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Volodymyr Shmalko, Oleg Zelensky and Maryan Rudkevich

TECHNOGENIC NANOPARTICLES FROM COAL CARBONIZATION PRODUCTS

SE «Ukrainian State Research Institute for Carbochemistry»,
7, Vesnina str., 61023 Kharkiv, Ukraine; v.shmalko@gmail.com

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Abstract. Experiments on the extraction of technogenic nanoparticles from coal carbonization products, namely, coke, pitch coke, coal tar, coke dust and carbon deposits from coke and coke-pitch chambers were carried out. With the help of transmission electron microscopy method extracted carbon nanoparticles were investigated. The rationale of the derived nanoparticles technologic origin is given in this paper. The obtained micro-diffraction patterns indicate that the extracted nanoparticles are crystalline solids. Energy-dispersive analysis showed that all of the nanoparticles and micro-particles are composed of carbon. With the help of scanning electron microscope method residual resulting from the storage of aqueous suspensions of nanoparticles were studied. It was found that the residual is composed mainly of carbon micro-tubes and micro-ribbons.

Keywords: carbon nanoparticles, technogenic nanoparticles, coke, pitch coke, carbon deposits, TEM, SEM.

1. Introduction

Today nanotechnologies use only artificially created nanoparticles. It is rather difficult to get information on world production of synthetic nanoparticles. However, it is obvious that the amount of synthetic nanoparticles is not enough for general use in all areas of production, particularly in the construction industry and other similar industries. Mass production of nanomaterials is necessary for further development of nanotechnology. In addition to the particles obtained in the result of physical and chemical synthesis, we can consider the following sources of receiving nanoparticles – natural and technogenic. Particles that are contained in the sedimentary rocks can refer to nanoparticles from natural sources (we do not consider viruses and other biological objects). Fullerenes are found in small quantities in shungites [1], in the bitumens of pillow lavas with inclusions of kerogenic shales [2] coals [3, 4], brown coals [5], oils [6], and some other minerals. Carbon nanotubes were also found in shungites. [7].

Due to the low concentration of nanoparticles in natural objects they represent a purely scientific interest, especially nanoparticles in extraterrestrial objects – fullerenes in meteorites [8] and in carbonaceous chondrites of protoplanetary dust [9]. Particles that are formed during the various processes of combustion (diesel engine exhaust, welding aerosols, *etc*.) as well as during industrial processes in the form of byproducts can refer to technogenic (secondary) nanoparticles. The most common are carbon nanoparticles that are formed during combustion of hydrocarbons. Carbon nanoparticles compose ~ 42 % of all nanoparticles in the environment. These include multi-walled carbon nanotubes (MWCNTs) produced at burning of natural gas in cookers and soot nanoparticles of different origin [10]. Ecologists all over the world carry out numerous studies on risk evaluation and the impact of nanoparticles on human health.

It was found that the technogenic nanoparticles can be formed not only by burning, but at intensive mechanical actions. Thus, at destruction of gas-saturated coal seams during the process of mining in the mines due to the development of shear deformation zones of highly dispersed coal with the size particle from 10 to 50000 nm [11] are formed. In addition, technogenic nanoparticles are found in highly dispersed sludge of metallurgical enterprises. As a rule, the content of ultrafine fractions with nanometer size of particles in sludge varies in the range of 1–1.5 % [12]. Taking into consideration the volume of production of mining and metallurgical complex, the amount of produced technogenic nanoparticles can be huge.

The processes connected with coking of coal can be one of the sources of technogenic carbon nanoparticles (CNP). Previously, our researches have shown that different types of CNP are formed in coke and coke-pitch chambers; these CNP are dissolved in the coke and coke-pitch and are carried away with coke gas [13].

The purpose of this paper is the evaluation of the possibilities of industrial production of carbon nanoparticles from coke products.

