DOI https://doi.org/10.32782/geotech2022.35.03
UDC 55.556

Ye. Nasedkin, O. Olshtynska, G. Ivanova, O. Mytrofanova

Nasedkin Ye., PhD (Geol.), senior scientist, Institute of geological sciences of NAS of Ukraine, ORCID 0000-0003-2633-9291, nasedevg@ukr.net
Olshtynska O., D. Sc. (Geol.), Head of Department, Institute of geological sciences of NAS of Ukraine, ORCID 0000-0003-3211-2106, ol-lesia@ukr.net
Ivanova G., PhD (Geol.), senior scientist, Institute of geological sciences of NAS of Ukraine, ORCID 0000-0002-5012-1084, a_1207@ukr.net
Mytrofanova O., PhD student, State Scientific Institution "Center for Problems of Marine Geology, Geoecology and Sedimentary Ore Formation of the National Academy of Sciences of Ukraine" ORCID 0000-0001-5971-9122, mitrof_ol@ukr.net

SOME FEATURES OF IRON DISTRIBUTION IN THE SUSPENDED MATTER OF THE DNIEPER RIVER WITHIN ZAPORIZHZHIA CITY

Abstract. *The main purpose of the research was determination of the peculiarities of iron distribution in the suspended matter of rivers in the industrialized regions of Ukraine, in particular the city of Zaporizhzhia. Long-term observations and continuous sampling of natural substances made it possible to determine the distribution features of the solid component of the river suspension containing iron oxide, study the morphological characteristics of these particles, and to preliminarily define their genetic affiliation to different technological processes of metallurgical production. Genetically, particles can be divided into two main categories related to the technological processes of crushing iron ores and their high-temperature processing. The first category (Fe_2O_3 spherules) includes spherical mineral aggregates represented by iron oxide of varying degrees of corrosion, sometimes with micro-impurities of ZnO, zinc, titanium, manganese, and copper oxides.. The second component of technogenic nature in the river suspension is fragments of Fe_2O_3, sometimes with MnO impurities, represented by a significant range of dimensions (from 5 to 70 and more microns) in the form of acute-angled, sometimes slightly rounded grains. In this case, the dispersed formation (in contrast to iron-containing condensed formations) is presented not only in the pelit and aleurite, but even the finely-psammite component. Morphological features of the particles of a technogenic component in the water suspension indicate that the condensed and dispersed components can be attributed by genetic affiliation to various technological processes of preparation and processing of iron ore at the metallurgical complex of the city. This was evidenced by laboratory examinations of matter of atmospheric emissions of a number of production units at the relevant metallurgical enterprises of the city of Zaporizhzhia. In the environmental field, our researches are very important because such particles are usually carriers of heavy metals (often with a high concentration of these metals).*

Key words: *suspended matter, Dnipro, glandular spherules, heavy metals, technological processes.*

Introduction

The city of Zaporizhzhia occupies the leading place among the most industrially loaded centers with a high potential of the metallurgical industry in Ukraine. Significant concentration of enterprises of ferrous, non-ferrous metallurgy, mechanical engineering causes in some areas of the city an intensive emission of a number of trace elements into the environment, in particular, in the Dnieper waters.

The distribution of pollutants released into the environment depends on a number of natural factors and is determined by the strength and direction of winds, hydrodynamic and hydrochemical regimes of surface watercourses, etc.

Analysis of recent research and publications

Until now, the processes of transformation of pollutants released into the environment, the features of their distribution and interaction with natural components remain insufficiently studied. First of all, this concerns the dynamic components of the environment (surface waters and atmospheric flows).

Considerable attention in the scientific world is paid to various aspects of the problem of monitoring the distribution of pollutants in the environment, as evidenced by a significant number of relevant publications [1, 4, 7, 8]. Largely, this concerns the state of the atmospheric environment, surface waters and land soils, to a lesser extent, bottom sediments and river suspension.

The purpose of the study

For a long time, Institute of Geological Sciences of the NAS of Ukraine has been undertaking continuous comprehensive studies of the sediment-forming substance transported in the atmospheric and aquatic environments within the city of Zaporizhzhia. Observations of economic activity impact on the natural environment include monitoring of quantitative and qualitative changes in the composition of the river suspension and atmospheric aerosol by the methods of continuous accumulation of natural matter for a month and its subsequent selection for analysis.

