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## AIR POLLUTANT EMISSIONS FROM PROCESS OF MIXING MATERIALS USED FOR MANUFACTURING SMALL PRODUCTS FROM CARBON AND GRAPHITE

The paper characterises the method of preparing the HCC and Rubba-type materials used to manufacture small products from carbon and graphite and the composition of waste gases escaping from the mixers for these materials. For the process of mixing the two materials under examination, two measurement series were completed, mainly covering the period between a binder adding to a properly preheated dry mass and a mixer discharging. The results shown apply only to those substances which occur just in the gaseous phase, that is CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, aliphatic hydrocarbons (C<sub>1</sub>–C<sub>6</sub>) and BTX (benzene, toluene, ethylbenzene and xylene) as well as solid substances, including total dust, tar substances, polycyclic aromatic hydrocarbons (PAH), and total organic carbon in solid phase.

### 1. INTRODUCTION

In recent years, market demand for refined carbon and graphite products has been continuously increasing. These products are used in the chemical industry, glassworks, ferrous and non-ferrous metals metallurgy, and the engineering industry.

SGL ANGRAPH from Nowy Sącz is the exclusive manufacturer of small products from graphite in Poland. The company specializes in the production of small-sized elements for industrial and commercial applications (electrodes, self-lubricating bearings, rings for high-pressure and deep-well pumps, metallurgical crucibles, brushes for power equipment, antennas for mobile phones, etc.) made of carbon and graphite-based materials.

The technology and type of the materials used to manufacture graphite products are subject to requirements which must be satisfied by final product. However, the manufacturing process usually consists of the following stages: charge preparation, compo-

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ment (material) mixing, moulding, sintering, proofing, graphitisation and final working (machining) of the product. Each stage of the manufacturing process involves air pollutant emissions, whose qualitative and quantitative characteristics are determined by the specificity of the technology and the type of the materials and binders used [1], [2].

The paper presents the results of measuring the content of selected gaseous and dust substances in waste gases escaping from the mixers while mixing HCC and Rubba carbon materials during the period between adding the liquid ingredients to the dry mass and the mixer discharging. The measurements were performed at SGL ANGRAPH in Nowy Sącz [3].

## 2. CHARACTERISTICS OF THE PROCESS UNDER EXAMINATION

The tests were performed in mixers, in which two material types, i.e., HCC and Rubba, were mixed for the manufacturing of small-sized carbon and graphite products [3]. The mixing process starts with pouring solid raw materials into the mixer. Then, natural gas-fired heating radiators are switched on to heat the solid ingredients up to a temperature of ca. 150 °C in the case of the HCC and 110 °C in the case of the Rubba material. The time required to heat up the solid raw materials to the specified temperature mainly depends on the initial mixer temperature while pouring the solid raw materials in, the ambient temperature, and the opening width of the choke valve in the duct carrying waste gases away from the mixer. On average, it is ca. 3 hours. As soon as the specified temperature of 150 °C (HCC)/110 °C (Rubba) is reached, the binder is added to the dry mass. This usually takes a few minutes. Once the binder has been added, the mixture is stirred and heated further, this time only by the radiators installed in its bottom. The mixture is heated until it has reached a temperature of ca.  $215 \pm 5$  °C (HCC)/ $127 \pm 5$  °C (Rubba). The process usually lasts approximately 4–5 hours (HCC)/1–3 hours (Rubba). Then, all the radiators heating up the mixer are turned off. The mixture reaches its final temperature, which should be ca.  $230 \pm 5$  °C (HCC)/ $135 \pm 5$  °C (Rubba), due to the heat radiating from the hot mixer itself. Samples of the mixture are taken as soon as the temperature necessary for the technological process is reached. In the case of a positive evaluation of the quality of the mixture, the mixer is emptied and its drive switched off. After cleaning, the mixer is ready for stirring solid raw materials again. Thus, the full mixing cycle is complete.

