

MAREK BOGACKI*, ROBERT OLENIACZ*,
MARIAN MAZUR*, PRZEMYSŁAW SZCZYGLÓWSKI*

AIR POLLUTANT EMISSIONS DURING BAKING OF SEMI-FINISHED GRAPHITE PRODUCTS IN A TUNNEL FURNACE

Baking of semi-finished graphite products in a tunnel furnace is the source of many air pollutants present in both the gaseous and solid phases. The goal of this study was to assess emission rates into the air of the substances such as: CO, NO_x, SO₂, H₂S, CH₄, aliphatic hydrocarbons C₁–C₆, BTEX, total dust, tar substances and PAHs. The research showed a small time-dependence of the emission rates for the majority of the substances analysed. Concentrations of the analysed substances in exhaust gases were in the majority of cases at a low level, except for BTEX and PAHs.

1. INTRODUCTION

The manufacturing technology of small graphite products consists in preparing a carbon mixture based mainly on ground calcinated anthracite mixed with a tar binder, then forming to obtain the desired shape of the product, baking the shapes manufactured in a tunnel furnace and finally, graphitising the semi-finished products in a graphitising furnace. The emission of a series of non-organic and organic substances into the air occurs at each production stage [1–6]. The goal of the research, carried out in one of the national plants manufacturing graphite accessories, was to estimate the emission rates into the air of the substances arising from the baking process of the formed graphite shapes in a tunnel furnace.

2. MATERIALS AND METHODS

The test object was a 35-chamber tunnel furnace with a monthly processing capacity of ca. 106 Mg of carbon material. Baking of carbon shapes (semi-finished prod-

*AGH University of Science and Technology, Faculty of Mining Surveying and Environmental Engineering, Department of Management and Protection of Environment, ul. 30 Mickiewicza, 30-059 Cracow, Poland. Corresponding author M. Bogacki, e-mail: bogacki@agh.edu.pl

ucts) takes place in this furnace type in a reducing atmosphere at a temperature of up to ca. 1400 K [7]. The furnace under test is fired with natural gas. The average gas consumption is 60 m³/h. There are 35 ceramic carts (one cart per chamber) inside the furnace. In each cart, there is a pressed shape made of carbon material covered with a coke backfill which reduces the heat and prevents the deformation of the shapes during the softening of their binder. The furnace is controlled based on the heating curve. Depending on the charge type and the heating curve applied, 6–8 carts are usually introduced into and removed from the furnace, thus the baking time amounts to 105–140 h for one charge.

There are three working zones in the furnace: I – pre-heating zone (chamber Nos. 1–19), II – baking zone (chamber Nos. 20–28), III – cooling zone (chamber Nos. 29–35). Zone I is heated by means of six burners mounted in chamber Nos. 8 (2 pieces), 12 (2 pieces) and 15 (2 pieces). The burners are supplied with air by a fan installed at the height of chamber No. 13. Two fans are installed, one is spare. Zone II (burn-out) is heated with the burners mounted in chamber Nos. 20–28. The burners are supplied with air by a fan installed at the height of chamber Nos. 30–31. Zone III (cooling) consists of chamber Nos. 29–35, in this zone the charge cooling with the force-fed ambient air and circulating air takes place. An exhaust (stack) fan, having a stand-by in chamber No. 3, works in chamber No. 2. The selection of the fan comes within the service personnel's duties. A door fan works on the door of chamber No. 1. A cart undercarriage cooling fan works in chamber No. 31. Gases released from the tunnel furnace have the temperature within the range of 520–570 K and one part of them is returned to the furnace and another part is released to air.

The following substances were subjected to the analysis: carbon oxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), sulfur hydrogen (H₂S), methane (CH₄), aliphatic hydrocarbons up to C₆, benzene and its homologues (BTEX), total dust and tar substances, and polycyclic aromatic hydrocarbons (PAHs) contained in the dust. The thermodynamic parameters of exhaust gases, necessary for determining their flux, were also measured.

Two series of measurements lasting almost four hours each and covering a period between two consecutive entries of new carts to the tunnel furnace were taken. For both the measurement series, carbon charge carried by each of 35 carts was identical as to type (90 wt. % – HCC material, 10 wt. % – Ruba 9001 material) and its total weight was (24.35 Mg). Assuming a mean baking time of 120 h for one cart, the mean mass flux passing through the furnace was 0.2029 Mg/h. Approx. 260 m³ of natural gas were used up for fuelling the furnace during these measurement series. There was a measurement point on the emitter.

