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Study of Fractional and Component Composition of High-Dispersed Dust Particles in Air of the Work Area of an Aluminum Smelter

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Abstract—The physicochemical properties of high-dispersed dust in the work area of an aluminum smelter have been studied by electron microscopy and X-ray diffraction analysis. It is shown that dust suspended in air is a complex heterogeneous mixture of chemically diverse crystalline and spherical-shaped, individual or agglomerated, fine and nanostructured particles. It is established that aerosol mixtures contain up to 95% of the fraction of up to 10 μm in size and up to 46.2% of the fraction of less than 0.5 μm, which occur predominantly in the work areas of crane operators and crane maintainers. The typical major dust components are fluorine, carbon, aluminum, sodium, oxygen, silicon, iron, sulfur, chromium, and nickel.

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INTRODUCTION

In view of the rapid development of nanotechnologies, the issues of assessing the hazard of nanosized aerosol particles for the state of health of workers of industrial enterprises have become increasingly important [1–4]. The current situation demands hygienic research focused on the registration, identification, and content evaluation of fine and ultrafine particles in the composition of industrial aerosols and the determination of their effects and consequences for the organism with the purpose of widening the scientific understanding of this problem [5–7].

These issues are relevant in a number of industries that keep using production technologies implemented for a long time, in particular, aluminum smelters. The industrial production of aluminum is based on the technology of electrolysis of alumina solved in an electrolyte and fluorine salts using self-baking and prebaked anodes. In the process of aluminum production, air in the work area is polluted with a dust–gas mixture of chemically diverse harmful substances (gaseous and solid fluorine compounds; metal, carbon, and sulfur oxides; tars; PAHs; disintegration and condensation aerosols; etc.), which can cause significant health problems to workers [8, 9]. However, there are very few studies focused on the physicochemical properties of complex aerosol suspensions formed under conditions of aluminum production [10, 11].

The data on the disperse and component compositions of fine and ultrafine particles in the work areas for workers of the core occupations are highly insufficient. The study of the morphological features of particles and their agglomerates is of concern. The lack of data on the fraction of finely dispersed particles in the total amount of suspended dust and the poor exploration of the chemical elemental composition of an aerosol complicates an assessment of the hazard and personalized health risks for workers of an aluminum smelter.

The morphology and fractional and material compositions of high-dispersed and nanostructured particles in dust–gas aerosol suspensions at an aluminum smelter are studied.

EXPERIMENTAL

The study of the weight concentration of dust and the dispersion and component compositions of particles suspended in air was performed at a large aluminum enterprise in East Siberia implementing traditional technology with self-baking anodes (SBAT) and an advanced one with prebaked anodes (PBAT). The total suspended particle (TSP) levels were evaluated by the gravimetric method using portable aspirators and sampling on perchlorovinyl filters [12].

For a detailed study of the morphology and the disperse and material compositions of aerosol suspensions, dust was sampled directly at dust sources in the work areas on PTFE filters during the key technological operations. Aerosol particles were visualized by high-resolution scanning electron microscopy (3.5 nm) using a FEI Company Quanta 200 microscope at the Ultramicroanalysis Center for Collective Use, Irkutsk Scientific Center, Siberian Branch, Rus-

Table 1. Disperse composition of dusts formed in the key technological operations of aluminum production

Technological operation	Particle fraction, %				
	<1 μm	1–10 μm	10–30 μm	30–50 μm	>50 μm
Technology using self-baking anodes					
Crust breaking (n = 749)	2.3 ± 0.5	41.8 ± 1.8	42.8 ± 1.8	11.8 ± 1.2	1.3 ± 1.2
Skull cutting (n = 648)	6.6 ± 0.9	78.1 ± 1.6	13.4 ± 1.3	1.6 ± 0.5	0.2 ± 0.2
Hardening (n = 273)	28.6 ± 2.7	58.2 ± 2.9	12.5 ± 2.0	0.7 ± 0.5	–
Blasting of tool surface (n = 1112)	14.2 ± 1.1	65.7 ± 1.4	14.6 ± 1.1	4.1 ± 0.6	1.4 ± 0.3
Stud pulling (n = 156)	9.0 ± 2.3	78.8 ± 3.3	9.0 ± 2.3	1.9 ± 1.1	1.3 ± 0.9
Loading of anode mass (n = 86)	57.0 ± 5.3	36.0 ± 5.2	3.5 ± 1.9	3.5 ± 1.9	–
Technology using prebaked anodes					
Replacing of anodes (n = 245)	14.3 ± 2.2	62.1 ± 3.1	20.4 ± 3.3	2.0 ± 0.9	1.2 ± 0.7
Covering of anodes (n = 509)	21.4 ± 1.8	68.2 ± 2.1	9.6 ± 1.3	0.6 ± 0.3	0.2 ± 0.1