## 3. TEST METHODS

The research was carried out to determine the content of certain gaseous and solid substances in the waste gases escaping during the HCC and Rubba material mixing process. Among gaseous substances there were found: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), oxygen (O<sub>2</sub>), hydrogen (H<sub>2</sub>), aliphatic hydrocarbons (C<sub>1</sub> to C<sub>6</sub>), ben-

zene and its homologues (toluene, ethylbenzene, xylenes), and their sum (BTX). The solid substances can be itemized as follows: total dust, tar substances, polycyclic aromatic hydrocarbons (PAHs) and the total organic carbon (TOC) in solid phase.

Two measurement series were completed, which consisted of two mixing cycles for each type of material. The measurements were performed only from the moment of adding the binder to the dry mass to the moment of mixer discharging.

The gases were determined as follows: (1) on average 3 times per hour for 5 min. (applies to: CO, CO<sub>2</sub>, O<sub>2</sub>), (2) once per hour (applies to: H<sub>2</sub>, aliphatic hydrocarbons C<sub>1</sub>–C<sub>6</sub>), (3) once per hour for 30 min. (applies to: BTX collected on active carbon). Measuring points were located in the duct carrying waste gases away, at a distance of ca. 1 m from the top of the mixer. CO, CO<sub>2</sub> and O<sub>2</sub> concentrations in the waste gases were determined with the LANCOM Series II (Land Combustion) type automatic exhaust-gas analyser. CO and O<sub>2</sub> concentrations were determined by electrochemical method, whereas CO<sub>2</sub> concentration – using the infrared radiation absorption method. Gas samples for the determination of aliphatic hydrocarbon content were collected and put into teflon bags of the a capacity of 1.0 dm<sup>3</sup>. Determination was carried out using the HP5890 gas chromatograph with flame ionisation detector (FID). Gas samples for the determination of the BTX concentration were collected at a rate of 30 dm<sup>3</sup>/hour in glass pipes filled with active carbon (50 mg/100 mg). The content of benzene and its homologues with a saturated side chain was determined using the gas chromatography method with a sample enrichment, according to Polish Standard PN-89/Z-04016.03.

Dust concentration and mass stream in waste gases were measured using the gravimetric method, according to Polish Standard PN-Z-04030-7:1994, with automatic EMIOTEST 2592-type gravimetric dust meter. Dusty gas samples were taken using an aspiration probe with internal dust separation. 50-mm diameter filters (series 1) and thimbles (series 2) made of glass microfibre were used as filtering media. Additionally, during measurement series 2, waste gas samples were first condensed in an oil dephlegmator and then collected in adsorption tubes filled with resin (XAD-2) in order to determine the tar substances, PAH and TOC.

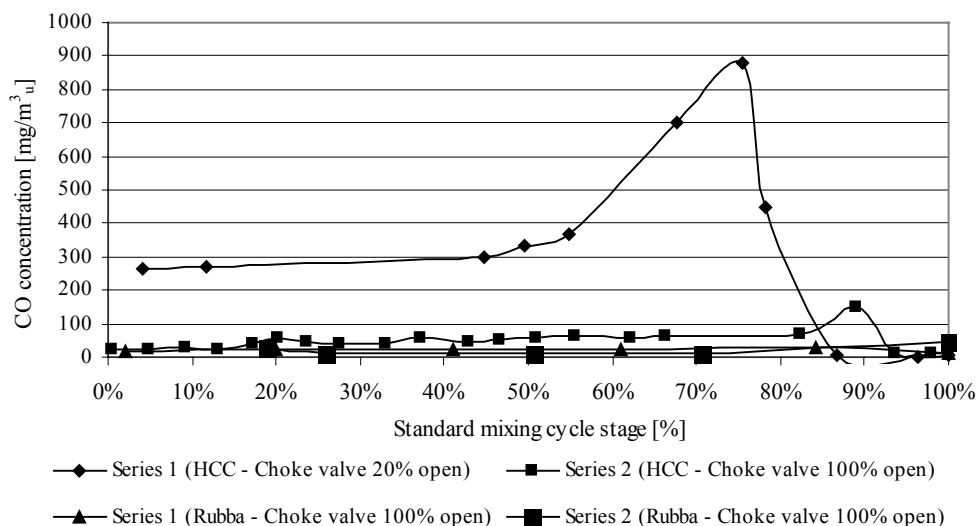
The tar content in the samples collected at the filters and the XAD resin concentration were determined using the gravimetric method according to procedure in [4]. Tar and resins were extracted with dichloromethane in Soxhlet apparatus for 8 hours. The extracts obtained were condensed to the volume of 10 cm<sup>3</sup> by means of solvent evaporation in the Kuderna–Danisch apparatus. The extracts were divided into two parts. One part was used to determine the content of polycyclic aromatic hydrocarbons (PAH) and the total organic carbon (TOC) in compounds at the boiling point ranging from ca. 100 to 300 °C, and the second part was used to determine the tar content (organic compounds, at the boiling point of 300 °C and above 300 °C).