2. Experimental

The nanoparticles determination was performed in aqueous suspensions of hard coking coal products. For the preparation of aqueous suspensions CNP samples (metallurgical coke, coke dust from the dust-free coke pushing plant (DFCP) and from coke dry-quenching plant (CDQP), pitch coke and carbon deposits from coke and coke-pitch ovens (samples characteristics are given in Table 1) were dispersed to grain size < 0.2 mm, and then they were exposed to ultrasonic treatment in distilled water for 15–30 min at the frequency of 22 kHz with ultrasonic generator power 100 W. The obtained suspension was centrifuged (rotor speed – 8000 rpm) for 15–30 min in order to remove amorphous carbon. The centrifugate was filtered in order to remove microparticles of amorphous carbon and we have obtained CNP aqueous suspension.

In addition, we prepared aqueous suspensions from the samples of pitch, characteristics of which are given in Table 2.

The obtained aqueous suspensions opalize due to light scattering on CNP particles. When we project red light laser wave with a length of 650 nm we observe Tyndall effect in all investigated suspensions.

The size and morphology of the CNP was determined with the help of transmission electron microscopy TEM 125K and EM-125, equipped with a digital image output system SEO-SCAN. The suspension sample was applied to a microscopic graphite grid (diameter 6 mm) and dried. The grid was placed in the electron microscope and electron microscopy was carried out. All images were obtained in bright-background mode at the accelerating voltage of 100 kV. With the help of scanning (raster) electron microscopes (SEM) Jeol JSM 840 and JSM-6390LV we investigated suspensions and suspension evaporated precipitation. Ultimate composition was determined with the help of energy-dispersive analyzer (EDA), an attachment to SEM.

With the help of optical microscopy method we have studied microstructures formed during spontaneous CNP assembly and solid precipitation after suspensions evaporation.

CNP output has been determined by gravimetric method.

3. Results and Discussion

All selected CNP are crystal, which is evidenced by the presence of micro-diffraction patterns obtained by reflection high-energy electron diffraction method. Micro-diffraction patterns (Fig. 1) were recorded on a TEM. As you can see from Fig. 2, CNP obtained from samples from the coke and coke-pitch ovens are very diverse. So we can see fractal structures, fiber, tubular, spiral, spherical [13], and pyramidal structures.

