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HYGIENE, SANITATION, EPIDEMIOLOGY AND MEDICAL ECOLOGY

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STUDY OF 1-HYDROXYPYRENE PAH EXPOSURE IN URINE OF WORKERS OF THE ALUMINUM SMELTER IN EASTERN SIBERIA

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Aim: to study the content of the biomarker of PAH exposure – 1-hydroxypyrene (1-OHPyr) in the urine of workers in modern aluminum production in Eastern Siberia.

Materials and methods. 159 workers of electrolysis workshops with the technology of self-baked and pre-baked anodes were examined. The I group included 142 workers of the main professions engaged in the servicing of electrolyzers, anodes and cranes, the group II included 17 workers of auxiliary professions for pouring metal. The control group consisted of 14 people. Determination of 1-OHPyr was carried out by chromatography-mass spectrometry on an Agilent 7890A gas chromatograph. The data was processed in the Statistica 6.1 program.

Results. Significant differences were established between the median levels of 1-OHPyr in urine among workers of the main (2.2–75.2 µg/l) and auxiliary (0.48–7.6 µg/l) occupations in comparison with the values of the control group (0.17 µg/l) and Biological Exposure Index (2.5 µg/l, AGGIH 2020). The concentrations of 1-OHPyr in anodes workers were 6.4–20.9 times higher than those of electrolyzers workers and crane operators, and 9.9–156.7 times higher than the levels of auxiliary professions. The lowest concentrations of 1-OHPyr were found in urine samples of workers - operators of workshops with the technology of pre-baked anodes.

Conclusion. The research results confirmed the increased professional impact of PAHs on aluminum production workers. The highest levels of 1-OHPyr in urine, characterizing the internal loads of PAHs and the associated high risk of health disorders, were found in operators servicing anodes of workshops with the technology of self-baked anodes.

Keywords: polycyclic aromatic hydrocarbons, 1-hydroxypyrene, aluminum production, workers.

Introduction. Polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent toxic substances, which can accumulate in the environment and in the body, have high toxicity, carcinogenic and mutagenic activity, and have a harmful effect on human health and his offspring [7, 9]. The increased content of PAHs and oncological diseases are noted in such carcinogenic industries as smelting of

aluminium, cast iron and steel, coal gasification, getting coke, bitumen and asphalt of roads etc. The impact of PAHs on workers in these industries is usually due to a different chemical mixture of PAHs. They include known (group 1), probable (group 2a) and possible (group 2b) carcinogenic compounds: benz(a) pyrene, dibenz(ah)anthracene, benz(a) anthracene, chrysene, benz(h)fluorene etc. Entering the body, chemical compounds of PAHs are biotransformed mainly by the monooxygenase enzyme system of the liver, forming specific indicative hydroxylated metabolites [13].

Based on a large number of studies conducted, it has been shown that the level of PAHs metabolites in urine can be used as a biological indicator of the adverse effects of PAHs. 1-hydroxypyrene (1-OHPyr) is recognized as a particularly preferred parameter for assessing the effects of PAHs among a number of metabolites, since pyrene is the main component in PAHs mixtures, and its metabolite correlates well with the total PAHs content in the air and DNA damage in persons exposed to benz(a)pyrene [5, 10, 11, 16]. The available foreign publi-

cations provide separate information about the levels of excretion of 1-OHPyr in urine and the risk of health disorders in workers of aluminum smelters in a number of countries [8, 11, 14], however, in Russia, such studies, to date, have not been properly reflected in the literature.

In this regard, the aim of the work was to study the content of the biomarker of PAH exposure – 1-OHPyr in the urine of workers of modern aluminum production in Eastern Siberia.

Materials and methods. The present study involved 159 workers of electrolysis workshops using the traditional technology of producing aluminum with self-baked anodes (TTSBA) and modernized – with pre-baked anodes (MTPBA). All employees participating in the study were classified into professional activity groups: group I consisted of the main professions engaged in maintenance electrolyzers, anodes and lifting cranes (average age 37.4–37.5 years and average experience 6.7–9.0 years), group II included auxiliary professions working the metal pouring and ladle farming (average age 40.3 years, average experience 5.8 years). The control group consisted of 14

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a person who does not have professional contact with PAHs. The persons included in the studies received information about the purposes of the examination and signed an informed consent issued in accordance with the Helsinki Declaration of the World Medical Association (2008).

Urine samples from workers were collected during a medical examination in the polyclinic of the plant in propylene containers, which were stored at a temperature of -20°C until analysis. Determination of concentrations of 1-OHPyr in urine was carried out by chromat-mass-spectrometry on an Agilent 7890A gas chromatograph with an Agilent 5975 mass selective detector using an improved method of analyte sample preparation [2]. The results of measurements of 1-OHPyr in the urine of workers were compared with the median level of the control group (0.17 µg/l) and the limit value of the biological exposure index (BEI) in urine established by the American Conference of Governmental Industrial Hygienists (ACGIH), which is 2.5 µg/l [15].

Statistical processing of the obtained results was carried out using the Statistica 6.1 program, using the nonparametric Mann–Whitney criterion with and without Bonferroni correction. The normality of the distribution of quantitative indicators was checked using the Shapiro-Wilk criterion. The results of the conducted studies are presented in the form of median, interquartile range and concentration interval, µg/l.