The objectives of these studies also include determining the features of the distribution of a number of heavy metals

in transit flows of sedimentary material, in particular in aqueous suspension, finding out and examination of redistribution patterns of their forms and concentrations depending on natural and anthropogenic factors.

Such observations, in comparison with the state system for monitoring the quality of surface waters, make it possible to obtain on a permanent basis samples of the river suspension in quantities sufficient for a number of additional studies, in particular, using an electron microscope, sedimentograph, and energy dispersive spectrometer.

Methods of investigation

The technique for suspended matter sampling is based both on the methodological recommendations presented in the literature [3], in particular, and on our own experience obtained during similar work in marine areas [6].

Monitoring observations of the Dnieper suspension were realized at the pier of the State Institution "Scientific Hydrophysical Center of the NAS of Ukraine" (Komunars'ky district of the city of Zaporizhzhia, lower reaches of the Dnieper river). Suspended matter accumulates in vertical sediment traps designed by Nasedkin Ye, Senior Researcher of IGN NAS of Ukraine (Fig. 1). The accumulated material is removed from the traps on a monthly basis for further laboratory research.

Fig. 1. Set of vertical sediment traps on the pier of the State Institution "Scientific Hydrophysical Center of the NAS of Ukraine"

Mineral, macro- and micro-component, chemical composition of samples of the sedimentary matter was identified by electron microscopy, as well as energy and water dispersion analysis in the laboratory of the Center for Collective Use of Scientific Equipment of the IGN NAS of Ukraine. A number of analytical studies (the distribution of trace elements and their chemical forms) were carried out in the laboratories of the Scientific and Educational Institute "Institute of Geology" of Taras Shevchenko Kyiv National University and Yuriy Fedkovich Chernivtsi National University.

Results of investigations

The generalization of the information obtained during the observation period made it possible to identify and evaluate the contribution to the complex of the suspended matter of such component which with a high probability can be considered anthropogenic. In particular, a comparison of the total iron content in the composition of the river suspension within Zaporizhzhia and the corresponding average values for the waters of the Dnieper [5] showed significant excesses of the content of the element in the area adjacent to the area of metallurgical enterprises. Here the total iron content in the composition of the river suspension reaches 12%. It significantly exceeds the corresponding average values for the Dnieper waters. Summarizing the data obtained over a five-year study period and averaging the distribution of the main components of the suspended matter by month showed that the second place in the total mineral content, after silica, is divided by iron oxide and calcium oxide (12% of each in total distribution of basic oxides) (Fig. 2). Minor fluctuations in the content of metal-containing components occur in different sampling periods, reaching a minimum in spring.

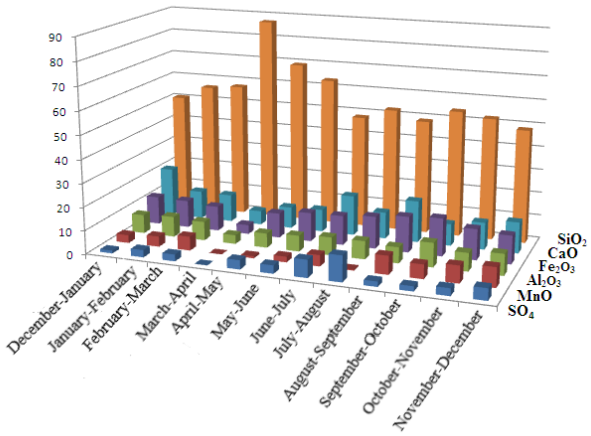


Fig. 2. The average monthly distribution of the main components of the river suspension substance (%) within the study area, 2015-2019.

Correlation coefficients indicate that this occurs most likely due to a significant increase in the content of organic silica, and to a lesser extent due to changes in the intensity of winds from land and the peculiarities of the hydrological regime.