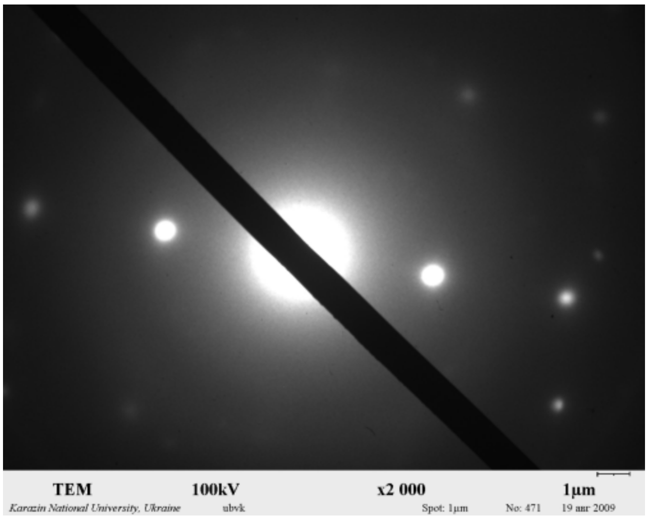


Fig. 1. Typical micro-diffraction pattern for carbon nanostructure

Table 1

Characteristic of the studied solid coking products

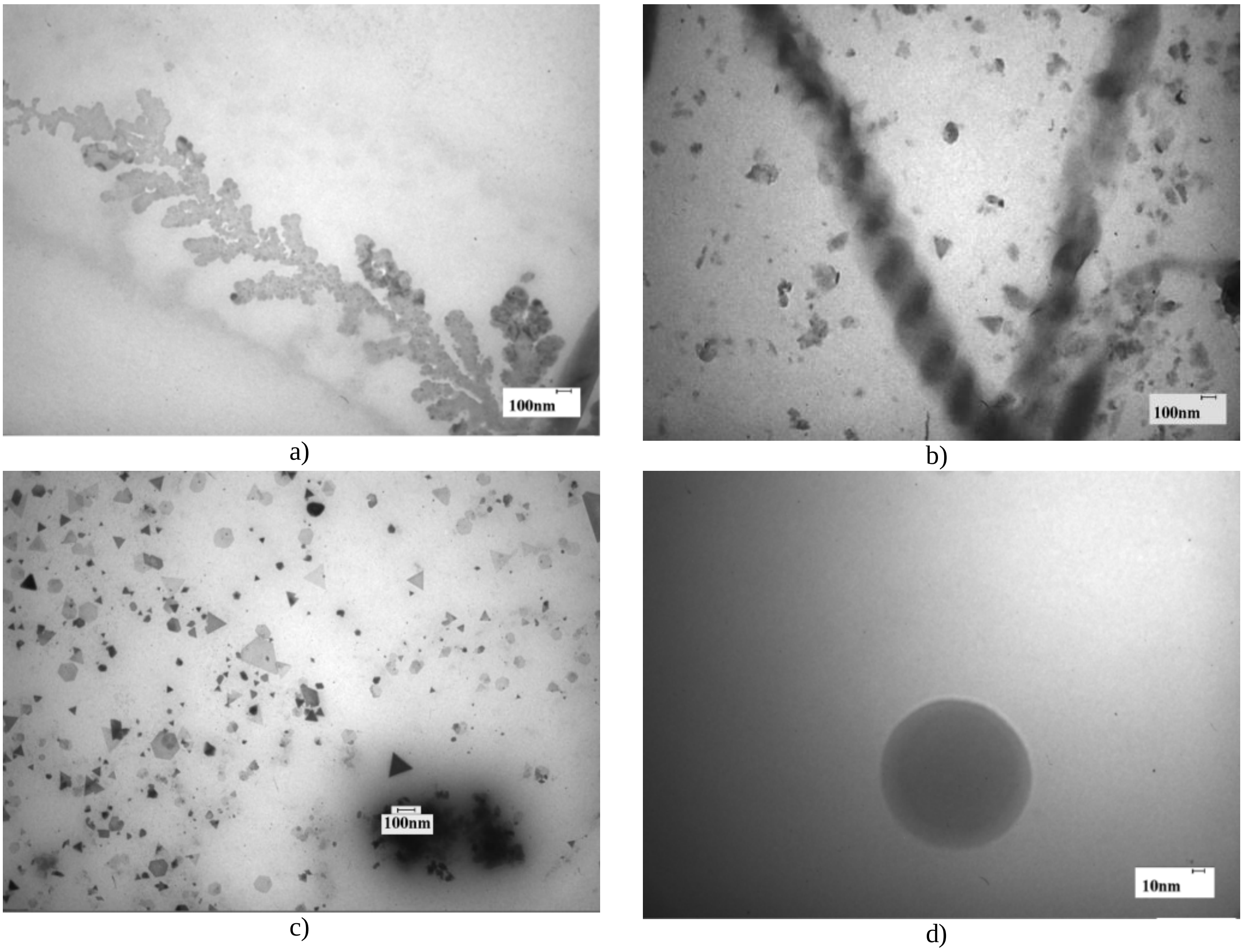
Sample	Element , %			Technical analysis , %		
	C^{daf}	H^{daf}	$N^{daf} + O^{daf}$	A^d	S_t^d	V^{daf}
Furnance coke	96.70	0.60	1.60	12.1	0.95	1.7
Pitch coke	97.84	0.43	1.18	0.6	0.54	0.6
Pyrocarbon 1*	97.41	0.32	0.82	3.1	1.46	0.9
Pyrocarbon 2**	98.10	0.49	1.07	0.3	0.36	0.4
DFCP dust	96.43	0.96	0.40	10.9	0.82	4.0
CDQP dust	97.79	0.68	0.40	13.3	0.99	2.3

Notes: * – carbon deposit from the coke oven; ** – carbon deposit from coke-pitch oven.

