Estimation of CO2-Equivalent Emission under the Copper Fire Refining Process

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Abstract. Non-ferrous metallurgy is one of the most energy-consuming and carbon-emissive sectors of industry. This is due to the fact that the volume of greenhouse gas (GHG) emissions is stipulated by energy consumption. Uralelectromed is a city-forming enterprise of the Verkhnyaya Pyshma. The situation is similar other cities of the old industrial regions of the Russian Federation (Krasnouralsk, Verkhnaya Salda, Karabash, etc.) Verkhnyaya Pyshma has many characteristics of "a clever city". It can be compared to Hamburg where blister copper is being produced at the center of the city at a copper smelting plant Aurubis. Following the example of such ecologically clean country as Germany and in order to assess how modern energy-efficient low-carbon technologies can provide a favorable habitat, and an acceptable level of carbon footprint, the authors estimated the level of greenhouse gas, i.e., carbon dioxide emission produced by the Uralelectromed. The emission of greenhouse gas – carbon dioxide in the process of fire refining of blister copper has been calculated. The anode melting process consists of several stages where the most important ones are melting of charge, oxidation, and copper melt reduction. Calculations are based on taking into account the mass of burnt carbon of natural gas and the thermal dissociation of fuel oil. It implies that a complete combustion of carbon takes place. The specific value of carbon dioxide emission of the copper refining process is averaged 181 kg CO_2 per 1 ton of anode copper.

Introduction

It is considered to be not typical for the so-called "clever" cities to have non-ferrous metallurgy enterprises in the city. However, since non-ferrous metallurgy has often a city-forming significance, enterprises are located within the city, for example, at the center. Thereby, it is desirable to estimate the emission of carbon dioxide from the refining process at Uralelectromed in Verkhnyaya Pyshma, which is a part of the Ural Mining and Metallurgical Company (UMMC) occupying the first place in Russia and is the eleventh largest producer of refined copper in the world. The article uses an array of random sample data for the period from 2016 to 2017 for seven variants of anode melting.

The copper refining enterprise was chosen for the following reasons:

- Russia has a significant raw material base and ranks third place in the world for copper ore reserves (about 90 million tons) after Chile and Peru;
- Copper has valuable mechanical (ductility and toughness) and corrosion properties and has high thermal, and electrical conductivity;
- 85 % of copper in the world is produced using pyrometallurgical method of processing the raw copper. This process consists of several operations: extraction, and beneficiation of ore to produce concentrate; production of blister copper; production of refined copper for providing the anodic and cathodic copper (Figure 1);
- Copper is currently the only alternative material in computational digital electronics (primarily computers) in various fields of electrical engineering, such as robotics, automation, measuring instruments, radio and telecommunication devices and many other digital devices.

The diagram in Figure 1 shows the steps of removal of iron and sulfur: in three stages (roasting, melting and converting), in two stages (melting, converting), or in one stage [1]. With the exception of the latter option including the direct melting of concentrates to produce a blister copper, the technology for its production is multistage.

The most common technology includes the obligatory use of the following metallurgical processes:

- matte smelting,
- matte copper converting,
- fire and electrolytic copper refining.

Refined copper is the main raw material for production of semi-finished copper goods. Nowadays 91 % of the UMMC production consists of copper rod, of non-ferrous rolled products 8 %, of copper powder 1 %.

At the center of any metallurgical process the principle lies of transferring the processed raw materials to a heterogeneous system. The process consists of several phases that differ from each other in composition and physical properties. During this process one of the phases can be enriched by the recovered metal and impoverished by the contaminants, while other phases, on the contrary, become impoverished by the main component.

One of the phases is the gas phase, which is subjected to high environmental requirements for non-ferrous metallurgy enterprises. Polluting emissions of copper melting enterprises mostly consist of such elements as

- sulfur dioxide,
- dust,
- nitrogen dioxide,
- carbon oxide and dioxide,
- metals and their compounds (depending on the composition of the feedstock, there are primarily cadmium, copper, arsenic, mercury, lead, etc.),
- volatile organic compounds (organic carbon, etc.).