Gas chromatography method was used to determine the PAH content in the samples of chloromethane extracts. The researchers used the HP6890 gas chromatograph with flame ionisation detector (FID) and 30-m long HP DB5 capillary column, work-

ing with a programmed temperature rise of 8 °C/min, from 40 °C to 280 °C. The samples were analysed for a total content of organic compounds, using the gas chromatography method according to the procedure described in [5]. The samples of extracts for TOC determination were analysed in a 1-m long column, with a programmed temperature rise of 15 °/min, from 40 °C to 280 °C, at an argon flow rate of 30 cm<sup>3</sup>/min. The samples were evaporated at a temperature of 260 °C; the FID detector working temperature was 300 °C.

#### 4. RESULTS

The results from the concentration measurements for the substances analysed are shown in figure 1 and tables 1–4. The test results were analysed with a special attention paid to the evaluation of variability range of the concentrations of individual substances in waste gases and to the dynamics of these changes in the function of the mixing process duration. At the same time, attention was also paid to the impact of the opening width of the choke valve in the gas collector on the concentration values registered. The measurement variant with the choke valve in the collector being open in 20% was applied only in one measurement series carried out while mixing the HCC material. During this series, the choke valve was closed in 80% for 75% of mixing time. Other measurements were performed with the choke valve fully open.



Variability of CO concentration in waste gases that escape during HCC and Rubba materials mixing process at various opening widths of choke valve in gas collector

Table 1

Variability ranges for CO, CO<sub>2</sub> and O<sub>2</sub> concentrations in waste gases escaping during HCC and Rubba materials mixing process

Meas. series	Value	Concentration of substances in waste gases*					
		CO		CO <sub>2</sub>		O <sub>2</sub>	
		[mg/m <sup>3</sup> ]	[% by vol.]	[% by vol.]	[mg/m <sup>3</sup> ]	[% by vol.]	[% by vol.]
HCC material			Rubba material				
1	Average	324.8	0.31	18.96	21.1	0.01	20.68
	Min.	2.4	0	16.74	13	0	20.49
	Max.	880.9	0.62	20.9	29.1	0.04	20.91
2	Average	46.5	0.08	20.81	21.6	0.01	20.68
	Min.	11.3	0	20.52	11.3	0	20.28
	Max.	148.6	0.21	20.92	44	0.04	20.89

\* In dry gas under reference conditions:  $T_n = 273$  K,  $p_n = 101.3$  kPa.

