DOI: 10.14739/mmt.2024.4.311754

UDC 613.632.3/.4.02:[622’18+669-044.964]-057

Ultrafine industrial aerosol as an occupational risk factor for sintering industry workers

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A – research concept and design; B – collection and/or assembly of data; C – data analysis and interpretation; D – writing the article; E – critical revision of the article; F – final approval of the article

Keywords:
metallurgical production, sintering factory, ultrafine industrial aerosol, suspended particulate matter, occupational risk.

Ключові слова:
металургійне виробництво, агломераційне відділення, ультрадисперсний промисловий аерозоль, зважені частки, професійний ризик.

Надійшла до редакції / Received: 18.09.2024

Після доопрацювання / Revised: 30.09.2024

Схвалено до друку / Accepted: 10.10.2024

Conflicts of interest:
authors have no conflict of interest to declare.

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Aim. Assessment of the physicochemical characteristics of suspended particulate matter of the ultrafine range present in the air of the working area of the sintering factory of a metallurgical plant.

Materials and methods. The assessment and analysis of the physicochemical parameters of ultrafine particles were carried out in different areas of the sintering factory of the metallurgical plant. The parameters were measured using a portable scanning spectrometer Nanoscan 3910 (USA). The chemical composition of the suspended particulate matter was determined by the method of optical emission spectrometry with inductively coupled plasma (OES-IZP) using the device “Ortima 2100 DV” (PerkinElmer, USA).

Results. It was estimated that the concentration of suspended particulate matter of ultrafine size in the main part of the sintering machine ranged from 3.02×10^4 to 3.12×10^4 per cm^3, in the tail part of the sintering machine – from 5.09×10^4 to 7.59×10^4 per cm^3, in the sintering machine control room No. 1 – from 2.06×10^4 to 2.38×10^4 per cm^3, in the workers of the control group – from 1.43×10^4 to 1.73×10^4 per cm^3. The quantitative concentration of suspended particulate matter by individual sizes at all workplaces of the sinter plant workers compared to workers of the control group had a significant difference. Values of the total surface area and surface volume of suspended particulate matter of the nano-sized range had their maximum in the tail part and near the head of the sintering machine, the lowest values were recorded around the control room and among the employees of the plant management department. The highest mass concentration of ultrafine particles was recorded in the tail part of the sintering machine (22.55 µg/m^3 to 508.35 µg/m^3), which is associated with a significant amount of suspended particulate matter of a larger size (≥115.5 nm). The chemical composition of the particles of the ultrafine range included aluminum, calcium, iron, magnesium, manganese, silicon, and phosphorus, which is explained by the specifics of the technological process, and the exceeding of the hygienic standard was observed for calcium, silicon and phosphorus.

Conclusions. It was established that during the sintering of the agglomerate in the agglomeration compartment, many suspended particles of the ultrafine range are formed. They included aluminum, iron, manganese, magnesium, silicon, phosphorus, and calcium. Significantly higher values of the number, mass concentration, surface area and surface volume of suspended particulate matter were determined at the workplaces of sintering factory workers, which had a statistically significant difference compared to the workers of the control group.

Modern medical technology. 2024;16(4):303-309

Ультрадисперсний промисловий аерозоль як фактор професійного ризику для працівників агломераційного виробництва

Л. П. Шаравара, Н. М. Дмитруха, І. М. Андрусишина

Мета роботи – оцінити фізико-хімічні характеристики зважених частинок ультрадисперсного діапазону, що містяться в повітрі робочої зони працівників агломераційного відділення металургійного заводу.

Матеріали і методи. Оцінювання й аналіз фізико-хімічних показників ультрадисперсних частинок здійснили на різних ділянках агломераційного відділення металургійного заводу. Показники встановили за допомогою портативного скануючого спектрометра Nanoscan 3910 (США). Хімічний склад зважених частинок визначено методом оптико-емісійної спектрометрії з індуктивно зв’язаною плазмою (ОЕС-ІЗП) за допомогою приладу Optima 2100 DV (PerkinElmer, США).

