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Analysis of changes in global warming potential during enrichment and production of battery-grade graphite using electrothermal fluidized bed technology

Semen Hubynskyi[1], **Artem Sybir**[2], **Serhii Fedorov**[2,5], **Andrii Usenko**[1], **Mykhailo Hubynskyi**[3] **and Tetyana Vvedenska**[4]

[1]Ukrainian State University of Science and Technologies, Lazaryana St., 2, Dnipro, 49010, Ukraine
[2]Iron and Steel Institute of Z. I. Nekrasov National Academy of Sciences of Ukraine, Akademika Starodubova Sqr., 1, Dnipro, 49107, Ukraine
[3]Thermal & Material Engineering Center SP. Z O. O., Ludwika Warynskiego St., 2, Opole, 46020, Poland
[4]Dnipro University of Technology, Dmytra Yavornytskoho Ave., 19, Dnipro, 49005, Ukraine

[5]Corresponding author: fedorov.pte@gmail.com

Abstract. The greenhouse gas emissions during the production of anode class graphite for the conditions of Ukraine have been calculated. Conventional technologies and technologies using electrothermal fluidized bed (EFB) for natural and synthetic graphite have been studied. Calculations are carried out with respect to the whole technological chain, starting from extraction and processing of raw materials and ending with finishing processing (coating). As a result, it is shown that the technology of using EFB for purification of natural graphite and graphitization of synthetic graphite is competitive in terms of global warming potential (GWP). In the production of natural graphite using thermal purification with EFB instead of chemical purification, emissions of greenhouse gases practically remain at the same level. At the same time, the use of acids is eliminated, and the environmental impact associated with them is reduced. Production of synthetic graphite of anodic quality in EFB furnaces allows to reduce greenhouse gases (GHG) emissions by 40-50% in comparison with traditional graphitization technologies in Acheson and Kastner furnaces. The effect is achieved by reducing energy and raw material consumption.

1. Introduction

One of the main trends in the development of modern economy has been a significant growth in the production of electric power accumulators based on lithium-ion batteries. This is explained by the development of renewable energy sources, electric vehicles, autonomous electronic devices and tools, and the rejection from the use of fossil fuels. Forecasts indicate an annual 20% growth in battery production [1, 2, 3, 4]. One of the main materials used in the manufacture of lithium-ion batteries is graphite which is used in manufacture of anodes. The share of graphite in anode material is more than 50% by weight [2]. Accordingly, the demand for production of anode quality graphite will increase, and at the same time the issue of the emissions impact on the environment during graphite production becomes relevant. In recent years, a number of works based on Life Cycle Assessment (LCA) has focused on this issue [3, 5-12]. The authors of the works, departing from the data on the technological sequence of anode-quality graphite production as well as used materials and energy carriers, determined the value of carbon emissions on the basis of generally accepted recommendations and taking into account direct and indirect emissions [13, 14]. The anode is composed of a mixture of natural and synthetic graphite, the content of which can vary from 40% to 60% [2]. Thus, the influence of both types of the used graphite determines the GHG emissions in the production of lithium-ion batteries.

A number of studies [9, 10] is devoted to the assessment of complex environmental impacts of anode material production, including GWP, Water Scarcity Footprint, Land Use Transformation, Acidification Potential and others. In this article we mainly limit ourselves to the assessment of GWP.

The purpose of this article is to assess the efficiency of GHG emission reduction while using electrothermal fluidized bed (EFB) technology for thermal treatment of natural graphite and graphitization of synthetic graphite. The process of thermal treatment of conductive carbon material in the EFB is associated with heating of the material when electric current passes through the fluidized bed [15] (figure 1).