The problem of capturing the sulfur dioxide SO_2 (accounting for 75–80 % of the total amount of pollutants in the waste gases) is being effectively solved at copper melting plants, for example, in the EU. Now, an average of 98.9 % of sulfur is extracted from emissions and used for production of sulfuric acid and liquid sulfur dioxide. Meanwhile, the issue of controlling and capturing other harmful components in the waste gases emitted by non-ferrous metallurgy enterprises remains quite acute. One of these undesirable components is the carbon dioxide CO_2.

Carbon dioxide CO_2 is the basic greenhouse gas (GHG). Presence of such gases in the atmosphere of our planet leads to the appearance of a greenhouse effect, namely to increasing the surface temperature and to climate change [2–6]. According to the IPCC Source Category, cast iron and steel belong to the category 1A2a, while nonferrous metals to 1A2b [4]. Generally, the most efficient practice is to use higher-level methods for the key categories, such as cast iron, steel, and non-ferrous metals. Decision-making schemes for each category help the GHG inventory compilers to follow the guidelines and select the appropriate multi-level methodology suitable for their conditions.
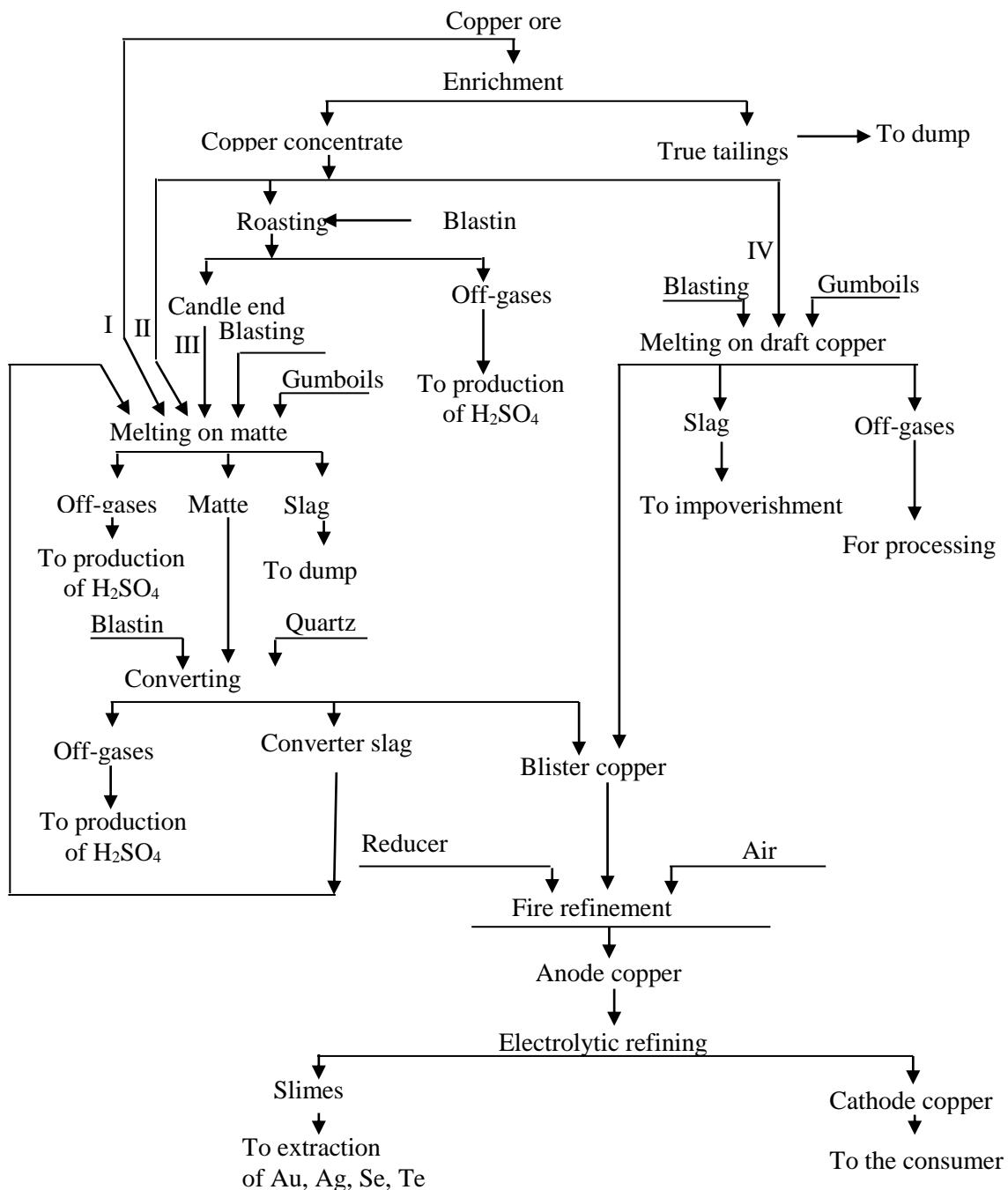
Figure 1. Principal technological scheme of pyrometallurgical copper production from sulphide ores; numericals indicate the possible options for processing the raw materials into thr blister copper