Результати. Концентрація зважених частинок ультрадисперсного розміру в головній частині агломераційної машини коливалася в межах від $3{,}02 \times 10^4$ до $3{,}12 \times 10^4$ на см^3, у хвостовій частині агломераційної машини – від $5{,}09 \times 10^4$ до $7{,}59 \times 10^4$ на см^3, у пульті управління агломераційної машини № 1 – від $2{,}06 \times 10^4$ до $2{,}38 \times 10^4$ на см^3, у працівників контрольної групи – від $1{,}43 \times 10^4$ до $1{,}73 \times 10^4$ на см^3. Кількісна концентрація зважених частинок за окремими розмірами на всіх робочих місцях агломератника порівняно з працівниками контрольної групи достовірно відрізнялася. Показники загальної площі поверхні та об’єму поверхні зважених частинок нанорозмірного діапазону були максимальними у хвостовій частині та біля головної частини агломераційної машини; найменші показники зареєстровано в зоні пульту управління та у працівників відділу заводоуправління. Найбільшу масову концентрацію ультрадисперсних частинок визначили у хвостовій частині агломераційної машини (22,55–508,35 мкг/м^3), що пов'язано зі значною кількістю зважених частинок більшого розміру (≥115,5 нм). До хімічного складу частинок ультрадисперсного діапазону входили алюміній, кальцій, залізо, магній, марганець, кремній і фосфор, що пояснюється специфікою технологічного процесу; перевищення гігієнічного нормативу встановлено для кальцію, кремнію та фосфору.

Висновки. У процесі спікання агломерату в агломераційному відділенні утворюється велика кількість зважених частинок ультрадисперсного діапазону. Вони містили алюміній, залізо, марганець, магній, кремній, фосфор і кальцій. На робочих місцях агломератників встановлено істотно вищі показники кількості, масової концентрації, площі та об'єму поверхні зважених частинок, що мали статистично вірогідні відмінності порівняно з параметрами, які визначені в працівників контрольної групи.

Сучасні медичні технології. 2024. Т. 16, № 4(63). С. 303-309

The metallurgical industry in Ukraine is one of the most harmful and dangerous industries in terms of working conditions due to insufficiently advanced technology and outdated equipment. Therefore, the working conditions of workers in sintering, cast iron, steel and rolled products workshops are particularly difficult and harmful [1].

Employees of this category work in harmful working conditions, they are affected by unfavorable microclimatic conditions, increased concentration of industrial dust and chemicals, industrial noise and vibration [2,3,4]. The complete exclusion of dangerous and harmful professional factors in metallurgical production is impossible, but developing and applying preventive measures to reduce their negative impact on workers' health is an urgent task for occupational hygiene. One of the main issues is a detailed analysis of dangerous and harmful production factors, especially industrial aerosol [5].

Among professional pathologies, dust lung pathology (pneumoconiosis, chronic bronchitis, chronic obstructive pulmonary diseases) is the most widespread in Ukraine. Today it also occupies a leading place among the causes of temporary incapacity, disability and mortality [2,6].

It is known that the main reason for the development of respiratory diseases is the increased level of industrial dust in the working zone air (WZA) of workers. In Ukraine, only the total dust mass is determined and regulated, not considering its finely dispersed and ultrafine components. It is known that suspended particulate matter (SPM) of the finely dispersed and ultrafine range affects health most negatively, causing pathological changes in various organs and systems of the human body [7,8,9,10,11,12].

Therefore, studying the SPM content of the ultrafine range in the WZA of employees of various enterprises, including metallurgical ones, is an urgent hygienic issue to determine, apply and implement effective measures to prevent occupational and industrial pathology.

Aim

The study aims to assess the physicochemical parameters of ultrafine particles present in the air of the working area of the sintering factory of a metallurgical plant.