sian Academy of Sciences (SB RAS) on the basis of the Limnological Institute, SB RAS.

Filters with dust-particle samples for microscopy were prepared by sticking them on a double-sided carbon tape and on a special table with the subsequent gold-coating deposition in a BALZERS SCD-004 sputter coater. The elemental analysis of aerosol suspensions of the work area was performed using an EDAX local elemental energy dispersive X-ray microanalysis system. The element ratio was calculated using the EDAX Genesis device software by the ZAF method. The processing and study of 14 filters and the size evaluation of 7340 particles was performed.

The statistical processing and analysis of the hygienic and physicochemical results was performed using Microsoft Excel and STATISTICA 6.1 software.

RESULTS AND DISCUSSION

As a result of the research, it was established that, in the process of aluminum production, ten technological operations generate the highest amounts of dust, including crust breaking, skull cutting, hardening, loading of anode mass, stud pulling, blasting of tool surface, and replacing and covering anodes.

The data analysis for the mean-shift dust concentrations showed that the aerosol content at all workplaces for the core occupations in SBAT electrolysis departments were 3 times higher than TLV, with the values of 12–14 mg/m^3 for anode operators and 15–17 mg/m^3 for electrode-handling crane operators. Meanwhile, for PBAT, the mean-shift concentrations in the work area were within 1.0–1.5 TLV, and the maximum one-time levels in the technological processes characterized by the highest dust release reached higher values.

The study of the disperse composition of dust established that particles suspended in air are characterized by size heterogeneity (Table 1). In the technologies using self-baking and prebaked anodes, the most hazardous for health finely dispersed fractions were registered during hardening (28.6%), covering of anodes (21.4%), and loading of anode mass (57.0%). The predominance of respirable particles with the size of 1–10 μm was registered during skull cutting (78.1%), stud pulling (78.8%), blasting of tool surface (65.7%), and replacing and covering anodes (62.1 and 68.2%, respectively).

The analysis and consideration of the fraction of high-dispersed suspended dust at workplaces for the core occupations is highly important for the evaluation of the hygienic consequences of their impact. It was established that, at workplaces of electrolysis operators, anode operators (SBAT), and electrolysis bath maintainers and anode beam racking operators in the automated aluminum production process (AAPP) (PBAT), particles of the size of 1–3 μm (41.9, 42.7, 43.8, and 31.8%, respectively) were predominant in air. In the work area of anode operators, the fraction of particles with the size of less than 1 μm was 2 times higher ($p < 0.05$) than at the workplace of electrolysis operators (16.3 and 8.2%, respectively).

In cabs for a crane operator (SBAT) and an AAPP crane maintainer (PBAT), the fraction of dust particles with a size of up to 10 μm was 95.7 and 91.4%, respectively; in this amount, the fraction of up to 1 μm was 50.1 and 65.3%, respectively (Fig. 1). Note that, in the work area of crane operators (SBAT), the major fractions of particles in the total amount of dust were those with the sizes of 0.5–1 μm (34.7%) and 1–3 μm (34.3%); for AAPP crane maintainers (PBAT), the major fraction in the total amount of suspended dust was that of a size of up to 0.5 μm (46.2%). This fact