The widespread notion of the carbon footprint is reduced to the concept of end-to-end emission of the carbon dioxide M_C, This value is the sum of carbon dioxide emissions that consistently occur in all processes of the technological chain starting with the extraction of raw materials and ending with the product. Moreover, we will distinguish between the emissions of the process M_P and the transit M_T due to the fractions of the total mass of analyzed carbon dioxide emissions generated in previous

processes. The end-to-end integrated emission of the carbon dioxide M_C is determined by the sum of emissions of carbon dioxide of the process and transit emissions

$$M_C = M_P + M_T. \tag{1}$$

Chemical Relations of the Process

Consider in details the methods for reducing the impact of production facilities onto the environment. These methods include ones integrated into the production process: the methods associated with preventing or reducing emissions from activities such as storage, chemical reactions, separation, and purification of various materials and substances [7]. As it was mentioned above, here, we take refining enterprise Uralelectromed (Verkhnyaya Pyshma) as an example. This plant receives supplies of blister copper from various producing factories and transforms it into the charge for anodic copper smelting. The full load of a single furnace is 350 tons.

The averaged chemical composition indicators of blister copper charge are the following:
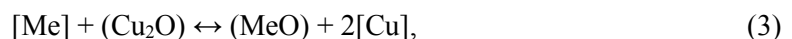
- 99.35 % Cu,
- 0.17 % Ni,
- 0.14 % Sb,
- 0.13 % Pb,
- 0.11 % As,
- 0.052% Sn,
- 0.00121 % Fe,
- 0.0001 % Bi.

The process of the copper fire refining in terms of greenhouse gas emissions was considered in [8, 9].

The refining process is based on the following regularities:

- High solubility of copper oxide (I) Cu_2O in liquid copper;
- Oxidation of the most contaminants by copper oxide (I) Cu_2O;
- Insolubility of contaminant oxides in copper (MeO);
- The reducibility of copper oxide (I) Cu_2O by various hydrocarbons after slag removal;
- The possibility of desorption of sulfur oxide (IV) SO_2, which is dissolved in liquid copper while mixing it with gaseous products of dry distillation of wood.