Materials and methods

The physical characteristics of ultrafine industrial aerosol (UIA) (number per cm^3, surface area and volume, mass concentration) were studied using a Nanoscan 3910 portable scanning spectrometer (USA), which allows the determination of suspended particles in the range from 10 to 400 nm. The device allows to measure the SPM in 13 channels for individual particle sizes: 11.5 nm, 15.4 nm, 20.5 nm, 27.4 nm, 36.5 nm, 48.7 nm, 64.9 nm, 86.6 nm, 115.5 nm, 154 nm, 205.4 nm, 273.8 nm and 365.2 nm. The study of the content of ultrafine particles in the WZA was carried out at the sinter factory workplace (WP) in different areas of the sintering department: the head part of the sintering machine (SM) ($n = 39$), the control room of SM No. 1 ($n = 130$), the tail part of the SM ($n = 52$), where workers spend a long time during their work shift, managing the sintering process, controlling the operation of equipment and machines.

The results obtained were compared with the results obtained at the WP in the area of the SM control room (isolated WP from the shop floor), as well as with the results at the WP of employees of the plant management department ($n = 130$) who are not exposed to industrial aerosol and have acceptable working conditions, so they were taken as a control group.

Statistically, the study results were processed using the Statistica, version 13 licensed software package (Copyright 1984–2018 TIBCO Software Inc. All rights reserved. License No. JPZ8041382130ARCN10-J). The normality of the distribution of quantitative features was determined with the Shapiro–Wilk test. Since all the values were distributed abnormally, the descriptive statistics were presented as the median with interquartile range – Me (Q_{25}; Q_{75}). The Mann–Whitney test assessed the reliability of differences in the compared values. Differences were considered probable at the level of statistical significance $p \leq 0.05$.

The chemical composition of the SPM isolated from the WZA was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using "Optima 2100 DV" instrument (PerkinElmer, USA) [NIOSH, 2001, GOSTISO 15202-2008]. The obtained results were processed using the software of the OES-IMP device WinLab32 in the Windows XP prof operating system. The results were compared with the maximum permissible concentrations (MPC) for the WZA according to Order

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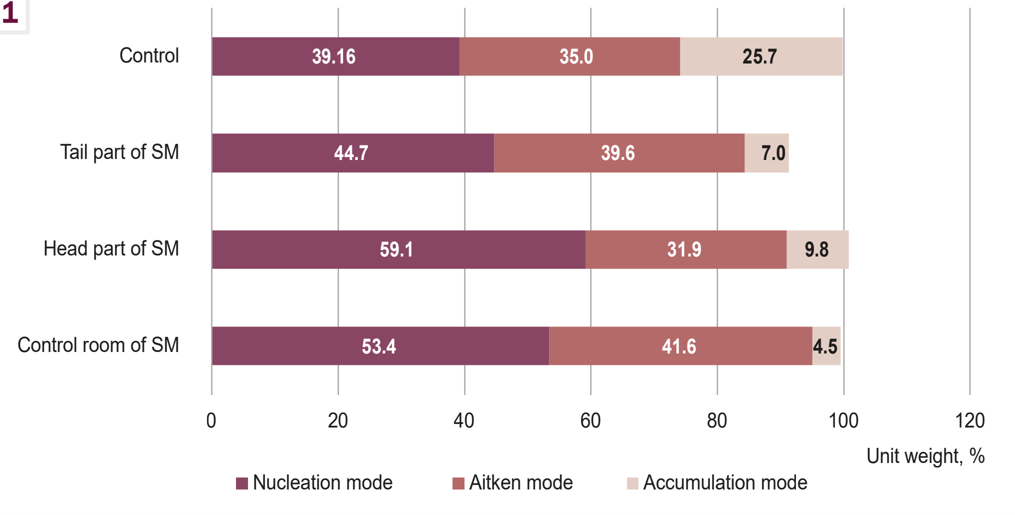

Fig. 1. Cumulative concentration of ultrafine suspended particles of the nanoscale at the workplace of sinter operators and control group workers, %.

No. 1596 “Hygienic regulations of chemicals in the working zone area” dated July 14, 2020.