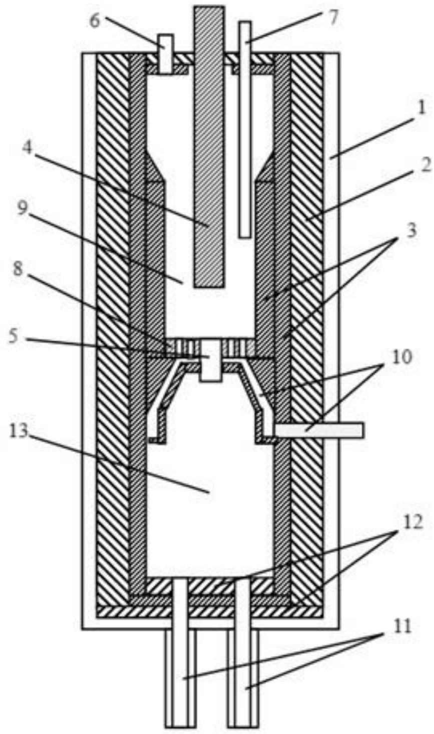

Figure 1. Schematic diagram of an electrothermal fluidized bed furnace: 1 - body, 2 - thermal insulation, 3 - graphite lining, 4 - central electrode, 5 - outlet pipe of the treated material, 6 - pipe for raw material loading, 7 - exhaust gas duct, 8 - gas distribution grid, 9 - working chamber, 10 - inert gas supply, 11 - cooler of the finished product, 12 - thermal insulation, 13 - chamber for material residence.

The heat treatment process is carried out in a continuous mode. The initial material enters the reactor through the feed pipe 6, the material treated in the bed after cleaning is removed from the reactor through pipe 5. Inert gas is supplied to the working chamber through the gas distribution grid, which ensures the formation of a fluidized bed of carbon material in the working chamber. When voltage is applied to the central electrode 4 and graphite lining 3, the electric current goes in the radial direction through the bed, which provides heating of carbon material to 2800 – 3000 °C due to Joule heat. The material with particle size up to 1 mm is processed in the furnace. In the course of heating, graphitization and purification of carbon material to the carbon content of 99.95% is performed [16, 17]. The oxide fumes from the ash are removed from the furnace together with exhaust gases.

2. Methods

The main factors determining GHG emissions are related to the consideration of all stages of the technological process of anode-quality graphite production and the quality of the inventory for the data related to the use of energy and other material resources.

Technological schemes of natural and synthetic graphite production presented in literature differ depending on the author's approach. For example, when assessing production of synthetic graphite, namely the finishing stage of its preparation; milling, classification and coating are often not taken into account. Below are the technological schemes for obtaining natural and synthetic anodic quality graphite obtained on the basis of analyzing the technological schemes [7-9, 11, 12, 18], which were used in the study.

The technological scheme for obtaining natural graphite of anodic quality based on the existing technology used at Chinese enterprises [8, 11, 12, 18] is shown in figure 2a. It includes the following main stages: ore extraction, enrichment via flotation, spheronization, purification, coating. The peculiarity of this scheme is that graphite purification is performed after spheronization, which ensures the yield of spherical graphite at the level of 40% of the initial graphite. This significantly reduces emissions at the purification stage.