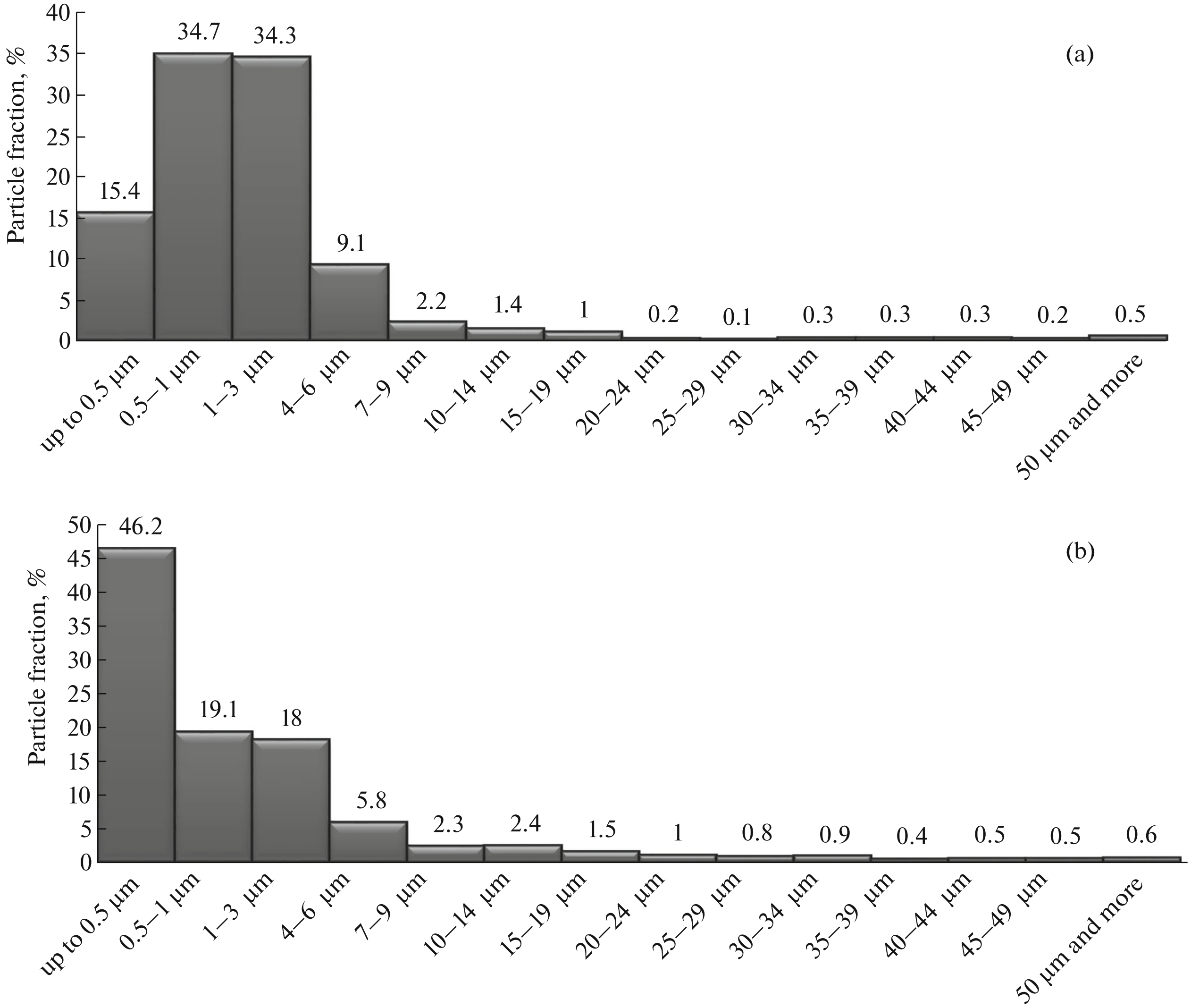

Fig. 1. Fraction histogram of dust particles at workplaces of a crane operator (a) and an AAPP crane maintainer (b).

demonstrates that ultrafine particles characterized by a large specific surface, which are the most hazardous for health of workers, are predominant in the work area of these professions.

The morphology study of dust particles showed that samples of suspended particles taken at workplaces at an aluminum smelter were characterized by shape heterogeneity (Fig. 2). Aerosol was predominantly formed in the technological operations from source raw materials used in the process of work and a condensed vapor during the high-temperature aluminum smelting. Dust particles detected in samples are both single and stuck to each other fine or agglomerated nanostructured particles of the size of 60 nm to 2 µm. In terms of shape and composition, most dust particles, which are polyhedrons of different shapes, form a typical disintegration aerosol, having a polymorphic structure with multiple sharp edges or a crystalline one. In the composition of suspended dust, individual, mostly oval or round, condensation aerosol particles are frequent. Note that the hygienic consequences of the impact of nanostructured particles identified in air on the organism are still poorly explored and need further studies.