Results

The metallurgical plant includes a sinter factory, which consists of the following divisions: car tipping division, receiving bins, raw material distribution division, raw material warehouses, charge bins, fuel and flux grinding and crushing divisions, sintering division, gas-treating facilities, sinter sorting and cooling divisions, and a “return” sorting division. The sinter factory is a complex set of structures, mechanisms and machines for producing iron ore sinter, which is subsequently used in blast furnace ironmaking to produce cast iron. The main equipment of the sintering division includes a sintering machine (SM), which agglomerates the sinter from iron ore and metallurgical waste using limestone and fine coke as fuel. The sintering process begins at the sintering head of the SM, where the raw material is loaded onto the sinter strand and passed under the SM ignition furnace, where natural gas with a combustion temperature of about 2200–3000 °C is burned, resulting in the agglomerating of the sinter. The finished sinter slowly moves on the sinter stand pallets, cooling down. At the tail end of the SM, the pallets enter the sinter strand rounding and are then fed to screens to screen out small pieces and return them to the previous stages. The finished sinter is cooled by atmospheric air and screened on vibrating screens in the sorting division for further transportation to the next technological processes.

The sintering department employs sinter operators who control the sintering process and monitor the operation of equipment and machinery. While performing technological operations, they are exposed to high concentrations of industrial dust and chemicals [13]. As a result of the study of the WZA on the sinter factory WP for the content of ultrafine SPM, it was found that ultrafine particles of the nanoscale range were present in all areas of the sintering department. It was found that the quantitative concentration of ultrafine SPM on the sinter factory WP in the head part of the SM ranged from 3.02×10^4 to 3.12×10^4 per cm^3, and in the tail part of the SM from 5.09×10^4 to 7.59×10^4 per cm^3. In the SM control room No. 1, where the sinter operator’s WP is isolated from the main factory, the quantitative concentration of SPM was lower than in the previous WPs and ranged from 2.06×10^4 to 2.38×10^4 per cm^3. The lowest quantitative concentration of SMP was recorded at the WP of workers in the control group – from 1.43×10^4 to 1.73×10^4 per cm^3.

When studying the concentration of ultrafine SPM by individual sizes, it was found that their amount on the sintering machine in the head part compared to the WP in the control room during agglomerating of the sinter was significantly higher for the following sizes: 11.5 nm, 15.4 nm, 20.5 nm, 27.4 nm, 36.5 nm, 48.7 nm, 115.5 nm, 154 nm, 205.4 nm, 365.2 nm ($p \leq 0.014$) and 273.8 nm ($p \leq 0.001$). At the WP in the tail part of the SM, the amount of SMP of 11.5 nm ($p \leq 0.008$), 15,4 nm, 36.5 nm, 48.7 nm, 64.9 nm and 86.6 nm ($p \leq 0.005$) was significantly higher compared to the WP in the control room. No significant difference was observed in the number of particles of larger sizes (from 86.6 nm to 365.2 nm) on these WPs.

The quantitative concentration of ultrafine SPM by individual sizes on all sinter factory WPs compared to control group workers had a significant difference *(Table 1)*. In the control group workers, the amount of larger-sized SPM (≥154 nm) was statistically significantly higher compared to the WPs in the head part of the SM and the control room. The data obtained allow us to conclude that pyrometallurgical technological processes, such as agglomerating of sinter, are a source of ultrafine SPM entering the air of the working area in a significant concentration.

When calculating the cumulative concentration of ultrafine nanoscale SPM (≤100 nm), it was found that the largest percentage of it was part of the industrial aerosol on the sinter factory WP in the head part of the SM, and in the SM control room – 91 % and 95 %, respectively *(Fig. 1)*. The highest percentage of larger particulate matter (accumulation mode) was recorded at the work-

Table 1. Analysis of the content of ultrafine suspended particles in the air of the working zone air of sintering division workers (number, amount/cm^3), Me (Q_{25}; Q_{75})