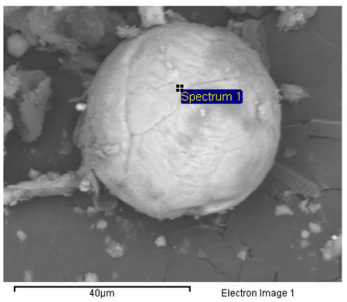
The results of electron microscopic analyzes of samples also indicated a significant role of metal-containing particles of silty dimension in the formation of the main phase of the mineral component of the suspended matter during the study period. Within the city of Zaporizhzhia, where such components as grains of quartz and feldspars, mixed-layered formations of chlorite-illite-montmorillonite, skeletal remains of siliceous microalgae dominate in the suspension matter, amount of metal-containing component can reach significant volumes. Iron is the predominant chemical element. Genetically particles could be divided into two main categories associated with the technological processes of iron ores grinding and their high-temperature processing. The first category is Fe_2O_3 spherules (spherical mineral aggregates)

and aluminosilicate spherules (Fig. 3) of varying degrees of corrosion with admixture of Fe and microimpurities of zinc, titanium, manganese, and copper oxides.

The particle size of the main phase averages from 0.1 to a few tens of micrometers, in rare cases it can reach $7 \cdot 10^{-5}$, while the silt-sized substance can contain impurities of manganese and titanium (up to 10% or more).

Based on the analysis of information sources [2], these formations are associated with the smelting of iron ores, metalworking, welding and other technogenic processes using high temperatures (operation of thermal stations, etc.) and are transported into the aquatic environment by air.

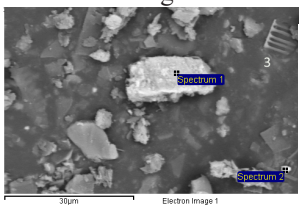
Our investigation showed that solid particles are a significant component of the suspended matter. These particles were formed and entered in the aquatic environment due to human activities. Some authors consider that ferruginous spherules are especially unstable to environmental factors and are easily amenable to decomposition processes in the river media [2]. Oxidation and other changes in such formations can adversely affect the ecological state of the environment.



Element	Weight%	Formula
Fe K	69.94	Fe2O3
O	30.06	
Totals	100.00	

Fig. 3. Fe_2O_3 spherules from Dnieper suspended matter, April-May 2016 (SEM).

Clastic fragments of Fe_2O_3 with microimpurities



Fragment 1

Element	Weight %	Formula
Si K	0.90	SiO2
Fe K	68.60	Fe2O3
O	30.50	
Totals	100.00	

Fragment 2

Element	Weight %	Formula
Si K	8.89	SiO2
Fe K	56.64	Fe2O3
O	34.47	
Totals	100.00	

Fig. 4. Fragments of Fe_2O_3 grains of different sizes (SEM) from the aqueous suspension of the Dnieper and fragments of siliceous microalgae. Sampling period January 15 – February 15, 2016.

of MnO are other technogenic components in the river suspension. They are represented by a significant range of dimensions from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-5}$ or more microns in the form of acute-angled, sometimes slightly rounded grains. The chemical composition of the clastic part of the suspended matter attracts attention primarily by the presence of a significant amount of heavy metal oxides (Cu, Cr, Ni, Ti, Zn), and the content of Fe_2O_3 according to microprobe chemical analysis can reach 80-95% (Fig. 4).

Conclusion

Our studies showed that a significant component of the suspended matter of the Dnieper within the city of Zaporizhzhia, in particular in the observation area, are solid particles formed or transferred from other areas (including mining sites) and also entered the aquatic environment due to human economic activity. According to morphological features, the particles of the technogenic component in the water suspension are divided into condensed and dispersed components which by genetic affiliation can be attributed to various technological processes of preparation and processing of iron ore at the metallurgical complex of the city. In particular, the dust obtained in the process of wet gas cleaning of open-hearth furnaces, as well as from the filters of electric steel-smelting furnaces, largely consists of iron-containing spherules and cenospheres, similar in chemical composition and external features to those studied by us in the suspended matter. The substance filtered out by the systems of wet-gas cleaning of process gases of sinter machines and electrostatic precipitators of the tail section of sinter machines, in turn, corresponds to the detrital component of iron oxide, which is also observed by us in samples of the river suspension.

Reference

1. Blackbern, A.A. (2001), O metodah rascheta balansa tyazhelyh metallov na vodosbornoj ploshchadi, *Geografiya i prirodnye resursy*, 1: 125-128.

2. Menshikova, E., Osovetsky, B. (2015), *Modern problems of science and education*, 1 (part 1). https://www.science-education.ru/ru/article/view?id=18203 (Accessed: 3 October 2017).