Basic parameters of the exhaust gases such as pressure, temperature, degree of moisture and density were determined within the measurement framework. The measurements of the exhaust gases, necessary for determining their volume flux, were made by means of an EMIOTEST 2592 measuring set using available exhaust gas composition data obtained by means of a LANCOM Series II (Land Combustion) flue

gas analyser. The volume gas flux was calculated as a function of the measurement cross-section area and measured mean gas velocity through the cross-section [8].

Measurements of the volume concentrations of basic gaseous pollutants such as CO, NO, NO₂, SO₂ and H₂S were made continuously using an automatic LANCOM Series II flue gas analyser which was saved to memory every 20 s.

Gas samples for the determination of aliphatic hydrocarbons were collected with gas pipettes of the capacity of 0.5 dm³. Three (series I) and four (series II) samples were accordingly taken at equal time intervals in individual series of measurements. The content of aliphatic hydrocarbons C₁–C₆ was determined using a HP5890 gas chromatograph with a flame ionisation detector (FID).

Samples for the determination of benzene and its homologues (BTEX) were collected by suction sampling with an ASP-2 (ZUP ZAM Kęty Sp. z o.o.) aspirator. Adsorption tubes with active carbon with a packing of 50 mg/100 mg were used as a collector. Four gas samples with the aspiration time ranging from 20 to 35 min were taken for each series of measurements. The contents of benzene and its homologues with a saturated side chain (toluene, ethylbenzene, xylene) were by the gas chromatography method with sample enrichment [9]. The extraction was conducted with carbon disulphide.

Dust concentration and mass flux in the exhaust gases were measured using the gravimetric method [8] with the EMIOTEST 2592 (PIW EMIO Sp. z o.o., Wrocław) automatic gravimetric dust meter. Altogether, 7 unit measurements (3 and 4 – in the first and second series, respectively) lasting from 60 to 90 min were taken.

Tar content was determined in the solid phase collected at the filter of the gravimetric dust meter according to the AEERL/12-9/2/86 procedure [10]. The determination of individual PAHs in the extracts of chloromethane samples taken by means of the dust meter was carried out by the gas chromatography method. The HP5890 gas chromatograph with the flame ionisation detector (FID) was used.

3. RESULTS AND DISCUSSION

Mean values of the measured and calculated basic parameters of the exhaust gases for both series of measurements are presented in Table 1. The mean, minimum and maximum concentrations of individual species in gases released into the air from the furnace under test and the mean values of emissions into the air, and emission factors related to the mass flux of carbon charge are collected in Tables 2–5. Mean concentrations for individual series are defined as arithmetic mean values weighted by the collection time of subsequent samples.

Though concentrations of individual components of exhaust gases (and, consequently, their emissions to air) varied, the differences were usually rather limited. The minimum variation was for CO and NO_x, whose content in the exhaust gases during both

series of measurements varied within the range of $330 \pm 100 \text{ mg/m}^3$ and $30 \pm 15 \text{ mg/m}^3$ (at $T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$, dry gas), respectively.

Table 1

Mean measurement results of basic substances released into the air from the tunnel furnace

Parameter	Series 1	Series 2	Mean
Absolute pressure in the stack, hPa	976	988	982
Flue gas temperature, K	454	456	455
Flue gas humidity ratio, kg/kg	0.032	0.033	0.0325
Dry gas density ^a , kg/m^3	1.290	1.295	1.292
Wet gas density ^a , kg/m^3	1.266	1.270	1.268
Wet gas density in measurement conditions, kg/m^3	0.734	0.742	0.738
Flue gas velocity, m/s	2.42	1.95	2.18
Wet gas flow rate ^a , m^3/h	1921	1535	1728
Dry gas flow rate ^a , m^3/h	1835	1463	1649

^a $T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$.

Table 2

Emission rates of CO, NO₂, SO₂ and H₂S

Species	Concentration [mg/m^3] ^a				Average	Mean emission rate	
	Series 1		Series 2			[g/h]	[kg/t feedstock] ^c
	Mean	Range	Mean	Range			
CO	341	233–451	312	229–551	327	541	2.67
NO _x ^b	26.5	19.5–34.6	35.8	21.6–54.0	31.2	50.5	0.249
SO ₂	24.2	0–39.1	18.1	0–36.1	21.1	35.4	0.175
H ₂ S	1.3	0–3.2	0.1	0–1.6	0.7	1.2	0.0059

^aIn dry gas and conditions: $T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$.

^bNO and NO₂ as NO₂.

^cEmission factors related to the mass flux of carbon charge assuming a mean baking time of 120 h.