Size	Head part of SM, n = 39	Tail part of SM, n = 39	SM control room, n = 130	Control group, n = 130
11.5	1130.27 (966.15; 1336.49)*,§	1733.98 (1204.963; 2053.43)*,§	709.58 (650.58; 763.57)§	359.69 (328.64; 460.28)
15.4	1743.64 (1276.66; 1988.06)*,§	1894.36 (1711.61; 2247.50)*,§	930.04 (867.49; 973.44)	826.71 (773.45; 911.43)
20.5	1936.72 (1445.63; 2028.59)*,§	1409.31 (896.88; 2411.39)	801.98 (777.45; 837.13)§	991.59 (970.54; 1071.37)
27.4	3864.64 (3309.15; 4099.98)*,§	4606.96 (3493.75; 5280.79)*,§	1884.11 (1874.13; 1951.86)§	1385.24 (1332.24; 1441.37)
36.5	4996.45 (4586.25; 5133.24)*,§	8694.64 (7540.79; 8989.50)*,§	3149.58 (3064.53; 3260.27)§	1234.26 (1167.83; 1319.88)
48.7	4935.93 (4797.18; 4971.93)*,§	11345.50 (9204.65; 11750.50)*,§	3879.41 (3797.62; 4142.79)§	1126.94 (967.87; 1175.57)
64.9	4193.93 (4114.54; 4212.06)§	9797.28 (8322.21; 11559.50)*,§	3813.07 (3756.85; 4147.71)§	1302.93 (1232.74; 1434.91)
86.6	3404.47 (3217.91; 3475.45)§	8352.93 (3969.55; 10785.50)	3051.63 (3009.14; 3345.51)§	1860.75 (1795.31; 2023.13)
115.5	2471.49 (2214.05; 2596.26)*	4695.19 (1265.40; 8320.89)	1902.26 (1821.69; 1954.23)§	2160,79 (2080,66; 2229,92)
154	1591.78 (1254.43; 1602.72)*,§	3918.62 (1592.57; 5337.01)	753.54 (720.89; 773.99)§	1841.39 (1788.77; 1904.39)
205.4	795.19 (605.99; 958.19)*,§	0.00 (0.00; 5977.00)	75.12 (32.42; 136.75)§	1203.25 (1166.88; 1231.23)
273.8	344.67 (338.86; 615.48)*	0.00 (0.00; 6736.00)	0.00	597.66 (559.73; 643.72)
365.2	416.13 (320.19; 535.51)§	277.27 (0.00; 4392.35)	129.28 (115.18; 159.05)§	275.30 (243.14; 312.76)

***:** statistically significant difference with the sinter operator's workplace in the SM control room (≤0.05); **§:** statistically significant difference with the control group (≤0.05).

Table 2. Chemical composition of ultrafine suspended particulate matter (number/cm^3) in the working zone air in different areas of the sintering division

Chemical element	Head part of SM		Tail part of SM		SM control room		MPC*
	min/max	median value	min/max	median value	min/max	median value	
Al	0.001/0.006	0.004	0.0003/0.0050	0.004	0.003/0.005	0.004	6.00
Ca	3.42/3.62	3.490	2.41/2.64	2.520	1.45/2.55	1.990	1.00
Fe	0.002/0.004	0.003	0.0003/0.0030	0.002	0.0003/0.0050	0.005	6.00
Mg	0.41/0.60	0.500	0.21/0.22	0.220	0.26/0.48	0.370	4.00
Mn	0.001/0.002	0.001	0.006/0.009	0.008	0.003/0.008	0.005	0.05
Si	1.32/2.23	1.770	1.54/1.66	1.600	1.52/3.41	2.460	1.00
P	0.39/0.64	0.500	–	–	–	–	0.20

***:** MPC is according to the Order No. 1596 "Hygienic regulations of chemicals in the working zone area" dated July 14, 2020.

place of workers in the control group (25.7 %) and accounted for almost a third of the studied air in the working area.

In the head part of the SM, the highest quantitative concentration of nanoparticles was observed in the size range from 27.4 nm to 115.5 nm *(Fig. 2),* which accounted for 67.9 % of the total number of detected SPM in the working zone air. In the tail part of the SM and the control room, the largest number was recorded among particles with a size of 36.5 nm to 86.6 nm and accounted for 60.6 % and 65.8 % of the total amount of detected SPM in the UIA, respectively. In the control group employees, the largest number of particles was in the size range from 86.6 nm to 154.0 nm, accounting for 38.5 % of the total number of detected SPM.