Table 2

Variability ranges for selected substances contained in waste gases escaping during HCC and Rubba materials mixing process

Meas. series	Value	Concentration of substances in waste gases [mg/m <sup>3</sup> ]*									
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> -C <sub>6</sub>	C <sub>1</sub> -C <sub>6</sub> (total)	Benzene	Toluene + ethylbenzene	Xylenes	BTX (total)
HCC material											
1	Average	3.54	1.38	0.84	2.11	14.4	22.27	0.204	0.030	0.113	0.347
	Min.	3.48	1.29	0	1.88	8.97	17.79	0.000	0.000	0.037	0.044
	Max.	3.74	1.38	1.67	2.35	17.76	26.16	0.330	0.055	0.258	0.596
2	Average	58.95	4.08	1.15	4.59	1.04	69.11	0.160	0.057	0.162	0.379
	Min.	8.22	0.51	0.36	0	0	8.74	0.093	0.031	0.099	0.272
	Max.	260.4	15.41	1.95	16.94	3.78	296.92	0.250	0.086	0.275	0.488
Rubba material											
1	Average	5.32	0.96	0	1.78	19.49	27.55	0.148	0	0.076	0.224
	Min.	4.04	0.69	0	1.16	12.42	22.37	0	0	0.020	0.050
	Max.	7.09	1.2	0	2.54	31.04	36.92	0.255	0	0.157	0.412
2	Average	5.94	0.87	0.62	1.82	6.13	15.07	0.255	0.138	0.158	0.551
	Min.	3.64	0.6	0.62	0	0	7.54	0.098	0.083	0.056	0.241
	Max.	6.94	1.58	0.84	7.85	22.7	36.61	0.416	0.244	0.211	0.710

\* In dry gas under reference conditions:  $T_n = 273$  K,  $p_n = 101.3$  kPa.

Due to the partial choking of the gas removal system, the concentration of CO in the waste gases considerably increased, even up to 200 times compared to the average value obtained for series 2 (figure 1, table 1). In the case of aliphatic hydrocarbons (C<sub>1</sub> to C<sub>6</sub>), it was observed that during the mixing of the HCC materials at the choke

valve partially closed (more reductive atmosphere), the concentrations of the substances analysed were from a few to several dozen times smaller than those obtained when the choke valve was fully open (table 2). This regularity was not observed in the case of BTX concentrations in any of the measurement series analysed. The concentrations of these substances at the choke valve partially closed were only slightly lower than those at the choke valve fully open (table 2).

The concentration measurements of the gaseous substances emitted while mixing the Rubba material were carried out only at the choke valve fully open. As a consequence, the results obtained in both measurement series were much more consistent. The differences in the concentrations registered in both measurement series never exceeded 100% of the average value (tables 1–2).

Table 3

Concentrations of total dust and tar substances in waste gases emitted during mixing process of HCC and Rubba materials

Measurement series no.	Parameter	Concentration [ $\text{g}/\text{m}_n^3$ ] *	
		Total dust	Tar substances
HCC material			
1**	Average value	44.73	34.65
	Minimum value	17.9	13.51
	Maximum value	89.9	69.93
2***	Average value	3.34	2.5
	Minimum value	0.65	0.52
	Maximum value	5.51	4.1
Rubba material			
1**	Average value	2.49	1.5
	Minimum value	0.95	0.41
	Maximum value	3.53	2.91
2***	Average value	7.76	3.97
	Minimum value	5.96	3.02
	Maximum value	10.9	5.68

\* In dry gas under reference conditions:  $T_n = 273 \text{ K}$ ,  $p_n = 101.3 \text{ kPa}$ .

\*\* Dust sample taken at 50-mm diameter filters.

\*\*\* Dust sample taken at thimbles.

Any clear relationship was not observed between the concentration of a particular substance in waste gases and the mixing cycle stage nor the temperature of the mixture during the second measurement series completed while mixing the HCC material, and during the first and second measurement series completed while mixing the Rubba material.

As a result of the high content of oil phase in the dust separated from the filter during the first measurement series and the analytical problems involved, the filtering medium was changed before the second series. A glass microfibre thimble was used in

place of the filter. This allowed the aspiration time for the gases to be extended and to ensure that the completed measurements were more representative. Additionally, dust-gas samples were collected during the second measurement series in adsorption tubes filled with the XAD-2 resin after oil phase condensation. The tar substances and PAH content were determined after extracting the adsorbed organic material from filters, thimbles, and adsorption tubes.