Table 2

Characteristics of coal tar

Indices	Medium temperature pitch
Softening temperature, °C	68.0
Volatile matter, %	61.9
Ash content, %	≤ 0.3
Mass fraction of substances, %, insoluble: in toluene	20.4
quinoline	5.6



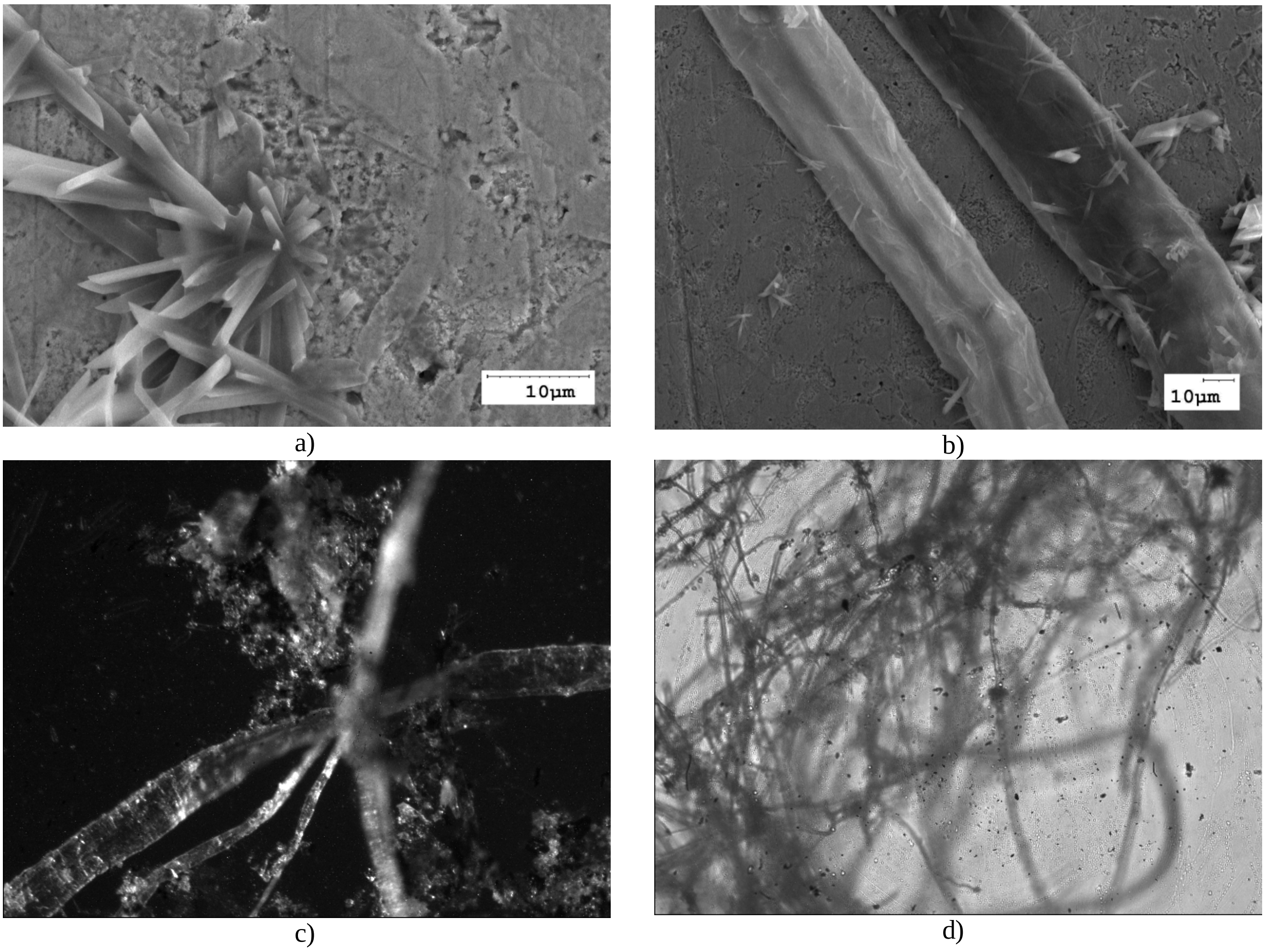
a) b) c) d)

