Evaluation of Nanoparticles Emission in Simulation of Experimental Model of Technological Process of Pig Lead Smelting

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Abstract. The results of investigations on determination of the peculiarities and regularities of lead fumes emission in the simulation of experimental model of technological process of secondary lead smelting are presented. Emission of the nanoparticles in a working zone air during secondary lead smelting under laboratory conditions has been evaluated. In the process of sample smelting a total concentration of the particles from 1 to 100 nm at 1 m distance from a muffle varied in the range of 24000-32000 particles/cm³. After dross removal the total concentration of nanoparticles in 1 minute has increased to a level of 50000 particles/cm³. The concentration of nanosized lead during smelting increased 3.1 times. Smelting of the secondary lead is accompanied by significant emission of nanorange particles (1-100 nm) into air of the working zone, in particular, lead nanoparticles in form of sulfide.

1. Introduction

Lead as a global pollutant of the environment and classical industrial poison is still in the focus of broad specialists, including environmentalists, toxicologists and occupational medicine professionals. In recent decades, the environmental and production aspects of lead influence have become particularly relevant [1,2,3] due to the fact that anthropogenic impact reached menacing proportions.

Lead has a sufficiently wide range of application in different branches of industry (lead smelting and coal combustion, lead-based paints, lead containing pipes or lead-based solder in water supply systems, battery recycling, grids and bearings, etc.) and household activities (everyday household products, children's toys), as well as large volumes of production and international trade, which promote its regular emissions into environmental medium, where it spreads far away from the pollution sources [4, 5]. This is a poison of cumulative action, which penetrates in a human body through a respiratory tract in the form of dust and vapors, enters an oral cavity by swallowing, from contaminated hands, through gastrointestinal tract. Lead is accumulated in all tissues, parenchymatous organs, but the main part of it (75%) forms a depot in bones [6]. Alcohol, overfatigue, fasting, harmful environmental factors mobilize lead from the depot. Entrance of lead into blood causes exacerbation of already existing diseases.

In Ukraine, the problem of lead danger has got special attention in the recent decades, when in the early 90's of the last century, the new, previously absent branches of industry start forming in the country due to restructuring the basic industries. The key place among them was production of the secondary lead and lead accumulators and batteries [7, 8].

It was assumed that the process of lead smelting can provoke formation of metal fumes with the particle size determined by their nanometric range. Under these conditions, the results of hygienic
studies on determination of lead concentration in the working zone air at the enterprises of battery industry can be understated. It is caused by the fact that the fumes with a particle size in the nanometer range have no ability to keep on the surface of AFA type filters, because they can easily penetrate through the filter pores, the size of which exceeds 100 nm.

Therefore, modern ideas about the peculiarities of biological effect of the nanosized fumes (1-100 nm) allow assuming that they have some contribution into development of the adverse changes in workers’ organism under condition of their presence in the working zone air. In particular, the experiments on laboratory animals show that lead nanoparticles, even at insignificant accumulation, exhibit high biological activity and reactive capability compared to macro-dispersed forms [9], while subchronic exposure of lead oxide nanoparticles have a profound negative effect on cellular as well as tissue levels [10].

Thus, the purpose of the work was to determine the peculiarities and regularities of emission of lead fumes in simulation of the experimental model of the technological process of secondary lead smelting.

2. Materials and investigation methods

An experimental model of the secondary lead smelting was simulated under laboratory conditions. For this, 1 kg of pig lead was placed in an open porcelain heat-resistant crucible of 250 mm diameter and melted in high-temperature muffle furnace "TermoLab" at 420 °C temperature (lead melting point 327.46 °C) for 60 minutes.

The samples were taken in sequence at 0.5 m distance from the muffle furnace during smelting (with closed muffle), muffle opening, removal of surface dross film.

To study the weight concentration of the suspended particles and concentration of the chemical substances, air with 0.5 l / min volume flow rate was aspirated using a TAYFUN P-20-2 sampler through Zaytsev absorber containing 10 ml of deionized water. The sample was filtered with the help of syringe, which was fitted with a filter holder including "Domnick Hunter" membrane disk filter (England) of 25 mm diameter and 100 nm pore size.

Composition of the air samples was studied by method of ICP atomic emission spectroscopy (ICP AES) using the atomic absorption spectrophotometer "Optima 2100 DV" (Perkin-Elmer, USA).

Concentration of the nanoparticles in the air of working zone was measured on diffusion aerosol spectrometer DAS-2702 (Russia).

The particle size was determined by scanning electron microscopy using Tescan MIRA3 microscope with local elemental energy-dispersive microanalysis system (Oxford Advanced Aztec Energy /EIE350 / X-max 80). The obtained results were processed using variation statistics methods applying Microsoft Excel and STATISTICA 6.0 Stat Soft Inc. software packages.