The results of X-ray diffraction analysis showed that most dust particles suspended in air of an aluminum smelter are particles of alumina (aluminum oxide), cryolite, fluorine carbon compounds, and a mixture of aluminum fluoride and alumina. Their most frequent components are fluorine, carbon, aluminum, sodium, oxygen, silicon, and metal compounds (Table 2). In SBAT, the fraction of alumina (aluminum oxide) particles containing aluminum and oxygen as the predominant elements was 36.3 ± 2.4%; in PBAT, it was 12.2 ± 2.2%. Aluminum fluoride occurred mostly in mixtures with alumina with stuck soot particles and with an admixture of sodium, nickel, iron, calcium, silicon, and sulfur compounds. The fraction of agglomerates of this

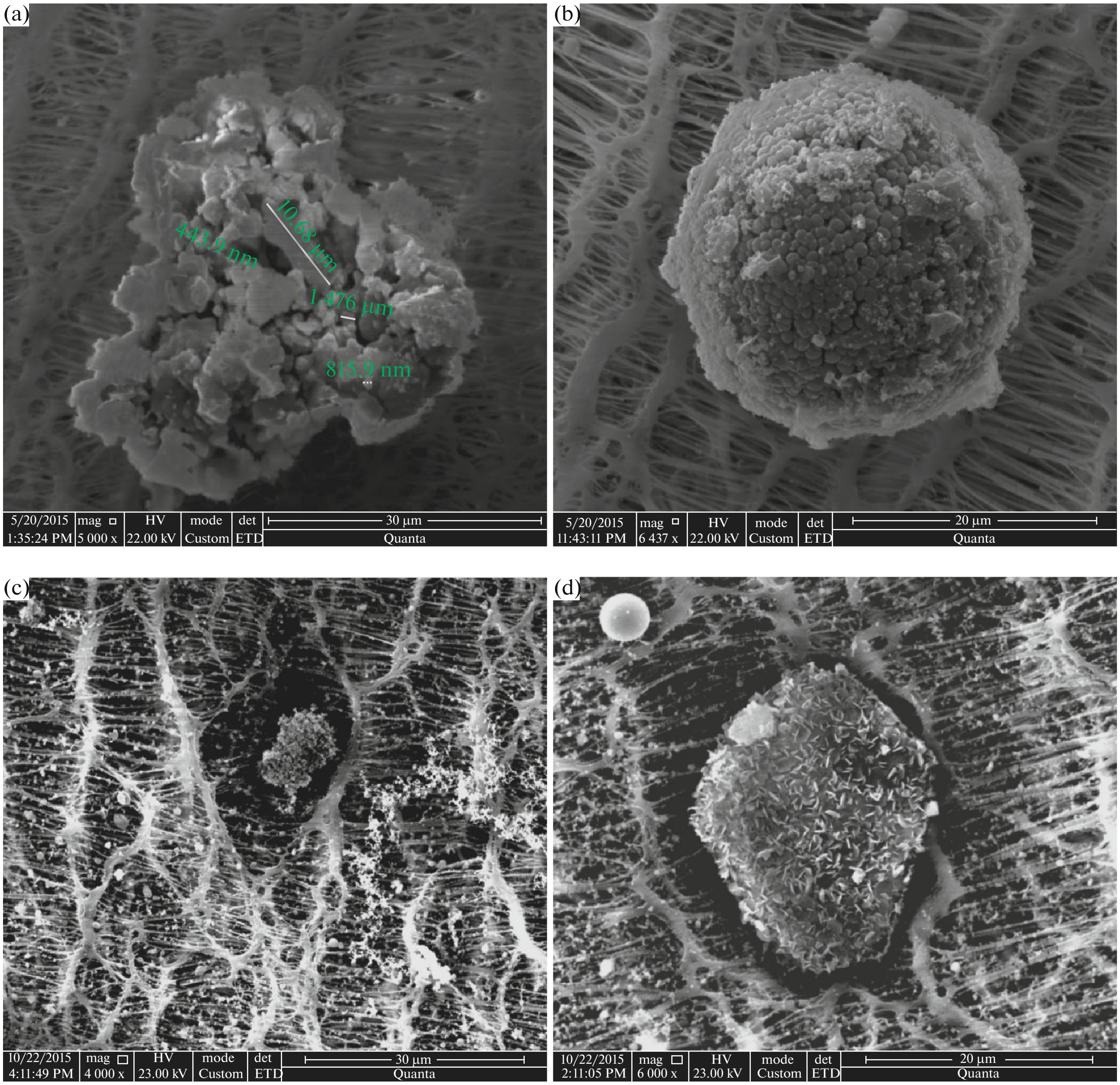

Fig. 2. (Color online) Microphotograph of disintegration aerosol and condensation aerosol samples consisting of stuck fine and nanostructured particle agglomerates.

dust mixture for SBAT and PBAT was 11.8 ± 1.6 and 19.2 ± 2.7%, respectively.

In collected aerosol samples, agglomerates consisting of fluorine, sodium, aluminum, and carbon were frequently registered. In terms of structure, according to the compositional analysis of the raw materials, these dust particles consisted of cryolite (Na_3AlF_6) with stuck soot particles. Apart from stuck soot components, cryolite particles contained admixtures of calcium, potassium, magnesium, nickel, sulfur, and silicon compounds. The fraction of these particles in the total amount of dust particles whose elemental composition was analyzed was 13.5 ± 1.7% in SBAT work areas and 29.6 ± 3.1% in PBAT work areas.

Among dust particles, there were agglomerates containing fluorine and carbon as major components, which consisted of soot or its mixture with fluorine compounds (e.g., HF) or fluorine–carbon compounds. In these agglomerates, microparticles containing admixtures of sodium, aluminum, nickel, sulfur, calcium, iron, magnesium, silicon, potassium, and chlorine compounds also occurred. The fraction of these agglomerates was 29.8 ± 2.3% for SBAT and 16.0 ± 2.5% for PBAT.