The main chemical reactions in this case are [1]

$$2[Cu] + 1/2O_2 \leftrightarrow (Cu_2O), \tag{2}$$

$$[Me] + (Cu_2O) \leftrightarrow (MeO) + 2[Cu], \tag{3}$$

$$(Cu_2O) \leftrightarrow 2[Cu] + [O], \tag{4}$$

$$[Me] + [O] \leftrightarrow (MeO), \tag{5}$$

$$Cu_2O + H_2 = 2Cu + H_2O_{steam}, \tag{6}$$

$$Cu_2O + CO = 2Cu + CO_2, \tag{7}$$

$$4Cu_2O + CH_4 = 8Cu + 2H_2O + CO_2. \tag{8}$$

As mentioned above, during this process, the carbon dioxide CO_2 is being produced. In practice, the temperature of the furnace working zone is maintained in the range from 1100 to 1200 ºC. The main condition for burning of natural gas is the presence of oxygen and, consequently, the presence of air which leads to a chemical reaction combining oxygen from the air with carbon and hydrogen in the fuel. The reaction occurs with the release of heat, light, as well as the carbon dioxide, and water vapor.

The amount of air depends on the calorific value of natural gas: the higher it is the more air is needed.

Regardless of the aggregate state of the substance, the amount of air necessary for complete combustion is determined by equation of the combustion chemical reaction compiled on the basis of the chemical composition of the combustible substance.

In order to calculate the value of fuel combustion, we calculate the material balance of the combustion process on the basis of relative molecular masses of the main substances involved in combustion, as well as, on the basis of composition (in percentage), and density ρ of natural gas (volume %), temperature T, and air pressure P.
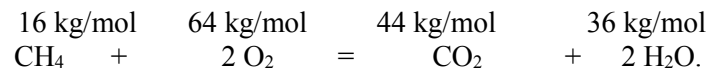
The calculation is carried out at $T = + 150\ °C$, $P = 760$ mm Hg, $P = 0.717$ kg/m³.

The equations of methane combustion reactions is

$$CH_4 + 2O_2 = CO_2 + 2H_2O. \tag{9}$$

Substitute the molecular masses of the elements in this equation.

Calculations are performed with the data for the methane combustion equation

$$
\begin{array}{ccccc}
16\ \text{kg/mol} & 64\ \text{kg/mol} & 44\ \text{kg/mol} & 36\ \text{kg/mol} \\
CH_4 + & 2\ O_2 & = & CO_2 & + & 2\ H_2O.
\end{array}
$$

From the methane combustion formula, find the mass of oxygen m_O necessary for the complete combustion of 1 kg of the component

$m_O = 64/16 = 4$ kg.

Find the volume V_O of oxygen required for the complete combustion of 1 m³ of the component by the formula

$$V = \frac{m_o}{\rho_o} \tag{10}$$

where ρ_O is the oxygen density.

Combustion of methane requires the following volume of oxygen:

$$V_{O_2} = \frac{4}{1.429} = 2.799\ \text{m}^3.$$

Define the required volume of air for methane combustion under the normal physical conditions, taking into account that concentration of oxygen in the air is 21 %:

$$Vacn = 2.799/0.21 = 13.33\ \text{m}^3/\text{m}^3.$$

Calculate the volume of air under the given conditions ($T = + 150C$, $P = 760$ mm Hg):

$$Vac = 13.33 \cdot (273 + 15)/273 = 14.06\ \text{m}^3/\text{m}^3.$$

Thus, complete combustion of 1 m³ of natural gas under the taken conditions requires 14.06 m³ of air. One kilogram of methane has a volume of $1/0.717 = 1.395$ m³ provided the methane density is $\rho = 0.717$ kg/m³. Therefore, in order to burn 1 kg of methane, $14.06/1.395 = 10.08$ m³ of air is needed. The amount of air determined in this way is called theoretically necessary. In practice, the combustion process in burners of various types has a much greater actual consumption.

Completeness of combustion is determined by the amount of air involved in the combustion process. With a sufficient supply of air, complete combustion of natural gas takes place and, as a result, are the following its combustion products are the following non-flammable gases:
- carbon dioxide CO_2,
- nitrogen N_2,
- H_2O water vapor.

If the amount of air is insufficient then the combustion of natural gas is incomplete or chemical undercooking of combustible constituents occurs. So, the following flammable gases appear in combustion products:

- carbon monoxide CO,
- methane CH_4,
- hydrogen H_2.