Results and discussion. Analysis of the results of the conducted studies showed that the median concentrations of 1-OHPyr in the urine of workers of the main professions of workshops with TTSBA varied in a wide range from 3.6 to 75.2 µg/l and were higher ($p < 0.05$)

than the level of the control group and the limit value of BEI (ACGIH, 2020) by 21.2–442.3 and 1.4–30.1 times, respectively (Table). At the same time, the highest median levels of 1-OHPyr content in urine exceeding the limit parameter BEI (2.5 µg/l) were observed in anodes workers (30.1 times) and crane operators (4.7 times), while in electrolyzers workers it was the lowest – 3.6 µg/l.

Quite other levels of 1-OHPyr excretion with urine were observed in workers in workshops with MTPBA. The median values of 1-OHPyr in the urine of operators of automated maintenance process of modern electrolysis baths were 2.2–6.8 µg/l, exceeding the limit value of BEI by 1.4–2.7 times only for operators servicing electrolyzers and crane operators. In general, the observed level of 1-OHPyr in the urine of the entire cohort of workshops operators with MTPBA was 3.1 times lower than that of workshops workers with TTSBA ($p < 0.05$). This may indicate higher levels of PAH exposure in workers of workshops using TTSBA.

Among workers of auxiliary professions, approximately the same parameters of the content of 1-OHPyr in urine (according to a median 0.48–7.6 µg/l) were noted as in workers of the main professions of new workshops with MTPBA. The excess of the median concentrations of 1-OHPyr in urine relative to the limiting level of BEI was observed only in metal pourers (brigade of pouring) (by 3.0 times).

The data obtained are consistent with the results of foreign studies carried out at aluminum plants in Sweden, France and Slovenia [8, 12, 14], indicating the presence of high PAH exposures and levels of 1-OHPyr in the urine of persons working near electrolyzers and anodes.

Some authors have suggested that exposure to PAHs at the level of 1-OHPyr in the urine of 4.4 µg/l may correspond to a relative risk of developing lung cancer at approximately 1.3, and the content of 1-OHPyr in the urine over 7.7 µg/l should be assessed as a higher risk of lung carcinoma for workers [3, 6]. However, it should be borne in mind that the harmful effects of PAHs on the body significantly depend on the chemical structure of the hydrocarbon itself and carcinogenic properties. After absorption in the body, many PAHs are metabolized to different types of reactive compounds capable of binding to DNA and initiating a carcinogenic process. Carcinogenic metabolites act on the principle of covalent binding to DNA, cause replication error, transcription changes and subsequent mutation, which leads to suppression of apoptosis, the onset of cell malignancy and the growth of a cancerous tumor [4, 13].

As our studies have shown, the anode workers of the workshops with TTSBA, serving coal anodes in electrolyzers, the levels of 1-OHPyr in urine were the highest, significantly exceeding the limit of BEI and the parameters of 1-OHPyr in workers of other groups of professions, which, combined with an increased content of PAHs (including benz(a)pyrene) in the air of these workshops [1] indicates a serious threat to their health. At the same time, the lowest concentrations of 1-OHPyr were noted among workers of new electrolysis workshops with MTPBA. Thus, the detected high levels of 1-OHPyr content and their significant excess of the BEI value in the urine of aluminum production workers may indicate the presence of an increased occupational carcinogenic risk of their health disorders. The performed pilot study confirms the feasibility of determining the PAH

Concentrations of 1-OHPyr in urine of workers of electrolytic aluminum production

Type of technology, profession	n	Me (Q25–Q75), µg/l	Min–Max, µg/l
TTSBA. All workers	112	11.0 (2.3–39.5)*. **	0.17–267.0
Electrolyzers worker	49	3.6 (1.5–13.3)▲	0.17–98.0
Anodes worker	26	75.2 (15.0–138.6)▲. ■. ♦	0.87–267.0
Crane operator	37	11.8 (2.7–30.0)■	0.18–57.7
MTPBA. All workers	30	3.5 (1.4–7.3)*	0.61–14.7
Operator of maintenance electrolyzers	16	3.5 (1.2–8.0)	0.61–14.7
Operator of maintenance anodes	6	2.2 (1.4–3.7)*	1.1–7.3
Operator of maintenance crane	8	6.8 (1.9–8.4)	0.81–10.9
The site of metal pouring and ladle farming. All workers	17	6.7 (0.96–9.1)**	0.21–29.8
Metal pourers:			
Brigade of pouring	10	7.6 (4.9–14.5)•	0.96–29.8
Brigade of cleaning	7	0.48 (0.37–4.8)•	0.21–9.1
Control group	14	0.17 (0.10–0.30)	0.08–0.9

Notes: *, **, ♦, • – the differences of the compared indicators are statistically significant at $p < 0.05$; ▲, ■ – the differences of the compared indicators are statistically significant at $p < 0.017$.

marker 1-OHPyr in urine to assess the harmful effects of PAH on the body and related major types of health disorders in aluminum plant workers.

Conclusion. The results of the conducted studies have shown that a particular problem in modern aluminum production is the continued exposure of workers to harmful chemical compounds of PAHs. The highest levels of 1-OHPyr in urine, characterizing the internal loads of PAHs and the associated high risk of health disorders, were found in the anodes workers in the workshops with TTS-BA. It is necessary to continue research on biomonitoring of 1-OHPyr in the urine of aluminum production workers during preventive medical examinations to prevent production-related diseases.

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