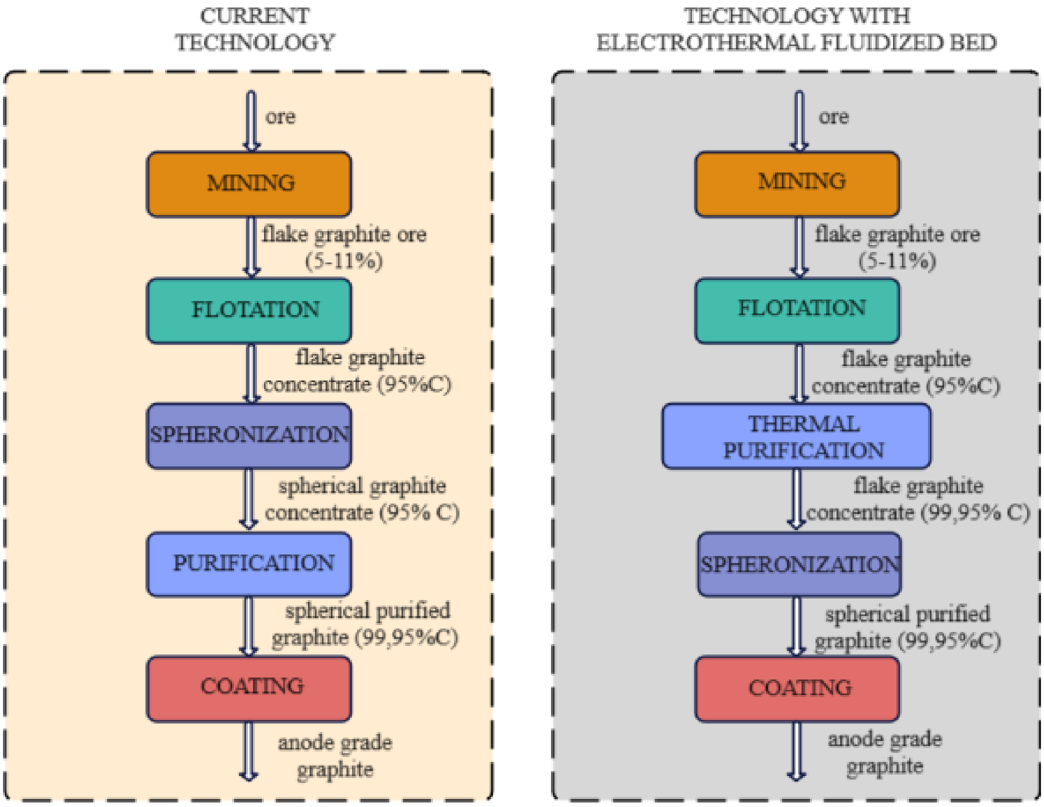

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Figure 2. Technological schemes for the production of anodic quality natural graphite.

The technological scheme of synthetic graphite production is based on the existing technologies of electrode production in Acheson or Kastner furnaces. The scheme (figure 3a) is based on the data given in [7-9, 11, 18]. The sequence of technological operations is as follows: calcination of green petroleum coke in a rotary furnace with natural gas heating or electric calciner, grinding of calcined coke and mixing it with binder (pitch), pressing of billets and their calcination in multi-chamber furnaces, graphitization at 2800-3000 °C, grinding and finishing of graphite. We calculated emissions associated with the production of petroleum coke and coal ash on the basis of works [19, 20, 21]. They provide data on GHG emissions during coal coking considering its extraction and transportation [19], as well as during oil extraction and processing [20, 21]. The value of global warming potential for ash was 5.06 $kgCO_2/kg$ of ash, and for green petroleum coke 0.55 $kgCO_2/kg$.