Table 3

Emission rates of aliphatic hydrocarbons

Species	Concentration [mg/m^3] ^a				Average value	Mean emission rate	
	Series 1		Series 2			[g/h]	[kg/t feedstock] ^b
	Mean	Range	Mean	Range			
CH ₄	8.23	5.52–13.2	11.74	10.9–12.5	10.0	16.1	0.0795
C ₂ H ₄	1.70	1.07–2.73	0.88	0.60–1.13	1.29	2.20	0.0108
C ₂ H ₆	1.61	1.50–1.68	1.61	1.57–1.63	1.61	2.66	0.0131
C ₃ H ₈ + C ₃ H ₆	0.95	0.86–1.10	0	not detected	0.47	0.87	0.0043
Total	12.49	9.14–18.7	14.23	13.1–15.1	13.4	21.9	0.1078

^aIn dry gas, $T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$.

^bEmission factors related to the mass flux of carbon charge assuming the mean baking time of 120 h.

Table 4

Emission rates of benzene and its homologues

Species	Concentration [mg/m ³] ^a					Mean emission rate	
	Series 1		Series 2		Average value	[g/h]	[kg/t feedstock] ^b
	Mean	Range	Mean	Range			
Benzene	7.18	4.31–10.1	3.15	2.84–3.39	5.17	8.90	0.0439
Toluene + Ethylbenzene	0.75	0.50–1.19	0.27	0.22–0.32	0.51	0.89	0.0044
Xylenes	1.77	0.86–3.16	0.39	0.21–0.66	1.08	1.91	0.0094
Total BTEX	9.71	5.67–14.46	3.81	3.30–4.25	6.76	11.69	0.0576

^aIn dry gas, $T = 273$ K, $p = 101.3$ kPa.

^bEmission factors related to the mass flux of carbon charge assuming a mean baking time of 120 h.

Table 5

Emission rates of dust, tar substances and PAHs

Species	Concentration [mg/m ³] ^a					Mean emission rate	
	Series 1		Series 2		Average value	[g/h]	[kg/t feedstock] ^b
	Mean	Range	Mean	Range			
Total dust	48.2	28.4–64.0	56.6	39.5–80.4	52.42	85.7	422.2
Tar substances	19.5	7.2–25.8	23.2	18.2–32.8	21.38	34.9	172.1
Naphthalene	0.001	0–0.006	0	not detected	0.0005	0.009	0.005
Acenaphthylene	–	not detected	–	not detected	–	–	–
Acenaphthene	–	not detected	–	not detected	–	–	–
Fluorene	–	not detected	–	not detected	–	–	–
Phenanthrene	0.282	0.048–0.481	0.533	0.227–0.857	0.407	0.649	3.20
Anthracene	0.138	0.065–0.198	0.083	0.052–0.142	0.111	0.188	0.92
Fluoranthene	1.528	0.279–2.57	2.752	1.06–4.25	2.140	3.415	16.8
Pyrene	0.800	0.144–1.33	1.342	0.570–2.13	1.071	1.716	8.45
Benzo(a)anthracene	0.645	0.205–1.02	0.731	0.540–1.05	0.688	1.127	5.56
Chrysene	1.724	0.503–2.81	1.800	1.49–2.12	1.762	2.898	14.3
Benzo(b)fluoranthene	1.197	0.607–1.79	1.093	0.820–1.49	1.145	1.898	9.36
Benzo(k)fluoranthene	0.432	0.234–0.627	0.415	0.343–0.605	0.424	0.701	3.45
Benzo(a)pyrene	0.306	0.155–0.454	0.286	0.247–0.421	0.296	0.490	2.41
Indeno(1,2,3- <i>cd</i>)pyrene	0.209	0.125–0.290	0.176	0.131–0.266	0.192	0.320	1.58
Dibenzo(<i>a,h</i>)anthracene	0.144	0.081–0.202	0.133	0.089–0.182	0.139	0.230	1.13
Benzo(<i>g,h,i</i>)perylene	0.149	0.088–0.207	0.123	0.064–0.186	0.136	0.227	1.12
Total PAHs	7.56	2.55–12.0	9.47	6.16–13.5	8.51	13.9	68.3

^aIn dry gas, $T = 273$ K, $p = 101.3$ kPa.

^bEmission factors related to the mass flux of carbon charge assuming a mean baking time of 120 h.

A slightly different behaviour was observed for concentrations of SO₂. After introducing a new cart into the tunnel furnace, these concentrations increased slightly, reaching a level of about 20–30 (maximally 40) mg/m³ after about 2–3 h from charg-

ing the furnace. Concentrations of H_2S remained all the time very small or their value was below the lower determinability limit of the measurement method used and the possible periodic maxima (in the magnitude of 3 mg/m^3) appeared during the first hour after introducing a new cart, only.