3. Morozov, N.P. (1979), On the relation between migration forms of trace elements in the waters of the rivers, bays, seas and oceans, *Geokhimiya,* 8: 1259–1263.

4. Mur, Dzh.V., Ramamurti, S.M. (1987), *Heavy metals in natural waters. Monitoring and assessment of impact*. Moscow.

5. Mytropolskiy, A.Yu., Bezborodov, A.A., Ovsyaniy, Ye.I. (1982), *Geochemistry of Black Sea*. Kyiv.

6. Nasedkin, Ye., Mytropolskyi, O., Ivanova, G. (2013). *Monitoring of sedimentation processes in the land and sea of interaction zone*. Sevastopol.

7. Splodytel. A. O., Kuraieva, I. V., Zlobina, K. S. (2020), Peculiarities of heavy metal accumulation in soils in urbanized landscapes of Brovary town, *Geological Journal*, 2: 39-51. https://doi.org/10.30836/igs.1025-6814.2020.2.200245.

8. Zhovinsky, E.Ya., Kuraieva, I.V. (2002). *Geochemistry of heavy metals in soils of Ukraine*. Kyiv.

9. Zyryanov, V.V., Zyryanov, I.V. (2009). *Zola unosa tekhnogennoe syr'e*. Moscow.

ДЕЯКІ ОСОБЛИВОСТІ РОЗПОДІЛУ ЗАЛІЗА У ЗАВИСЛІЙ РЕЧОВИНІ Р. ДНІПРО В МЕЖАХ МІСТА ЗАПОРІЖЖЯ

Насєдкін Є.І., Ольштинська О.П., Іванова Г.М., Митрофанова О.А.

Насєдкін Є.І., канд. геол. наук, старший науковий співробітник, Інститут геологічних наук НАН України, https://orcid.org/0000-0003-2633-9291, nasedevg@ukr.net
Ольштинська О.П., доктор геол. наук, завідувач відділом, Інститут геологічних наук НАН України, ORCID 0000-0003-3211-2106, ol-lesia@ukr.net
Іванова Г.М., канд. геол. наук, старший науковий співробітник, Інститут геологічних наук НАН України, ORCID 0000-0002-5012-1084, a_1207@ukr.net
Митрофанова О.А., аспірантка, Державна наукова установа "Центр проблем морської геології, геоекології та осадового рудоутворення НАН України", ORCID 0000-0001-5971-9122, mitrof_ol@ukr.net

Анотація. *Основною метою досліджень було визначення особливостей розподілу заліза в завислій речовині річок у промислово навантажених регіонах України, зокрема місті Запоріжжі. Тривалі спостереження та безперервний відбір проб натурної речовини дозволили визначити особливості розподілу твердого компоненту річкової завісі, що містить оксид заліза, дослідити морфологічні характеристики зазначених частинок та попередньо з'ясувати їх генетичну належність до різних технологічних процесів металургійного виробництва. Генетично частинки можна розділити на дві основні категорії, пов'язані з технологічними процесами подрібнення залізних руд та їх високотемпературної переробки. Перша категорія – сферули Fe2O3 – включає сферичні мінеральні агрегати, представлені оксидом заліза, різного ступеня кородованості, іноді з мікродомішками оксидів цинку, титану, марганцю, міді. Другою складовою техногенного характеру у річковій завісі є уламкові фрагменти Fe2O3, іноді з мікродомішками MnO, представлені значним діапазоном розмірності – від 5 до 70 і більше мікрон у вигляді гострокутних, іноді незначно обкатаних зерен. При цьому, на відміну від залізовміщуючих конденсаційних утворень, диспергаційні за розмірністю присутні не тільки в пелітовій та алевритовій, але й навіть дрібнопсамітовій складовій. Морфологічні ознаки частинок техногенної складової у водній завісі свідчать, що конденсовану та диспергована компоненти за генетичною належністю можна віднести до різних технологічних процесів підготовки та переробки залізної руди на підприємствах металургійного комплексу міста. Останнє засвідчили лабораторні досліджень речовини атмосферних викидів низки ланок виробництва на відповідних металургійних підприємствах Запоріжжя. В екологічній сфері ці дослідження важливі тим, що такі частинки, як правило, є носіями важких металів, нерідко включаючи суттєві концентрації останніх.*

Ключові слова: *зависла речовина, Дніпро, залізисті сферули, технологічні процеси.*