Table 4

PAH concentrations in waste gases emitted during mixing process of HCC and Rubba materials \*

Parameter	Unit	HCC material						Rubba material					
		Series 1**			Series 2***			Series 1**			Series 2***		
		av.	min.	max.	av.	min.	max.	av.	min.	max.	av.	min.	max.
Sum of PAHs	[mg/m <sup>3</sup> ]	10.26	3.5	20.21	0.46	0.031	0.779	1.51	0.26	2.57	0.51	0.44	0.603
including:													
Naphthalene	µg/m <sup>3</sup> <sub>n</sub>	858.3	183	2184	126.1	0	228.6	1041	65.5	1625	50.1	0	150.4
Acenaphthylene	µg/m <sup>3</sup> <sub>n</sub>	129.1	99.01	153.2	0	0	0	2.45	0	6.06	0	0	0
Acenaphthene	µg/m <sup>3</sup> <sub>n</sub>	3615	1098	8414	0	0	0	137.9	89.7	206	15.2	0	45.7
Fluorene	µg/m <sup>3</sup> <sub>n</sub>	363.8	94.5	872.2	29.3	0	95.0	43.93	32.4	53.4	15.2	0	45.7
Phenanthrene	µg/m <sup>3</sup> <sub>n</sub>	2697	6.27	4437	23.6	0	94.8	201.8	51.4	471	25.5	0	59.2
Anthracene	µg/m <sup>3</sup> <sub>n</sub>	1511	295.2	3648	0	0	0	24.04	8.13	49.9	0	0	0
Fluoranthene	µg/m <sup>3</sup> <sub>n</sub>	310.4	11.18	463.7	15.04	0	79.74	31.76	5.61	77.4	106	73.2	144.2
Pyrene	µg/m <sup>3</sup> <sub>n</sub>	353.5	234.5	586	0	0	0	16.88	3.45	40.9	0	0	0
Benzo(a)anthracene	µg/m <sup>3</sup> <sub>n</sub>	320.7	90.5	581.8	202.1	0	503.2	9.72	0.68	26.9	0	0	0
Chrysene	µg/m <sup>3</sup> <sub>n</sub>	62.78	21.14	118.7	0	0	0	2.29	0.69	5.23	0	0	0
Benzo(b)fluoranthene	µg/m <sup>3</sup> <sub>n</sub>	15.16	6.08	29.15	0	0	0	0.655	0.16	1.59	0	0	0
Benzo(k)fluoranthene	µg/m <sup>3</sup> <sub>n</sub>	13.31	4.8	25.4	22.0	0	62.0	0.654	0.14	1.65	38.1	0	84.3
Benzo(a)pyrene	µg/m <sup>3</sup> <sub>n</sub>	9.35	4.22	16.76	0	0	0	0.451	0.09	1.12	0	0	0
Indeno(1,2,3-cd)pyrene	µg/m <sup>3</sup> <sub>n</sub>	3.03	1.38	5.56	27.22	0	50.41	0.121	0.03	0.29	0	0	0
Dibenzo(ah)anthracene	µg/m <sup>3</sup> <sub>n</sub>	1.34	0.84	2.07	0	0	0	0.081	0.02	0.19	0	0	0
Benzo(gh)terylene	µg/m <sup>3</sup> <sub>n</sub>	1.5	0	3.09	14.6	0	79.2	0.087	0	0.24	255	172	308.9

\* Concentration in dry gas under reference conditions:  $T_n = 273 \text{ K}$ ,  $p_n = 101.3 \text{ kPa}$ .

\*\* PAHs determined in dust taken at 50-mm diameter filters.

\*\*\* PAHs adsorbed in tubes filled with the XAD-2 resin.