A variation analysis of the concentrations of other substances measured did not show the existence of any distinct trend. The concentrations changed in an unpredictable way, oscillating around the calculated mean value. Examples of the variation of the concentrations of aliphatic hydrocarbons, BTEX and total dust, and tar substances in exhaust gases during individual series of measurements are presented in Figs. 1–3.

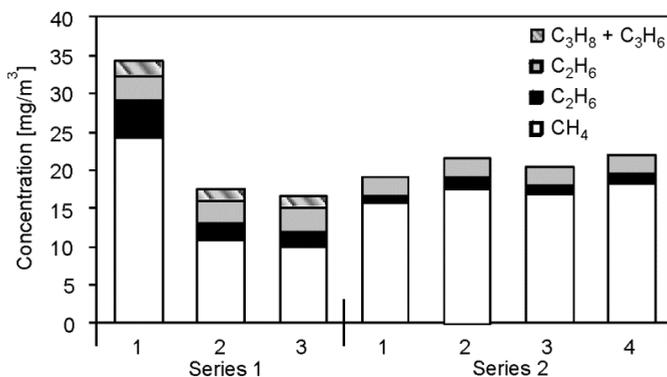


Fig. 1. Concentrations of aliphatic hydrocarbons up to C_6 in exhaust gases from the tunnel furnace for both series of measurements ($T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$, dry gas)

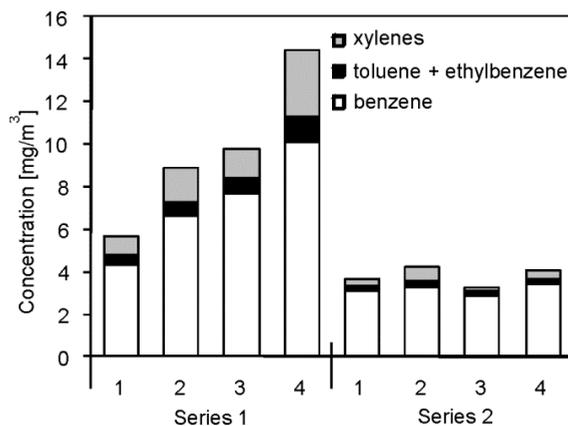


Fig. 2. Concentrations of BTEX in exhaust gases from the tunnel furnace for both series of measurements ($T = 273 \text{ K}$, $p = 101.3 \text{ kPa}$, dry gas)

Dusts emitted into the air contained 25–46 wt. % (39 wt. % on average) of tar substances, while the PAHs content in tar amounted to 18–55 (38 wt. % on average).

Fluoroanthene and chrysene had the highest share among all substances determined, numbered among PAHs.

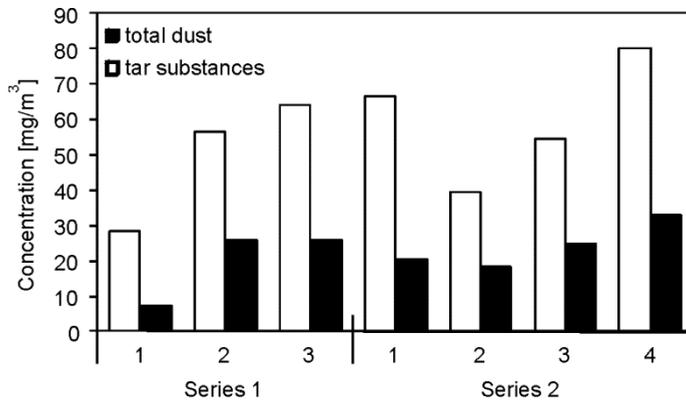


Fig. 3. Concentrations of total dust and tar substances in exhaust gases from the tunnel furnace for both series of measurements ($T = 273$ K, $p = 101.3$ kPa, dry gas)

The variation of concentrations obtained for the analysed substances or groups of substances in the gases emitted from the baking process of semi-finished graphite products in the tunnel furnace is within the range specified for this process type in the BAT reference document [6]. This range depends, among others, on the method of exhaust gas cleaning applied. For various cleaning systems, it fluctuates within a very wide range and equals (at $T = 273$ K, $p = 101.3$ kPa): 1–90 mg/m³ for total dust, 2–150 mg/m³ for SO₂, 10–40 mg/m³ (and in the case of thermal reheat: 50–250 mg/m³) for NO_x, 1–250 mg/m³ for total amount of hydrocarbons, 0.1–11 mg/m³ for benzene and 0.002–19.45 mg/m³ for total amount of 16 PAHs [6]. As there was no exhaust gas cleaning system (only their partial re-circulation for the furnace under test), it is no wonder that the concentrations of certain substances were maintained at the level close to the upper range limit specified in document [6].