Fig. 2. Carbon nanoparticles from products of coking coal: fractal clusters (coke) x10000 (a); spiral nanofibers (pitch coke) x10000 (b); triangular and hexagonal structures (coke, pitch coke) x12000 (c) and spherical (pitch) x80000 (d)

It was previously shown [13] that CNP of such morphology in the initial coals do not occur, so we can assume that they have a technologic origin, *i.e*. they are formed in the result of the coal pyrolysis in coke ovens. In addition, these CNP are not formed at ultrasonic dispersion, because special experiments have shown that the same particles are formed at desalination of initial samples with particle size 0.2 mm. DFCP dust, which was not dispersed in the process of samples preparing, contains practically all types of nanoparticles, found in other coking products, that is the direct evidence of technologic origin of the studied CNP.

When storing the CNP aqueous suspensions form grey gelatinous precipitates, consisting of nanoparticle aggregates formed in the result of their self-organization.

The main part of the precipitations from furnace coke and DFCP dust suspensions consists of fractal structures (fern leaves, fish-bone, *etc*.). At the same time, the CNP from more structurally ordered material (pitch coke) are aggregated into microtubules (diameter from 2 to 8 mm) and micro-ribbons (Fig. 3) with a width of up to 30 microns.



a) b) c) d)

Fig. 3. Precipitation of CNP suspensions from pitch coke SEM: x1000 (a) and x2000 (b) and from optical microscope: x150 (c) and x150 (d)

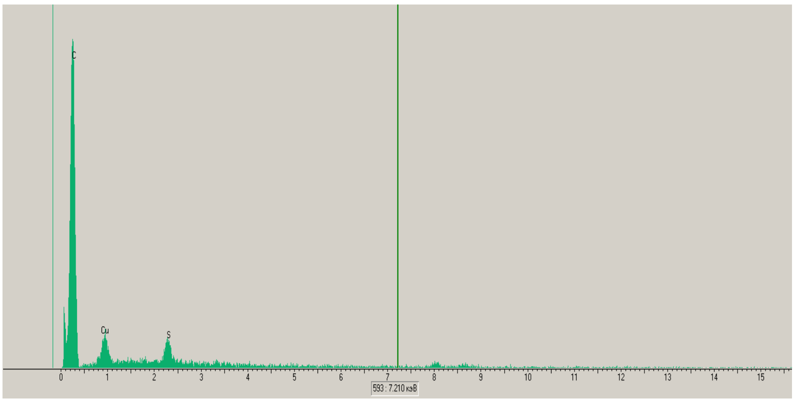


Fig. 4. Energy-dispersive spectrum of CNP suspensions precipitations from pitch coke (the peaks of Cu and Zn are calibrating)

