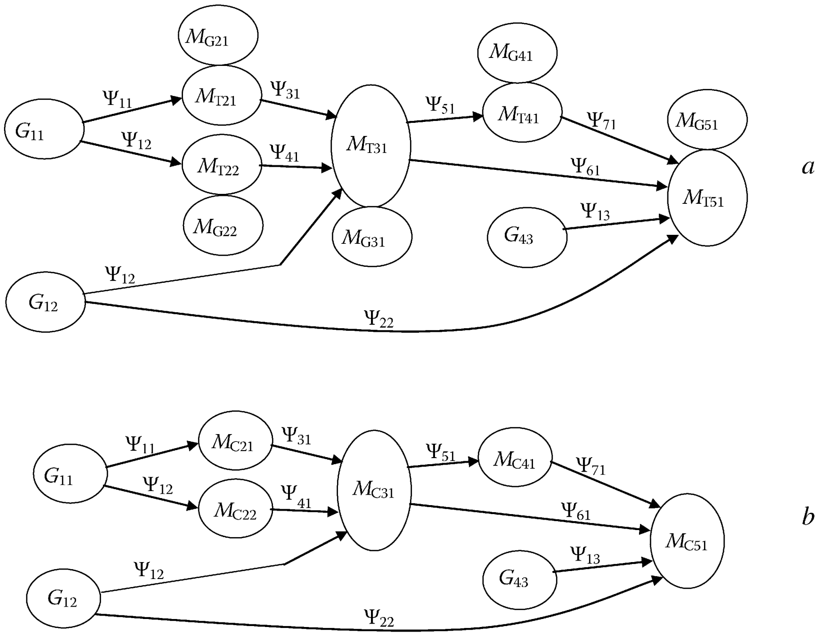

Fig. 1. Graph of emissions from conversions in metallurgical processing: *a*) complete graph with allowance for process and transit emissions; *b*) graph of net emissions; Ψ_{ik} – unit weights of the arcs.

For signal graphs, the value of a signal at a vertex is equal to the sum of the signals arriving from other vertices with allowance for the transmission factor of the arc. It can then be found that

$$M_{C51} = M_{G51} + G_{43}\Psi_{13} + M_{C31}(\Psi_{51}\Psi_{71} + \Psi_{61}) + G_{12}\Psi_{22} \tag{10}$$

and

$$M_{C31} = M_{G31} + G_{11}(\Psi_{11}\Psi_{31} + \Psi_{21}\Psi_{41}) + G_{12}\Psi_{12}.$$

Inserting M_{C31} into Eq. (10), we obtain

$$M_{C51} = M_{G51} + G_{43}\Psi_{13} + M_{G31}(\Psi_{51}\Psi_{71} + \Psi_{61}) + G_{11}(\Psi_{11}\Psi_{31} +$$

$$+ \Psi_{21}\Psi_{41})(\Psi_{51}\Psi_{71} + \Psi_{61}) + G_{12}\Psi_{12}(\Psi_{51}\Psi_{71} + \Psi_{61}) + G_{12}\Psi_{22}.$$

After opening the parentheses and grouping the respective terms in the formula, we obtain

$$M_{C51} = M_{G51} + G_{43}\Psi_{13} + M_{G31}(\Psi_{51}\Psi_{71} + \Psi_{61}) + G_{11}(\Psi_{11}\Psi_{31}\Psi_{51}\Psi_{71} +$$

$$+ \Psi_{21}\Psi_{41}\Psi_{51}\Psi_{71} + \Psi_{11}\Psi_{31}\Psi_{61} + \Psi_{21}\Psi_{41}\Psi_{61}) + G_{12}(\Psi_{12}\Psi_{51}\Psi_{71} + \Psi_{12}\Psi_{61}) + G_{12}\Psi_{22}.$$

We will refer to the products of the unit weights of the arcs – $\Psi_{11}\Psi_{31}\Psi_{51}\Psi_{71}$, for example – as transfer functions of the corresponding path P_j; the lengths of the paths differ. Thus, the net emission at the *k*th vertex for the *i*th conversion is determined from the formula

$$M_{Cik} = M_{Gik} + \sum_{i=1}^{L}\left(G_{Cik} \sum_{j=1}^{N} P_j \right), \tag{11}$$

where *L* is the number of sources, *N* is the number of paths from a vertex-source to the vertex being analyzed.