The total surface area of nano range ultrafine SPM at a sinter operator's WP near the head part of SM ranged from 7.22 × 10^8 to 9.20 × 10^8 nm^2/cm^2; near the tail part of the SM, it ranged from 7.41 × 10^8 to 1.19 × 10^9 nm^2/cm^2, at the control group's WP – from 6.74 × 10^8 to 7.93×10^8 nm^2/cm^2, but at the WP in the control room it was the smallest – from 3.61 × 10^8 to 4.13 × 10^8 nm^2/cm^2. The surface area of this SPM by individual dimensions is demonstrated in *Fig. 3.* It was determined that the surface area was larger for the SP with the highest quantitative concentration.

The surface volume of ultrafine nanoscale SPM had different values in different parts of the SM with maximum values at the WP in the tail part of the SM – from 1.88 × 10^{10} to 4.24 × 10^{11} nm^3/cm^3 and at the WP near the head part of the SM – from 2.29 × 10^{10} to 3.19 × 10^{11} nm^3/cm^3, the lowest values were recorded in the control room – from 8.03 × 10^9 to 1.10 × 10^{10} nm^3/cm^3 and in the control group – from 2.19 × 10^{10} to 2.83 × 10^{10} nm^3/cm^3.

The mass concentration of ultrafine SPM at a sinter operator's WP near the head of the SM ranged from 27.49 μg/m^3

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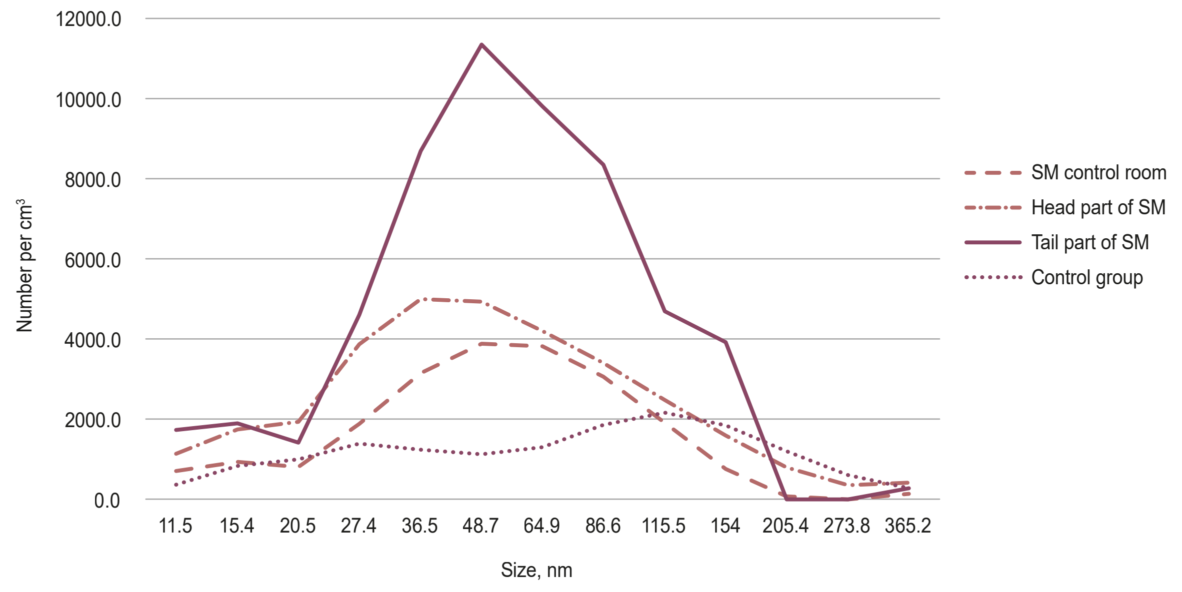

Fig. 2. Quantitative concentration of ultrafine suspended particles (number/cm^3) in the air of a sinter operator's working zone in different areas of the sintering division, and control group employees.