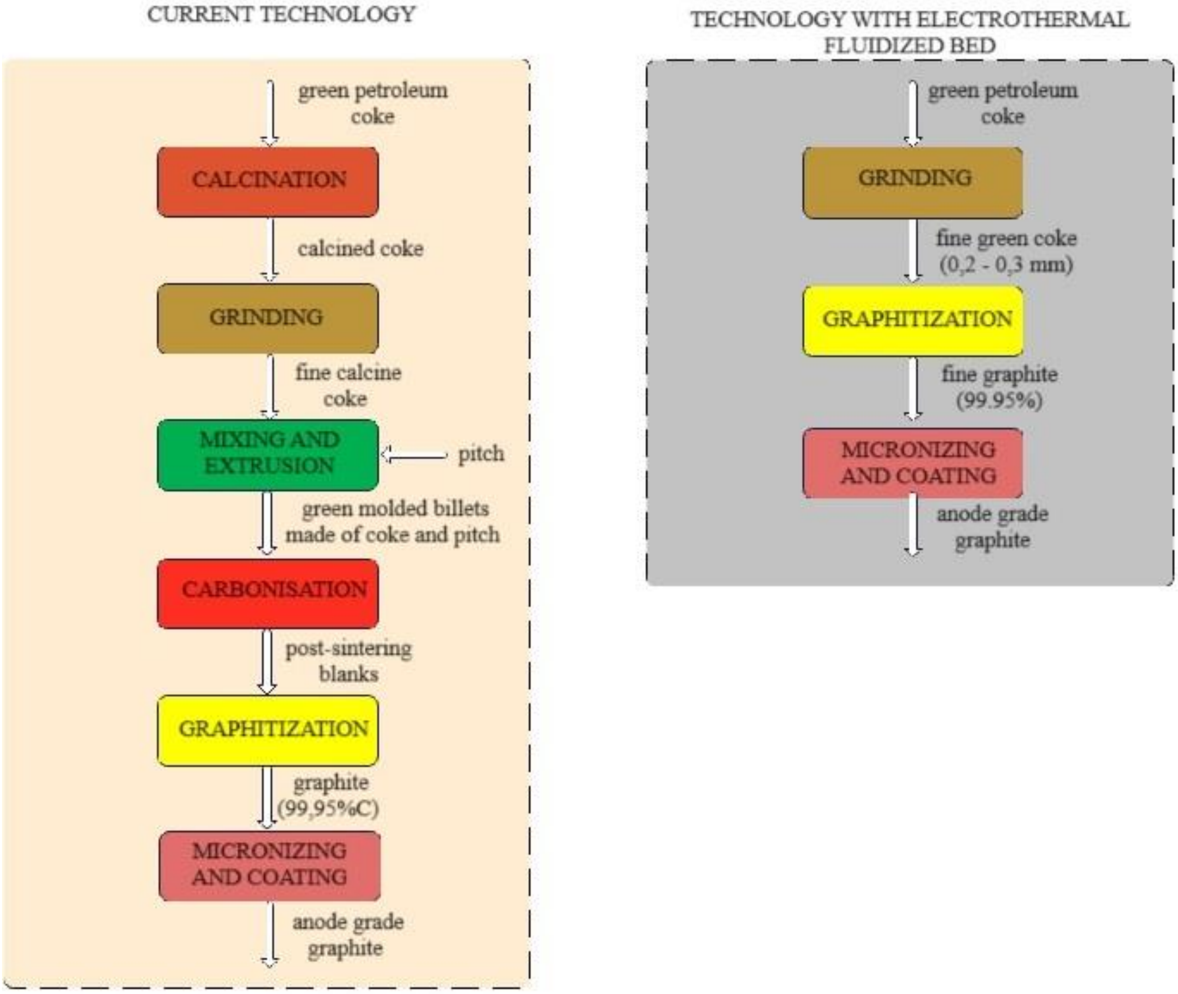

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Figure 3. Technological schemes for production of anodic quality synthetic graphite.

The use of EFB technology changes the technological schemes for purification of natural graphite (figure 2b) and synthetic graphite (figure 3b).

Thermal purification of natural graphite in the EFB can be carried out for the particle size more than 200 microns. Thus, the purification stage takes place before micronization and spheronization, since the particle size distribution of spheroidized graphite is almost an order of magnitude smaller than the required particle size for EFB. In this regard, the entire volume of natural graphite is subjected to thermal purification, and the sequence of technological operations takes the following order: ore extraction, its enrichment via flotation, thermal purification, spheronization, coating.

Unlike natural graphite, the technology of graphitization and purification of synthetic graphite changes radically due to thermal treatment of petroleum coke in a fluidized bed with particle sizes over 200 microns without addition of pitch. Thus, energy-consuming operations of green coke calcination, formation of green billets and their calcination in multi-chamber furnaces are excluded. And the whole process boils down to grinding of green coke, its graphitization in furnaces with EFB and finishing treatment of cleaned graphite (micronization and coating).

The GHG emissions were calculated on the basis of energy consumption at each technological stage, available in literature [12,11,7,8,19,22,23]. Calculations were carried out for the conditions of electricity generation in Ukraine [22]. Specific GHG emissions from electricity generation are assumed to be 0.339 $kgCO_2/kWh$ and natural gas combustion 56.1 $kgCO_2/GJ$.

3. Results and discussion

Calculations of GHG emissions at the stages of spheronization and purification by conventional technology and EFB technology are based on the data given in [12, 22], presented in table 1. Emissions at the stages of ore mining, flotation and coating remained unchanged except for the reduction of emissions for electricity use in conditions of Ukraine compared to China. Altering the sequence of technological operations of spheronization and purification changed not only the direct energy costs, but also the amount of processed material at each technological stage (figure 4). The amount of spheroidized material increased significantly when switching to thermal purification, while the extraction of initial graphite ore and its flotation slightly decreased.

Table 1. Inventory of energy and material use at the stages of spheronization and purification of natural graphite.

Technology	Conventional technology [12]		EFB technology [12, 22]	
Technological stage	Spheronization, per tonne of graphite concentrate after flotation	Chemical treatment, per tonne of purified spheronized graphite	Thermal purification, per ton of purified graphite	Spheronization, per tonne of purified spheronized graphite
Energy consumption				
Electricity, kwh/t	2100	305	2300	2100
Diesel fuel, kg/t	0.415	0.249		0.415
Natural gas, MJ/t		1050		
Materials used				
Graphite concentrate (95%C), kg/t	2220		1100	
Graphite concentrate (99.95%C), kg/t				2220
Spheronized graphite, kg/t		1130		
Hydrofluoric acid, kg/t		180		
Hydrochloric acid, kg/t		200		
Nitric acid kg/t		100		
Water, m^3/t		25		
Lime kg/t		400		
Waste				
Graphite fines, kg/t	1215			1215
Water vapor, kg/t		320.1		
CO2 emissions, kg/t		57.75		
Wastewater, m^3/t		24.8		
Industrial waste kg/t	0.25	917	100	

The results of calculations showed that the global warming potential of the traditional technology in relation to the conditions of Ukraine is 5494 kgCO_2/t of anode-grade graphite, the similar indicator for the technology using EFB thermal treatment being 5934 kgCO_2/t of graphite. The structure of emissions for both technologies is presented in figure 5.