Thus, the lack of air leads to incomplete combustion of natural gas, while the excess of air leads to excessive cooling of the flame temperature. To provide complete combustion of fuel, it is necessary to supply air to the furnace somewhat more than required by the calculations, which is regulated by the air excess coefficient.

Besides emissions from burnt natural gas necessary to maintain the melt temperature, appearance of significant concentrations of the carbon monoxide is possible in the recovering atmosphere of the furnace. Removal of the carbon monoxide CO is carried out by burning furnace gases with the consumption of additional fuel; so, the amount of the carbon dioxide CO_2 in the plant emissions increases.

Provided that all carbon is oxidized to the carbon dioxide CO_2 and with availability of data from the plant's practice, calculations of carbon dioxide emissions can be simplified without using formulas (2)–(8). Articles [10, 11] give us the formula from the industrial method for determining carbon dioxide emission E_{CO2}

$$E_{CO2} = (M \cdot C_M - P \cdot Cp) \cdot K_u. \tag{11}$$

Here, M is consumption of carbon-containing materials in thousand tons; C_M is the carbon content in the material, t/t; P is output of carbon-containing products, t/t; Cp is the carbon content of the product, t/t; K_u is the coefficient of conversion of the carbon C mass into the mass of the carbon dioxide CO_2, equal to $44/12 \approx 3.667$. In paper [12], we find calculations of carbon dioxide emissions based on generalized coefficients made by enterprises. However, there is no data for non-ferrous metallurgy in this study. Let us use formula (9), taking into account that the output of carbon-containing products is absent in non-ferrous metallurgy.

Calculations of emission of the carbon dioxide

On elaboration of blasting 1 m^3 of air it is needed about 0.43 kWh of electric power that leads to emission of the carbon dioxide 1.086 kg/m^3 [13].

Taking it into account, calculation of values of emissions of the carbon dioxide is carried out by the following formulas:

$$E_{ghg} = V_{ghg} \cdot \rho_{ghg} \cdot C_{ghg} \cdot 44/12, \text{ kg } CO_2, \tag{12}$$

$$E_{fo} = m_{fo} \cdot C_{fo} \cdot 44/12, \text{ kg } CO_2, \tag{13}$$

$$E_a = 1.086 \cdot V_{ghg} \cdot V_a, \text{ kg } CO_2. \tag{14}$$

where V_{ghg} is the volume of natural gas, m^3; ρ_{ghg} is density of natural gas, kg/m^3; C_{ghg} is the content of carbon in natural gas, %; m_{fo} is the mass of fuel oil, kg; C_{fo} is the content of carbon in fuel oil, %; V_{ghg} is a specific consumption of air for burning of 1 m^3 of natural gas; 44 and 12 are the molar massed of the carbon dioxide.

According to practice of Uralelectromed for chosen the furnace charge at fire refinement of copper in the reflective furnace, usually it is spent of 28 855 m^3 or $m_{ghg} = 28\,855 \cdot 0.717 = 20\,689$ kg of natural gas of density $\rho_{ghg} = 0.717$ kg/m^3 with content of the carbon $C_{ghg} = 75$ %. Combustion of natural gas requires $V_a = 275\,784$ m^3 or $m_a = 337\,835$ kg of air.

Resultant emission of process of the carbon dioxide (if in it there is no transit emission of CO_2 of power plant) at the rate of full load of the furnace (350 t) of the considered process is

$$E_{pr} = E_{ghg} + E_{fo}, \text{ kg } CO_2, \tag{15}$$

Taking into account emission of the carbon dioxide at power generation the through emission of CO_2 at process of manufacturing the draft copper at anode will be

$$E_{ti} = E_{pr} + E_a + E_{fo}, \text{ kg } CO_2, \tag{16}$$

From the loaded furnace charge m_{ac} of tons of anode copper be received. Specific emission of the carbon dioxide of process of fire refinement then will be

$$E_{scfr} = E_{da}/m_{ac}, \text{ kg CO}_2, \tag{17}$$

As mentioned above, the basic data are taken from practice of the plant, which were used for calculations for formulas (12)–(17) and are given in Table 1. Existence of data for these concrete swimming trunks significantly increases the accuracy of calculations. The last line represents average values of basic initial and calculated data.