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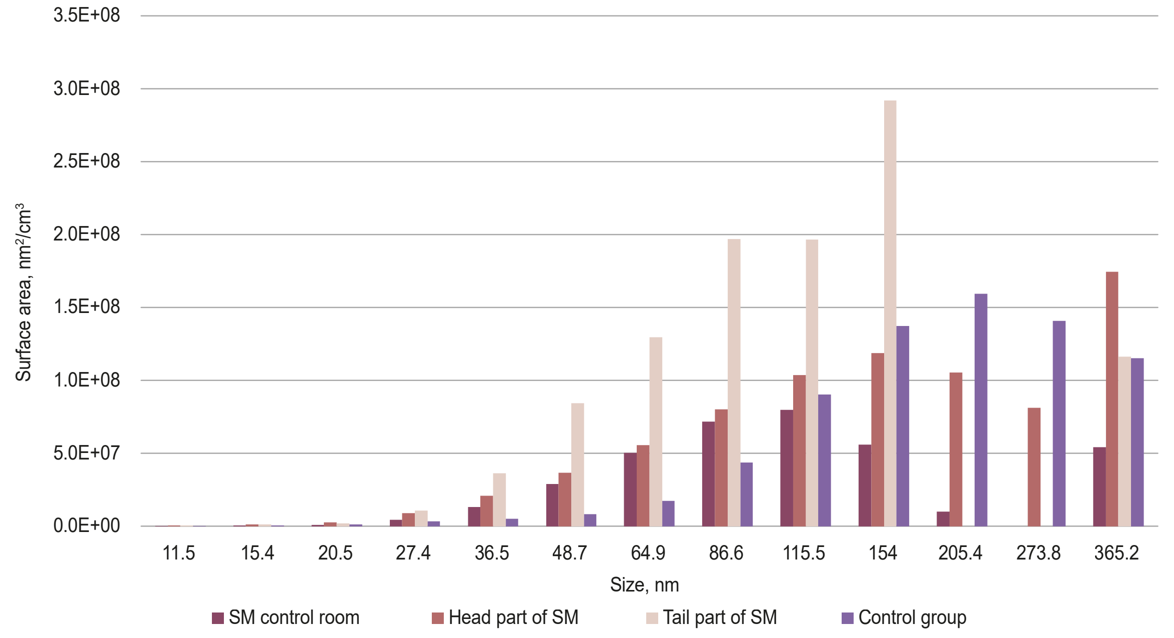

Fig. 3. The surface area of ultrafine suspended particles of different sizes (nm^2/cm^3) in the working zone air in different areas of the sintering division, and for control group employees.

to 38.24 µg/m^3, in the tail of the SM – from 22.55 µg/m^3 to 508.35 µg/m^3, in the control room the concentration was the lowest – from 9.63 µg/m^3 to 13.20 µg/m^3, and the maximum mass concentration in the control group was 33.91 µg/m^3. The high mass concentration of ultrafine SPM in the tail part of SM is associated with the highest number of larger SP (115.5 nm and 154.0 nm). High indicators of mass concentration, area and surface volume in workers of the control group were noted due to a greater number of large SP in the UIA composition (≥115.5 nm).

The study of the chemical composition of ultrafine particulate matter at a sinter operator's WP is presented in *Table 2,* showing that the air contains particles containing aluminum, calcium, iron, magnesium, manganese, silicon, and phosphorus. According to Order No. 1596 "Hygienic regulations of chemicals in the working zone area" dated July 14, 2020, the MPC in the WZA was exceeded by 2.0–5.5 times for calcium, 1.6–2.5 times for silicon, and 2.5 times for phosphorus, while other chemical elements did not exceed the MPC and met the hygienic requirements.