The obtained results confirm the conclusion [12] that the main influence on the structure and absolute value of greenhouse gases emissions is produces by the emission associated with the use of electricity.

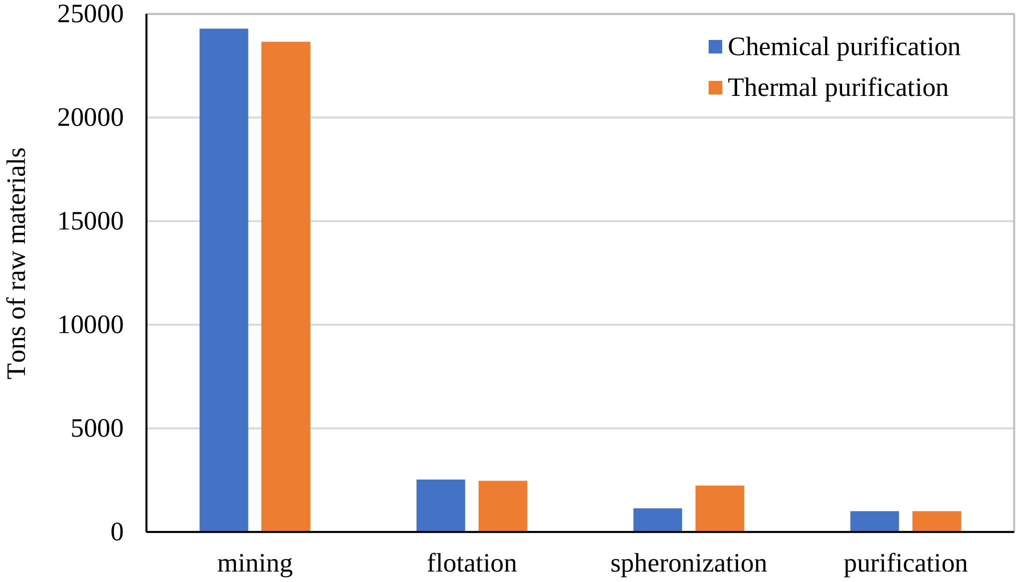

Figure 4. Raw material quantities at each process stage for production of 1 ton of anode graphite from natural graphite.

The use of EFB for thermal treatment of natural graphite instead of chemical treatment showed that GHG emissions practically remain at the same level. However, the use of acids and lime is completely eliminated. As a result, water treatment and the amount of industrial waste, requiring treatment and disposal, are significantly (about 10 times) reduced.

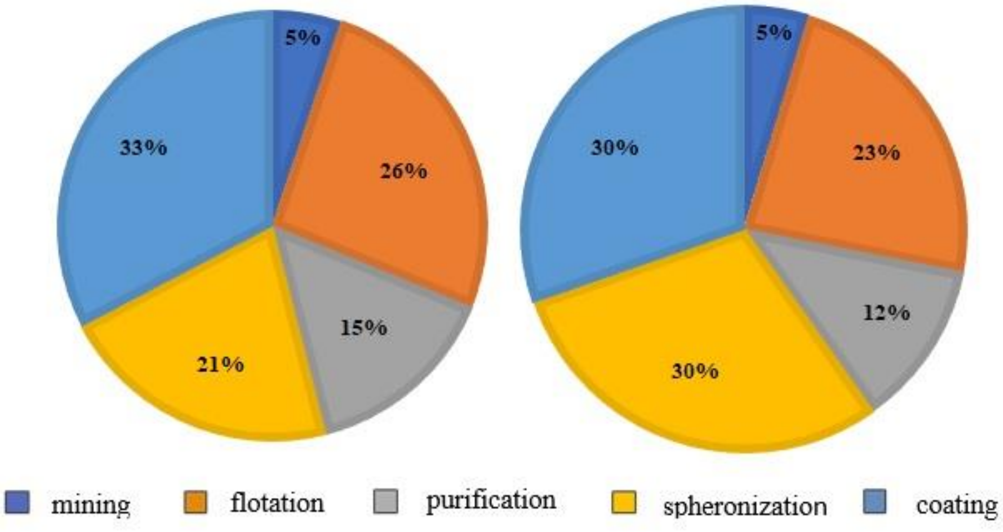

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Figure 5. Structure of greenhouse gases emissions by technological stages: a - traditional technology with chemical purification; b- technology with thermal treatment using EFB.