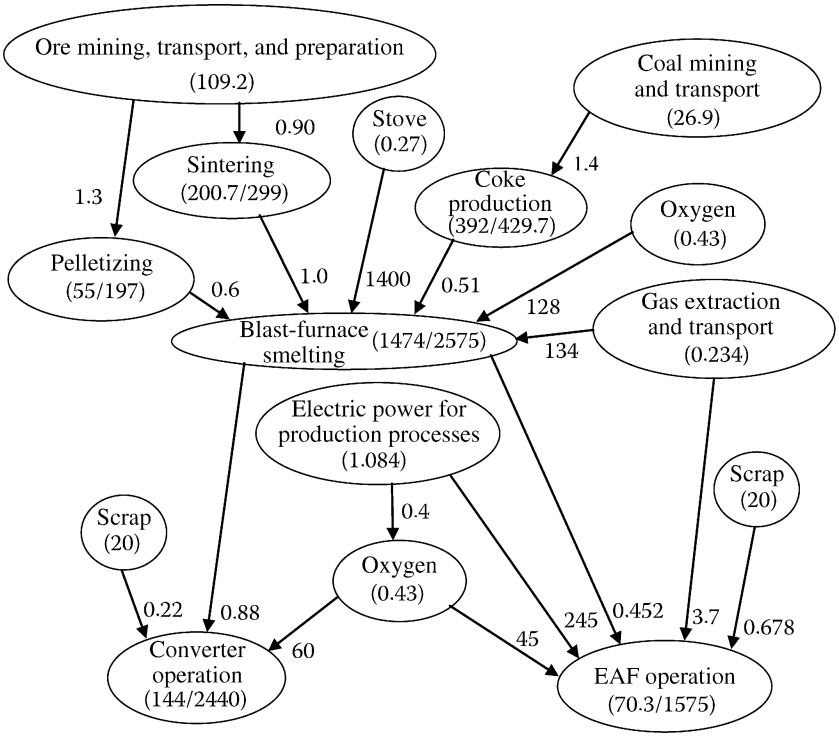

Fig. 2. Graph of process emissions and net emissions (by conversion) of carbon dioxide.

As an example, let us examine the construction of an emissions graph for the production of iron and steel in a basic oxygen converter (BOC) and an electric-arc furnace (EAF). In the ironmaking process, carbon dioxide is formed during the preparation of the ore (sintering), the production of oxidized pellets, and coke production. The following data is used to perform calculations of the net emission of carbon dioxide:

pig iron: $C_P = 4\%$, $Si_P = 1.2\%$, $Mn_P = 1\%$, $P_P = 0.2\%$, $S_P = 0.05\%$ (the total impurity content is 6.45% and the remainder is iron);

scrap: $C_S = 0.12\%$, $Si_S = 0.2\%$, $Mn_S = 0.5\%$, $P_S = 0.04\%$, $S_S = 0.05\%$ (total impurity content 0.91%);

steel: $C_{ST} = 0.3\%$, $Si_{ST} = 0.2\%$, $Mn_{ST} = 0.3\%$, $P_{ST} = 0.04\%$, $S_{St} = 0.05\%$ (total impurity content 0.89%).

We further assumed that the charge for the BOC consists of 80% pig iron and 20% scrap and that the EAF is operated with the use of liquid pig iron (which is the practice at several plants). The metallic part of the charge for the EAF consists of 40% pig iron and 60% scrap. The net emission of CO_2 will be even lower if the EAF is operated on a charge whose metallic part consists of up to 80% solid scrap.

Equations (1)–(8) were used to determine the emissions from the different processes and Eqs. (9) and (11) were used to calculate the transit and net emissions. The following were chosen as the energy sources: coal, ore, natural gas, oxygen, compressed air, electric power. The values for their net emissions were taken from the data in [7].

It follows from Fig. 2 that in blast-furnace smelting the integral emission of carbon dioxide is 1474 kg/ton pig iron and the net emission is 2575 kg/ton pig. The net emission for the converter process is 2440 kg/ton steel. The EAF has a net emission of 1575 kg/ton steel, which is lower than that of the converter. However, this difference is due less to the nature of the steelmaking operation than it is to the fact that the charge used on the EAF contains less pig iron than the converter charge. Thus, more carbon is burned in the converter than in the EAF.

Conclusion. The use of mathematical models of production processes in graph form is a convenient means of calculating the net emissions of carbon dioxide at metallurgical plants.

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