Discussion

Our study of the samples of WZA for the presence of ultrafine SPM at sinter operators' WP during agglomerating of sinter confirmed their presence in various quantitative concentrations at all stages of the technological process, which coincides with the studies of Gabriele Marcias et al. [14], who determined the content of SPM in WZA at a steel plant and M. Järvelä et al. [15] at a ferroalloy plant. As in our study, the authors quantified ultrafine particulate matter in the metallurgical industry workers' WZA to determine the number of particles and their size distribution. Their investigations confirmed the presence of many ultrafine particles in the WZA directly next to the metal melting point and a gradual decrease in their concentration at the WPs located at a distance from the melting process. Our studies also found that the largest amount of ultrafine SPM is formed at WPs near the melting point (the head and tail parts of SM), while workers not involved in the melting process are exposed to the lowest quantitative concentration. The authors state that studying the amount of ultrafine SPM, its size distribution, and the determination of its chemical composition is an important step in determining occupational risks levels for workers in these conditions.

Contrary to other studies, we measured and analyzed not only the quantitative concentration of SPM but also its other physical characteristics: total surface area and volume, mass concentration for SPM in general and separately for different sizes. According to the scientists, the value of the total surface area of suspended particles, which we measured in different areas of the sintering division, is important. The largest surface area was characteristic of the SPM, whose quantitative concentration was the highest. This value is undoubtedly important since with an increase in surface area, the possibility of adsorption on the SP and the transport of additional pollutants from the environment to the worker's body rises, which increases their toxicological properties to biological structures of the body [16].

In our work, we also determined the chemical composition of suspended particles. We found that WZA of the sintering division contained suspended particles comprising aluminum, iron, manganese, magnesium, calcium, silicon, and phosphorus, which corresponds to the technological process of agglomerating sinter with the addition of various impurities. Our data on the chemical composition of suspended particles is confirmed by several foreign studies that have established the presence of these elements in the air from emissions of various industrial enterprises, including the metallurgical industry. The presence of these metals in the nanoscale range is due to the peculiarities of the technological process when during pyrometallurgical technological operations of melting or sintering, SPs of various sizes are formed and enter the workers' WZA [14,17].

It is worth mentioning that our studies confirm the effectiveness of collective means of protection of workers (isolated sinter operator's WP in the control room) against the effects of ultrafine range SPM. It has been determined that the SPM quantitative concentration and surface area in the control room were significantly lower by 1.3–2.5 times compared to the WP near the sinter melting site. These data can be used in the risk management system from exposure to ultrafine SPM.

Thus, the study of WZA for the content of the ultrafine range SPs and their physicochemical characteristics is necessary for the hygienic assessment of production factors and determination of occupational risk levels at different WPs at metallurgical plants and other industries to develop and implement effective measures for the prevention of occupational and industrial pathology.

Conclusions

1. It has been established that in the process of agglomerating the sinter in the sintering division, a large amount of ultrafine nanorange SPM is formed. The concentration of SP in the sintering division during agglomerating of the sinter had a statistically significantly higher amount of ultrafine SPM ($p \leq 0.05$) compared to WPs of the control group employees who were not involved in melting processes.
2. The chemical composition of ultrafine industrial aerosol includes iron, manganese, magnesium, silicon, phosphorus, and calcium, which is explained by the use of these substances during the agglomeration of the sinter. Exceeded values of the MPC according to Order No. 1596 "Hygienic regulations of chemicals in the working zone area" dated July 14, 2020, were determined for calcium, silicon and phosphorus. Other chemicals did not exceed the MPC, but it should be noted that due to their ultra-small size, they can have an increased toxic effect on the biological structures of the body.
3. The studies conducted at a sinter operator's WP in the control room confirm the effectiveness of collective protective measures in the system of occupational risk management against the effects of ultrafine SPM (reduction in quantitative concentration by 1.3–2.5 times).

Prospects for further research. In the future, it is planned to study the health status of workers in the studied occupational group by calculating the level of occupational risk for the purpose of early and effective prevention of occupational and occupation-related pathology. In the future, it is planned to study the health status of workers of the studied occupational group by calculating the level of occupational risk for the purpose of early and effective prevention of occupational and occupationally induced pathology

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