For the estimation of GHG emissions resulting from synthetic graphite production, four technological options were analyzed, as presented in table 2. The technologies differ in calcination units (rotary furnaces, electric calcinators) and graphitization units (Acheson furnace, Kastner furnace, EFB furnace). Inventory sources for these technologies are shown in table 2.

Table 2. Inventory of energy carriers in the production of synthetic graphite.

No.	Technology	Specific consumption of natural gas, GJ/t	Specific consumption of electricity, kWh/t	Percentage of finished product yield, %, [25]
1	**Calcination in a rotary furnace** [22, 26]	6.07	-	78
	Grinding [24]	-	25	97
	Mixing and extruding	-	-	99
	Carbonization [27]	4.5	-	92
	Graphitization in Acheson furnace [22, 26]	-	6425	95
	Coating [12]	-	4550	99
2	**Calcination in a rotary furnace** [22,26]	6.07	-	78
	Grinding [24]	-	25	97
	Mixing and extruding	-	-	99
	Carbonization [27]	4.5	-	92
	Graphitization in Kastner furnace [22, 26]	-	3575	95
	Coating [12]	-	4550	99
3	**Calcination in an electrocalciner** [22, 26]	-	1392	90
	Grinding [24]	-	25	97
	Mixing and extruding	-	-	99
	Carbonization [27]	4.5		92
	Graphitization in Kastner furnace [22, 26]		3575	95
	Coating [12]		4550	
4	**Grinding** [24]		52	97
	Graphitization in an electrothermal fluidized bed furnace [22, 23]		2300	90
	Coating [12]		4550	99

In the calculations, energy costs and GHG emissions at the finishing stage of synthetic graphite processing (coating) were assumed to be similar to those associated with coating of spheronization natural graphite [12]. Energy costs at the milling stage were taken according to the literature data for coal milling systems [24]. Energy costs during mixing of oil slash and pitch, as well as pressing of green billets were not taken into account due to the lack of data.

The results of the GWP calculations for the four technologies are presented in figure 6.

Significant emission reduction occurs due to the reduction of energy consumption when using EFB technology compared to the existing graphitization processes in Acheson and Kastner furnaces (figure 7), as well as due to the elimination of calcination and roasting stages. In addition, the reduction of emissions is determined by the reduction of indirect emissions associated with the consumption of raw materials - petroleum coke and pitch (figure 8).