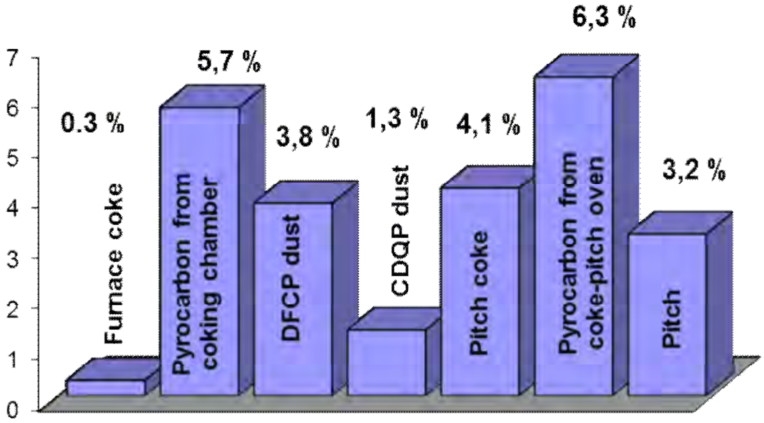


Fig. 5. The distribution of the CNP in coking products

Energy-dispersion analysis showed that all of the nanoparticles and micro-particles are composed of carbon. The example of energy-dispersion spectrum is shown in Fig. 4.

Energy-dispersive spectra of micro-particles from furnace coke and DFCP dust may contain small amounts of oxygen and other elements, which obviously got to the suspension from the initial coal (sulfur, chlorine, phosphorus, *etc*.). We still have to understand the cause of the oxygen presence in some CNP suspensions precipitations.

The results of CNP output determination from various solid coke products are shown in Fig. 5. The greatest number of nanoparticles was obtained from coke and coke-pitch oven carbon deposits 5.7 and 6.3 %, respectively. Quite a lot of nanoparticles are contained in pitch coke, coal tar and DFCP dust (Fig. 5). The amount of CNP in furnace coke was the least. We think that in the case of wet-quenched coke most CNP is gone from the surface of the coke with quenching water, in the case of dry-quenched coke, CNP go to coke dust (CDQP dust) at coke grinding.Indeed, in the content of CNP in DFCP dust is four times higher than in the coke itself. By the presence of light scattering the presence of CNP in quenching water is determined qualitatively.

The distribution of the CNP in the coke near-surface layer and its high content in carbon deposit of coke chamber indicates that the most possible cause of the technogenic nanoparticles presence in the coke chamber is their synthesis from the gaseous phase at decompounding of volatile coking products on the surface of coke and coke chamber refractory masonry.

As it seems to us, in coke-pitch chamber, besides the synthesis from the gaseous phase, there is a high probability of technogenic nanoparticles formation both in fluid-plastic state at coal tar pitch coking. This assumption was made by us before [14] from the analysis of the amount of nanoparticles in the coke in relation to their amount in the carbon deposits. This value for nanoparticles from the coke chamber is equal to 5.6 %, and from coke-pitch chamber it is equal to 65.1 %. This means that technogenic nanoparticles are synthesized not only in the surface layer, but also in the coke-pitch load volume.

During evaluation of possible resources of technogenic CNP in coke production we can focus on the side-products of coking – carbon deposits from coke and coke-pitch chambers, as well as DFCP and CDQP dust. Despite the high content of CNP in carbon deposits in coke and coke-pitch chambers (~ 6 %), they cannot be used as raw material for the production of nanoparticles. The main reason is their limited resources and the absence of real way of their removal from oven chambers.

Thus, now dust from DFCP is the most promising and technological raw materials. This dust does not require cost for dispersion, because about 90% of the dust is of grain size < 0.5 mm. In addition, dust from DFCP contains about 4 % of the CNP and has sufficient capturing volume. According to the data [15], the number of dust captured by DFCP plants on batteries 9-bis and 10-bis of OJSC "ALCHEVSKKOKS" is 406 t/y and 710 t/y, respectively. Thus, only with the dust of these two batteries about 34 tons of the CNP are utilized annually (at an estimated CNP content not less than 3 %).

Without utilization of this dust nanoparticles are released to the atmosphere and these emissions are particularly dangerous [16-17].

4. Conclusions

Carbon nanoparticles extracted from the solid coke products have technologic origin. Thus coking furnace battery is the reactor for production of carbon nanoparticles, which are formed on coke surface and coke chamber refractory masonry, and, probably, in the coke-pitch load volume.