Table 2. Particles of different chemical compositions and their fractions (%) in the total amount of suspended dust in air of the work area for different aluminum production technologies ($M \pm m$)

Group of particles	Elemental composition of dust particles	Technology	
		self-baking anodes (n = 400)	prebaked anodes (n = 213)
Aluminum oxide (alumina)	Al, O, C, F, Na, K	36.3 ± 2.4	12.2 ± 2.2
Aluminum fluoride	Al, F, C, Na, K, Ca, N, O	0.8 ± 0.4	2.8 ± 1.1
Mixture of aluminum fluoride and alumina	Al, F, O, C, Na, Ni, Fe, Ca, Si, S	11.8 ± 1.6	19.2 ± 2.7
Cryolite	F, Na, Al, C, O, Ca, K, Mg, Ni, S, Si	13.5 ± 1.7	29.6 ± 3.1
Mixture of aluminum oxide and cryolite	F, Al, Na, O, C, Fe, K, Ca, S	4.0 ± 1.0	14.1 ± 2.4
Fluorine–carbon compounds	C, F, Na, Al, Ca, Fe, Mg, Si, K, Cl, Ni, S	29.8 ± 2.3	16.0 ± 2.5
Particles of other mixtures and compounds	Fe, F, O, C, Si, Al, Na, Ca, K, Mg, Cl, Cr, Fe, Zn, S	3.8 ± 1.0	6.3 ± 1.7

Italics denotes the major elements in the corresponding groups of particles.

CONCLUSIONS

A dust–gas aerosol of an aluminum smelter consists of chemically diverse individual or agglomerated micro- and nanostructured particles containing fluorine, carbon, aluminum, sodium, oxygen, silicon, iron, sulfur, chromium, and nickel. In air of the work area for operators that deal with electrolysis, anodes, baths, and anode beam racking, dust particles of the sizes of 1–10 μm are mostly registered (up to 68.2%). At workplaces of crane operators and AAPP crane maintainers, particles with sizes of up to 0.5 μm (up to 46.2%) are predominant. The combined effect of high-dispersed combined aerosol mixtures containing chemically diverse harmful compounds on the organism can cause highly negative consequences, which is important for an adequate analysis of the exposure and the health risk assessment for workers.

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