The analysis of the measurement results compiled in tables 3–4 shows a considerable variability in the dusty substance concentrations in the waste gases while mixing the HCC material. This effect is very clearly visible while analysing the first measurement series results. The progress in total dust and tar substances releasing during the HCC material mixing (the second measurement series) and the mixing of the

Rubba material (both series) was more stabilised. The computed concentrations of the substances analysed were at comparable level. The measurement results for the PAH content in the samples of waste gases collected in the filtering medium (series 1) and in adsorption tubes (series 2), as shown in table 4, are incomparable, since in tubes only those hydrocarbons were adsorbed, which were not condensed with oil phase in the dephlegmator installed before the tube, whereas all PAH fractions occurring in the solid phase were retained by the filter.

Gases escaping during the mixing process were also analysed for TOC content in the solid phase. The average results for the solid TOC concentrations in the waste gases escaping during the mixing of HCC and Rubba materials were  $42.1 \text{ mg/m}_n^3$  (HCC) and  $36.8 \text{ mg/m}_n^3$  (Rubba). The proportion of tar substances in TOC in solid samples collected from filters ranged from ca. 80 to 94% (on average 92.5% for the HCC material and 86.3% for Rubba material), and in the samples collected from the XAD-2 resin – from ca. 41 to 74% (on average 59.4% for the HCC and 56.1% for the Rubba).

## 5. CONCLUSIONS

The mixing of HCC and Rubba-type carbon materials is mainly associated with the emissions of solid and liquid substances and, in a smaller degree, gaseous substances. Dust emission is featured in high variability of mixing time. The biggest emission is observed directly after addition of the liquid ingredients to the dry carbon mass. Depending on the type of the material subjected to mixing, the total dust concentration in flue gases can periodically achieve the level of  $90 \text{ g/m}_n^3$ , with average concentrations during mixing between  $1\text{--}45 \text{ g/m}_n^3$ . The maximum concentration of tar substances (found in the solid phase) does not exceed  $70 \text{ g/m}_n^3$ . High concentration of TOC in the first phase of mixing is correlated with high concentration of PAH that ranged from  $0.03$  to  $10 \text{ mg/m}_u^3$  with the maximum of ca.  $20 \text{ mg/m}_u^3$ . Average emissions of solid TOC are similar for both materials analysed (ca.  $40 \text{ mg/m}_u^3$ ).

Of the gaseous pollutants emitted to the air during the mixing process, carbon monoxide, aliphatic hydrocarbons C1–C6 and BTX occur in the highest proportions. Their concentrations in flue gases also considerably change, depending on the mixing process time. The maximum values during measurements do not exceed  $881 \text{ mg/m}_u^3$  (CO),  $297 \text{ mg/m}_u^3$  (the sum of aliphatic hydrocarbons C1–C6) and  $0.7 \text{ mg/m}_u^3$  (BTX). Average concentrations of gaseous substances reach 90% of their maximum values, depending on the type of carbon materials and a relative time of mixing.



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PODCZAS MIESZANIA SUROWCÓW STOSOWANYCH DO PRODUKCJI  
DROBNYCH WYROBÓW WĘGLOWYCH I GRAFITOWYCH

Scharakteryzowano metody przygotowania tworzyw typu HCC i Rubba stosowanych do produkcji drobnych wyrobów węglowych i grafitowych, a także skład gazów odlotowych odprowadzonych z mieszarek tych tworzyw. Dla procesu mieszania każdego z dwóch tworzyw wykonano po dwie kompletne serie pomiarowe, obejmujące przeważnie okres od zalania lepiszczem odpowiednio podgrzanej suchej masy aż do momentu rozładunku mieszalnika. Otrzymane wyniki pokazują zawartość takich substancji występujących w fazie gazowej jak: CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, węglowodory alifatyczne (C<sub>1</sub>–C<sub>6</sub>) oraz BTX (benzen, toluen, etylobenzen i ksylen), a także substancji pyłowych z uwzględnieniem pyłu ogółem, substancji smołowych, wielopierścieniowych węglowodorów aromatycznych (WWA) oraz całkowitego węgla organicznego w fazie stałej.