Table 1. Basic and calculated data of emissions of the carbon dioxide

m_{cop}, t	V_{ghg}, m³	m_{ghg}, kg	E_{ghg}, kg CO_2	V_a, m³	E_a, kg CO_2	m_{fo}, t	E_{fo}, kg CO_2	E_{ghg}, kg CO_2	E_{ti}, kg CO_2	E_{scfr}, kg CO_2
342	28442	20393	56081	398188	432432	1.22	3802	59883	492315	175
341	29411	21088	57991	411754	447165	1.34	4173	62164	509329	183
338	28605	20510	56402	400470	434910	1.22	3815	60217	495127	178
332	29867	21415	58890	418138	454098	2.03	6336	65226	519324	197
353	31517	22598	62144	441238	479184	1.08	3350	65494	544679	185
346	27186	19492	53604	380604	413336	1.56	4865	58469	471805	169
344	28855	20689	56895	403970	438711	1.28	3989	60884	499596	177
342	29126	20883	57429	407766	442834	1.39	4333	61763	504596	181

Emission of the carbon dioxide of E_{ti} is not a carbon trace of copper production since here the transit emissions of the carbon dioxide passing from processes of receiving draft copper and electrolytic refinement of anode copper are not considered. Formation of a carbon trace of copper production illustrates columns of emissions of the carbon dioxide (Figure 2) made for one chain of possible chains of production of copper production. The notations TE_i correspond to specific through emission of the carbon dioxide in this or other process. The symbol Ψ_j has designated expenses (consumption) of this or other resource. The through emission at each top point is calculated as sum of emission corresponding to this point with the through emissions of joined top points multiplied by values of consumptions of spent resources.

For example, through emission (a carbon trace) of fire refinement of copper is defined by the sum
$TE_5 = (TE_{ghg} \cdot \Psi_{2ghg} + TE_4 \cdot \Psi_4 + TE_a \cdot \Psi_{3a} + TE_{fo} \cdot \Psi_{fo})/342 + 181$ kg CO_2/t of anode copper,
where

$$TE_a \cdot \Psi_{3a} = (TE_I \cdot \Psi_{2I}/342) \cdot \Psi_{3a} = 1\ 474 \text{ kg CO2/t of anode copper.}$$

Division by 342 serves for reduction of total emissions to specific ones. Value of a through emission of the carbon dioxide is at production and transportation of $TE_{ghg} = 0.234$ kg of CO_2/m³ of fuel oil, $TE_{fo} = 233$ kg of CO_2/t [14, 15]. Values of the sizes TE_4, Ψ_{2ghg}, Ψ_4, Ψ_{fo} are unknown. For this reason, it is only possible to claim that through emission or a carbon trace of process of fire refinement of copper exceeds the value

$$181 + 504\ 596/342 = 1\ 655 \text{ kg CO2/t of anode copper.}$$

Appendices
1. Specific emission of the carbon dioxide in fire refinement of draft copper process makes 181 kg of CO_2 on ton of anode copper.

2. Annual emission of the carbon dioxide on the Uralelectromed is no more than 0.12 % of the total volume of emissions of greenhouse gases by all enterprises of Sverdlovsk region.