3. Results and their discussion

The technology of lead metal production consists of four stages, namely agglomeration, melting, removal of dross and pyrometallurgical refining. The so-called pig lead, obtained as a result of concentrate melting, contains ≥97% of lead, the rest is the impurities, which deteriorate its properties. Therefore, the pig lead is not used for any purposes in the industry, and comes to refinement. The task of refinement is removal of the impurities and increase of lead content to a standard level. Before refining the ingot of pig lead usually requires preliminary boiler treatment. In dross removal, it falls into slag of a boiler for impurities transfer and cooled to 370-425 °C temperature, which is slightly higher than its solidification point. The dross consisting of lead oxide, as well as copper, antimony and other elements, moves to the top and solidifies over molten lead, after which the dross is removed and fed into dross furnace for obtaining other useful metals. In turn, refining of the pig lead involves the sequential removal of the impurities taking into account chemical properties of the impurities or their compounds. At each refining stage, there is formation of the intermediate products, to which the impurities and part of the lead are transferred. The refined lead has 99.90 - 99.99% purity [8].
Application of the diffusion aerosol spectrometer DAS 2707 allowed studying the dynamics of particle concentration from 1 to 100 nm during melting of the secondary (pig) lead (as simulation of preparation before refinement). It should be noted that a background concentration of nanoparticles in the laboratory made from 8535 to 15000 particles / cm$^3$ (air temperature 26 °C and relative humidity 28%).

It is interesting fact that in the beginning of the experiment there were almost no particles of up to 10 nm size (the main amount is in 15-45 nm limits, Figure 1).

![Dynamics of concentration of particles in air during melting of unalloyed lead.](image)

Figure 1. Dynamics of concentration of particles in air during melting of unalloyed lead.

In turn, heating of the muffle furnace (temperature 480°C) promotes rise of the number of 5-10 nm size particles. During sample melting, the total concentration of particles from 1 to 100 nm at 1 m distance from the muffle varied from 24000 to 32000 particles / cm$^3$. At muffle opening (in 25 minutes after placing the lead sample in it), the total concentration of nanoparticles did not change significantly and made about 30000 particles / cm$^3$. In 12 minutes, the process of lead sample melting was prolonged by another 30 minutes, at that the total concentration of nanoparticles varied in 26000-30000 particles / cm$^3$ range. During the next opening of the muffle, the total concentration of particles from 1 to 100 nm at 25-30 cm distance from the sample did not significantly change and made around 30000 particles / cm$^3$. Instead, after shifting the dross with a pallet-knife, the total concentration of nanoparticles has increased to a level of 50.000 particles / cm$^3$ for 1 minute (Figure 2). At that, the main increase of concentration took place due to the following fractions of nanoparticles:

- 0-5 nm (from 498 to 5577 particles / cm$^3$);
- 5-10 nm (from 2924 to 9824 particles / cm$^3$);
- 10-15 nm (from 4617 to 8818 particles / cm$^3$);
- 15-20 nm (from 3889 to 5725 particles / cm$^3$);
- 20-25 nm (from 3008 to 3900 particles / cm$^3$).
Figure 2. Distribution of particles of 1-100 nm by size in air after dross shift.

At open muffle, the total particle concentration from 1 to 100 nm at a level of 40000-50000 particles / cm³ was registered during 20 minutes, after what it began gradual decrease.

In other words, these results can reflect the situation, which takes place at production during dross removal. Removal of the dross in process of pig lead melting before refining as well as removal of the impurities in the process of refining during liqation is accompanied by significant emission of nanoparticles.

Presence of lead nanoparticles in form of sulfide in the selected samples (Figure 3) was proved by electron microscopy.

In turn, application of atomic emission spectroscopy allowed determining the concentration of nanosized lead in the selected air samples during (sample 1) and after (sample 2) melting (Table 1).

It was determined that the content of nanosized lead after the experiment increased 3.1 times. Therefore, these results can represent the situation that takes place in the production at dross removal, namely, removal of the dross during pig lead melting as before refining, as well as removal of impurities in the process of refining during liqation is accompanied by significant emission of nanoparticles.

Presence of lead nanoparticles in form of sulfide (Figure 3) in the selected samples was confirmed by electron microscopy.

In turn, application of atomic emission spectroscopy allowed determining the concentration of nanosized lead in the selected air samples (sample 1) and after melting (sample 2) (Table 1).

It was determined that the content of nanosized lead after the experiment increased 3.1 times.
Figure 3. Identification of nanoparticles by raster electron microscopy (a) and their material composition according to the spectrum of EEDM (b)/

Table 1. Content of nanosized lead in the samples selected in air during and after melting of unalloyed lead [mg/m³]

| Element | Sample 1 | Sample 2 |
|---------|----------|----------|
| Pb      | 0.00013  | 0.0004   |

Thus, the results of the experiment can explain the situation that is observed at metallurgical plants from time to time, when the workers have the signs of lead intoxication without exceeding the current hygienic standards on content of chemical elements in the working zone air. At the same time, certain contribution of polluted environment, especially in the areas with unfavorable man-caused burden, also shall be taken into account.

4. Conclusions

1. It was determined that melting of the secondary lead is accompanied by significant emission of nanorange particles (1-100 nm) into the working zone air, in particular, lead nanoparticles in form of sulfide.

2. It was determined that the concentration of nanosized lead during melting increased 3.1 times.

3. It is reasonable to carry out thorough hygienic researches on assessment of nanospecific risk for workers of the corresponding industries.
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