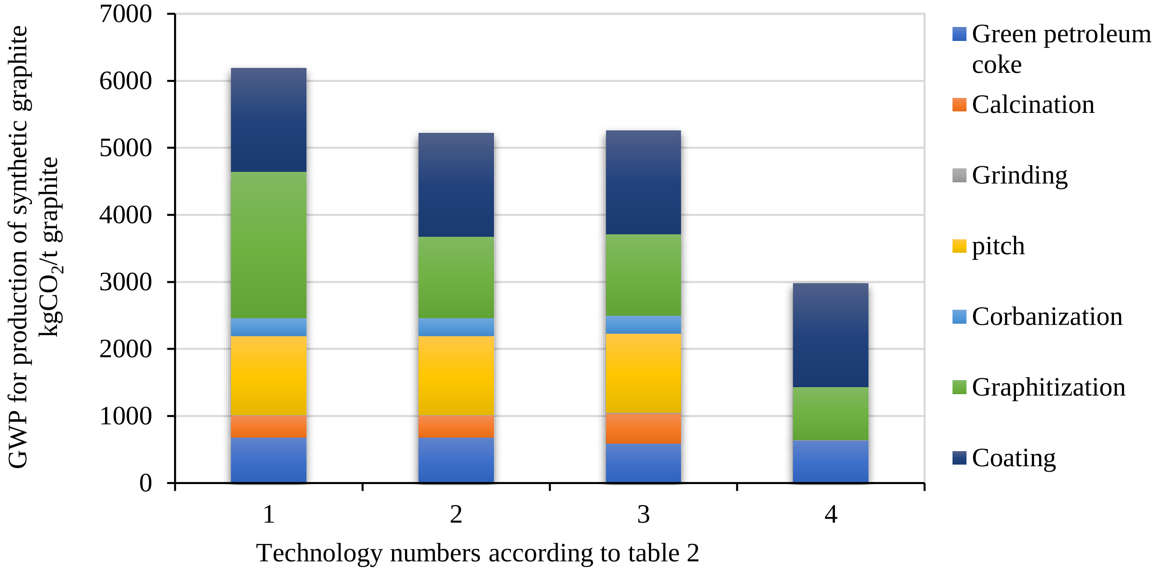

Figure 6. Greenhouse gas emissions from synthetic graphite production.

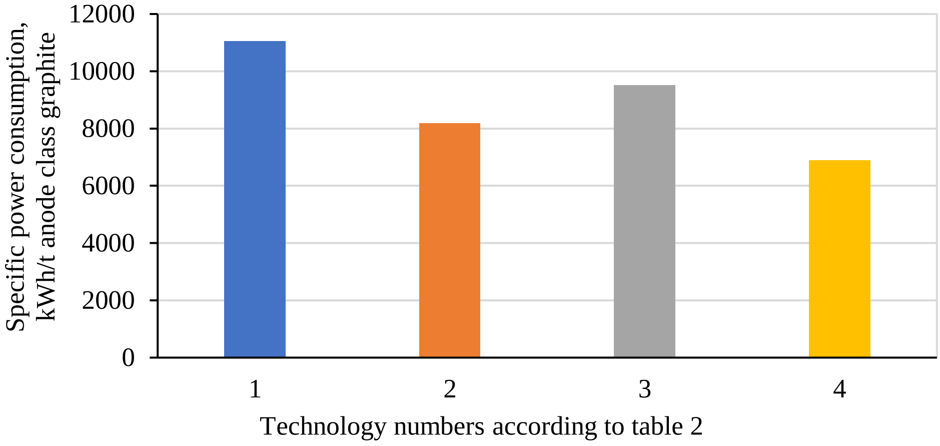

Figure 7. Specific energy consumption in the production of synthetic graphite.

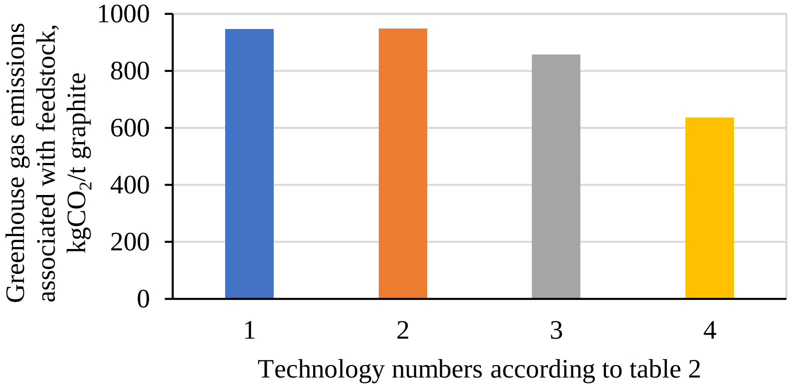

Figure 8. Specific greenhouse gases emissions associated with the use of petroleum coke and pitch.

4. Conclusions

On the basis of calculation of GHG emissions in the production of anode class graphite for the conditions of Ukraine, it is shown that the technology of using EFB for the purification of natural graphite and graphitization of synthetic graphite is competitive in terms of global warming potential.

In the production of natural graphite using thermal treatment with EFB instead of chemical treatment, GHG emissions practically remain at the same level. The difference is no more than 8%, which is commensurate with the accuracy of calculations. At the same time, the use of acids and lime is completely eliminated. As a result, the need for wastewater treatment is significantly reduced and the amount of industrial waste requiring treatment and disposal is reduced by 10 times.

Production of synthetic graphite of anodic quality in EFB furnaces allows to reduce greenhouse gases emissions by 40-50% compared to traditional graphitization technologies in Achenson and Kastner furnaces. The effect is achieved by reducing energy and raw material consumption.

Comparison of emission values for natural and synthetic graphite is not quite correct, as the level of emission inventory for natural graphite is much more detailed than that for synthetic graphite. Nevertheless, it can be said that the orders of magnitude of GWP for anode-quality graphite based on natural and on synthetic graphite coincide.

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