3. Calculations are carried out according to the concrete swimming trunks determined by method of random selection.

4. Results of article confirm that work of the refining shops placed in the urban environment does not lead to significant growth in a carbon trace and critical level of ecological damage to the environment and the population Verkhnyaya Pyshma. It is one of the main indicators, on which Verkhnyaya Pyshma can be referred in the short term to category of "the clever cities".
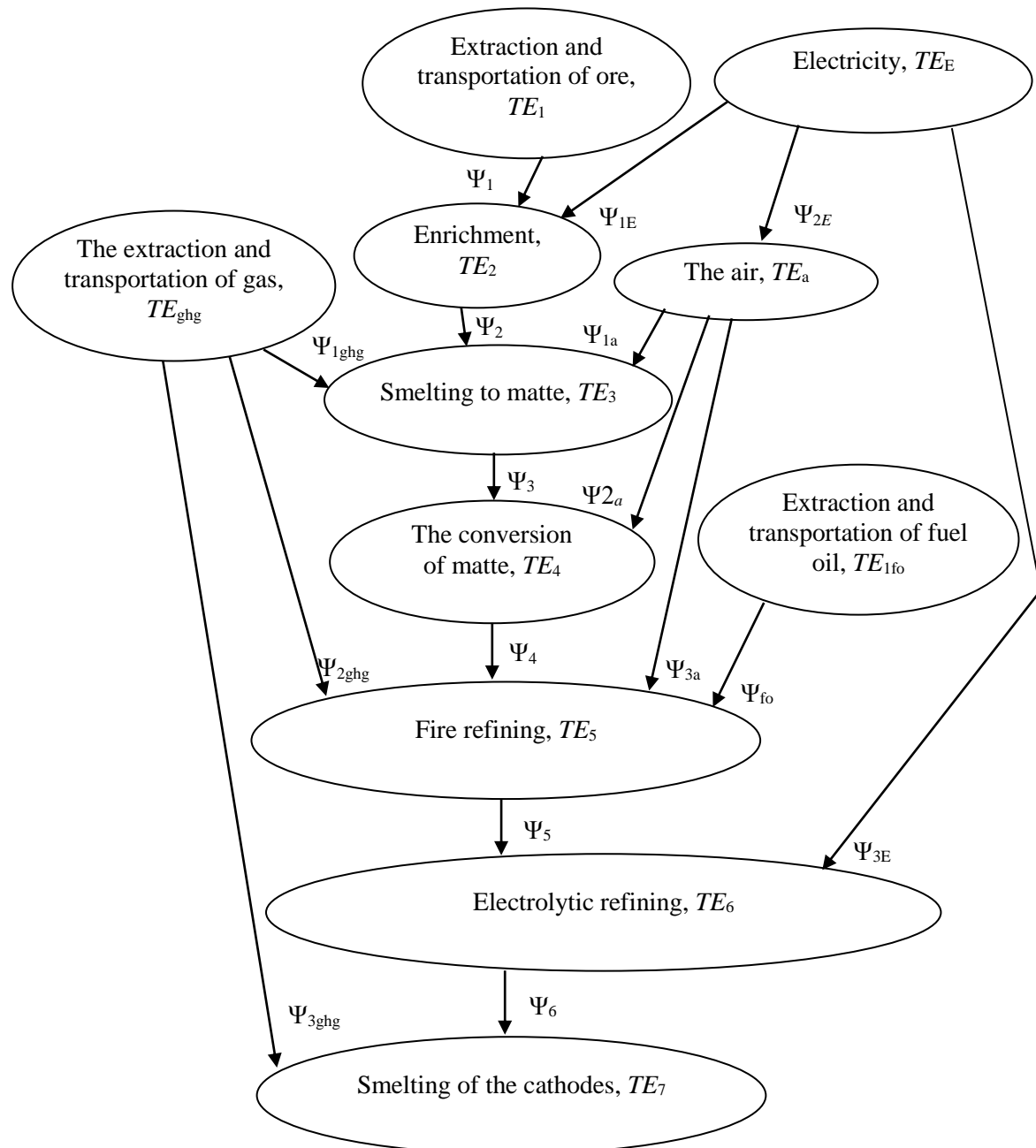

Figure 2. Chart of emissions of the carbon dioxide of process of manufacturing of copper production

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