Technogenic nanoparticles have different sizes and morphology, depending on the initial material. Dust from DFCP, which is not the aim product of coking, contains about 4 % of the CNP and has sufficient capturing volume, can be considered as the most promising and technologically advanced material for release of technogenic carbon nanoparticles.

Acknowledgments

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References

[1] Buseck P., Tsipursky S. and Hettich R.: Science, 1992, **257**, 215.
[2] Jehlichka J., Osawa M., Slanina Z. and Osawa E.: Fullerene Sci. Tech., 2000, **8**, 449.
[3] Fang P. and Wong R.: Mat. Res. Innovat., 1997, **2**, 130.
[4] Fang P., Chen F., Tao R. *et al.*: Fullerene in Some Coal Deposits in Chine. [in:] Rietmeijer F. (Ed.), Natural Fullerenes and Related Structures of Elemental Carbon (eBook). Springer, 2006.
[5] Zubrik A., Skybova M., Cuvanova S. *et al.*: Acta Montanistica Slovaca, 2005, **1**, 77.
[6] Evdokimov I. and Losev A.: Promysh. Bezopasnost' i Ekol., 2009, **10**, 8.
[7] Bechkiy O., Kislov V., Kreniczkiy A. *et al.*: Biomed. Techn. i Radioelektronika, 2006, **3**, 25.
[8] Harris P. and Vis R.: Proc. R. Soc. Lond. A, 2003, **459,** 2069.
[9] Bogatikov O.: Vestnik Ross. Akad. Nauk, 2003, **73**, 426.
[10] Murr L. and Garza K.: Atmosph. Environ., 2009, **43**, 2683.
[11] Trubeczkoy K., Viktorov S., Galchenko Yu. *et al.*: Vestnik Ros. Akad. Nauk, 2006, **76**, 318.
[12] Kovalenko I., Kovzun I., Ul'berg Z. *et al.*: Nanosystems, Nanomat., Nanotechn., 2008, **6**, 443.
[13] Shmalko V. and Zelensky O.: Karbo, 2010, **3**, 130.
[14] Zelenskiy O., Shmal'ko V. and Bogatyrenko S.: Uglekhim. Zh., 2010, **1-2**, 15.
[15] Shmal'ko V.: Khimia, Fizika ta Techn. Poverkhni, 2012, **1**, 102.
[16] Trembach T., Lanina E. and Solovyov M.: Uglekhim. Zh., 2009, **3-4**, 93.
[17] Maysinger D., Behrendt M. and Przybytkowski E.: Nanopharm. Online J., 2006, **1**. Access mode: http://www.nanopharmaceutical.org/.
[18] Kurlandskiy B.: Toksikolog. Vestnik, 2007, **6**, 3.

ТЕХНОГЕННІ НАНОЧАСТКИ З ПРОДУКТІВ КОКСУВАННЯ ВУГІЛЛЯ

Анотація. *Проведені експерименти з виділення вуглецевих наночасток технологічного походження з продуктів коксування вугілля, а саме: коксу, пекового коксу, пеку, коксового пилу і вуглецевих відкладень з коксової і пекококсової камер. Методом просвічуючої електронної мікроскопії були досліджені наночастки, які були виділені з продуктів коксування. Наведено обґрунтування технологічного походження виділених наночасток. Отримані мікродіфракційні картини свідчать, що виділені наночастки є кристалічними тілами. Енергодисперсійний аналіз показав, що всі наночастки і мікрочастки складаються з вуглецю. Методом скануючої електронної мікроскопії досліджено осад, який утворюється під час зберігання водних суспензій з отриманих наночасток. Встановлено, що осад являє собою, головним чином, вуглецеві мікротрубки і мікрострічки.*

Ключові слова: *вуглецеві наночастки, техногенні наночастки, кокс, пековий кокс, вуглецеві відкладення, ТЕМ, СЕМ.*