With regard to the emissions of BTEX and PAHs from large annular furnaces (fired with natural gas) used for baking carbon products, the exhaust gases from them being cleaned in a two-stage electrofilter with a pipe cooler and coke filters [1, 5], one may find that the concentrations of these substances obtained for the gases released from the tunnel furnace are similar (especially for BTEX) or one order of magnitude higher (especially for PAHs) than for the plants fitted with a high-duty exhaust gas cleaning system. These emissions can be considered relatively high.

4. CONCLUSIONS

Air pollutant emissions from the baking process of semi-finished carbon products may be differentiated, among others, according to the used furnace type (and

baking technology), exhaust gas cleaning system, and type of the baked material and binder.

A relatively small variation of concentrations is observed for polluting substances in the exhaust gases from the process in the case of the tunnel furnace and use of the carbon charge moderately stabilised in respect to quantity and type as well as overlapping emissions arising from various phases of the baking process of separate portions of the charge material (regularly introduced to and removed from the furnace).

The introduction of successive carts with the charge to be baked into the furnace does not usually cause any substantial change in the amounts of the emitted substances, except for SO₂ and H₂S in the case of which the emission rate is to a great extent determined by the processes occurring at the beginning of the manufacturing (during the pre-heating phase).

Of the substances analysed, the emissions of PAHs as well as of benzene and its homologues (BTEX) seem to be of special importance. The emission factors derived (being source emission factors at the same time owing to the lack of exhaust gas cleaning system) can be used for estimating the mean source emission and the release of substances into the air from the baking process of small semi-finished graphite products in the tunnel furnace. One should however be aware of the fact that the rate of this type of the process is determined by the large number of parameters, the most important of which are: the composition and mass of carbon mixture, form of the baked shapes, furnace heating curve (adjusted to the above mentioned parameters) as well as the operating efficiency of a possible exhaust gas cleaning system.

ACKNOWLEDGEMENTS

The work was completed within the scope of AGH University statutory research No. 11.11.150.008 and the contract No. 5.5.150.633.

REFERENCES

- [1] MAZUR M., SZCZYGLOWSKI P., OLENIACZ R., BOGACKI M., *BTX emission from production of graphite and coal wares*, [In:] J. Koniecznyński, R. Zarzycki (Eds.), *Air Protection in Theory and Applications*, Wyd. IPIS PAN, Zabrze, 2004, 249–256 (in Polish).
- [2] MAZUR M., OLENIACZ R., BOGACKI M., SZCZYGLOWSKI P., *Environ. Eng.*, 2006, 11 (2), 145.
- [3] MAZUR M., BOGACKI M., OLENIACZ R., SZCZYGLOWSKI P., *Environ. Prot. Eng.*, 2008, 34 (4), 119.
- [4] BOGACKI M., OLENIACZ R., MAZUR M., *Evaluation of gas emissions from graphitizing of carbon products*, [In:] L. Pawłowski, M.R. Dudzińska, A. Pawłowski (Eds.), *Environmental Engineering III*, CRC Press/Balkema, Taylor & Francis Group, London, 2010, 9–14.
- [5] MAZUR M., OLENIACZ R., BOGACKI M., SZCZYGLOWSKI P., *Emission of polycyclic aromatic hydrocarbons (PAHs) during the production of carbon and graphite electrodes*, [In:] L. Pawłowski, M.R. Dudzińska, A. Pawłowski (Eds.), *Environmental Engineering III*, CRC Press/Balkema, Taylor & Francis Group, London, 2010, 59–66.
- [6] European Commission, IPCC Draft Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries, Draft July 2009 (<<http://eippcb.jrc.es/reference>>).
- [7] PIECH J., *Ceramic and Glass Furnaces*, AGH University Press, Cracow, 2001 (in Polish).

-
- [8] PN-Z-0404030-7,1994, *Air purity protection – Tests for dust content – Measurements of concentration and mass flow rate of particulate matter in waste gases by gravimetric method* (in Polish).
- [9] PN-Z-04016-7,1999, *Air purity protection – Tests for benzene and its homologous compounds with saturated side chain – Determination of benzene, toluene, ethylbenzene, (m+p)-ksylene, and o-ksylene in flue gases (emission) by gas chromatography* (in Polish).
- [10] AEERL/12-9/2/86 Procedure, *Standard procedure for gravimetric analysis of organic extracts* (based on, EPA-600/S7-82-048, NTIS PB82-239, p. 30–36, March 1982 and EPA 6000/7-78/201, NTIS PB293-795, p. 140–142, October 1978).