Quantities and Distribution of Nano Metal and Micro-Particles at a Melting Furnace for Lead Wastes

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Abstract  Lead wastes are melted in the complex of Kovohutě Příbram nástupnická, a.s., mostly from discarded (broken) lead starter accumulators. Burning of coke in a charge inside a blast furnace causes melting of lead and its reduction. The melting is continually discharged into a siphon and subsequently tapped into moulds. Measurements of distribution of nano- and micro-particle were performed during the described operations. Meanwhile, the particles were collected on filters to analyse their shapes and chemical compositions; we also measured efficiency of regular respirators. Spherical, cubic, cuboid, cylinder and amorphous particles were found, with the prevailing composition of Pb and PbS alloys. However, the atmosphere in the furnace proximity contained also particles of other heavy metals that are considered high-risk elements from the viewpoint of toxicity. The work also includes a discussion about toxicity and how it is affected by composition and shape of the particles.

Keywords  Metal nano- and Micro-Particles, Respirator, Lead, Heavy Metals, Toxicity

1. Introduction

The complex of Kovohutě Příbram nástupnická a.s. Czech Republic [1 - 2] is organization, where is engaged in the production of raw lead from its waste in the blast furnace, with the subsequent refinement in rotary furnaces.

The charges into blast furnace are broken starter accumulators (including other waste containing lead), without electrolyte (H₂SO₄), as well as return slag, limestone, iron and iron oxides. The purpose of adding iron into the charge is sulphur separation – residual acid from accumulators. Sulphur and iron are chemically bonded to produce iron sulphide (so-called “matte”), which forms the separate separable part of the slag.[3]

Burning of coke in a charge causes melting of lead metal and its reduction. The temperature of molten lead in the furnace reaches the values of 1000 to 1100°C and a layer of oxidized lead enriched with other substances – slag is formed on its surface. This slag is skimmed (tapped) and cast into special containers (moulds), in which it is left to cool down. After cooling, the slag is removed out of the moulds and part of hedenbergite is separated to be partially returned back into the furnace and part of iron sulphide is separated, which is not yet further used and is stored. The tapping of the slag is carried out every 15-20 minutes. The molten lead runs out of the furnace into the trap (Fig. 1), and when it is full, it is tapped into the moulds to solidify (Fig. 2).
By emptying the casting mould we obtain raw lead in the form of a large brick with dimensions 500x1000x400 mm and weight of 1500 kg. The capacity of the blast furnace is approximately 120 t of lead per day.

When melting lead waste (mainly accumulators) in the blast furnace, the raw lead with the high content of impurities is tapped. This lead is subsequently subjected to a step-by-step refining process in order to remove copper (reaction with sulphur), Sn, As, Sb (by oxidation), precious metals Ag (by adding Zn – the Parkes process, i.e. formation of Zn – Ag alloy deposited on the surface of the melting) and to remove then Zn by vacuum distillation.

The aim of this study was to measure the distribution layout of Nano- and Micro-Particles, chemical composition, morphology and test the performance of respirators in the area of the blast furnace.

2. Experimental Part

The area around the blast furnace in the part at the tapping of molten lead was used to place the measuring technology for determining the quantity and distribution of nano- and micro-particles, the efficiency of respirators and for taking particles in order to determine their morphology or element composition. For layout of measuring technology, the distance from the tapping of lead (Fig. 1) out of the blast furnace was 3 - 4 m from the tapping of hot slag approximately 10 m.

The area in front of the blast furnace, where the tapping of the slag was carried out, was open to the outdoor room. The temperature around the measuring technology was approximately 8 – 10°C, the outdoor temperature was +3 to -2°C (rapid cooling was associated with snowstorm).

2.1. Used Measuring Technology

- The measurement of aerosol particles in the area of nano was performed by means of SMPS (Scanning Mobility Particle Sizer) 3934, comprised of the CPC 3022 system (Condensation Particle Counter) working in the low mode and the EC 3071 system (Electrostatic Classifier) equipped with the DMA probe 3081 (Differential Mobility Analyzer) and impactor 0.0457 cm.
- The measurement of aerosol particles in the area of micro was performed by means of APS (Aerodynamic Particle Sizer Spectrometer 3321 TSI, USA).
- The instrument for measuring and evaluating aerosol of solid particles in two areas (in front of and outside the respirator) compared to absolutely pure air was the Porta Count PRO‘ 8038 of the company TSI Incorporated, U.S.A.
- Selection for the purpose of chemical analysis and morphology determination of particles by means of Nano – ID sampler.
- The measurement of aerosol particles by means of SMPS 3934 and APS 3321

2.2. Tested Respirators

The area of the blast furnace was chosen to be the place for efficiency testing of respirator or its ability to prevent the respiration of nano- and micro-particles. The type Refil 530 FFP2 of uni size was used as the respirator; this is a disposable whole-filtering half mask meeting the requirements of ČSN 149 (czech standard). This standard respirator (affordable) should protect the user in the polluted working atmosphere against solid particles. Another tested respirator was SEGRE FFP2U, which is suitable as protection against solid and liquid aerosols. It has a low breathing resistance, soft sealing under the nose bridge stiffener, stable filtering capacity, the country of origin - Sweden. The test was performed on one testee (man) in the form of measuring the FIT factor $F$, which is the value defined as the ratio of concentration of the particles in front of the respirator and behind the protection of the respirator. The higher the value $F$, the safer protective equipment for the user. So-called efficiency of protective equipment $S$, given in %, is more practical expression (1):

$$S = 100 - \frac{100}{F} \text{ [%]}$$  (1)

Prior to the measurement, the respirators were provided with a hole for inserting the detector for measuring behind the respirator, followed by sealing and the tested person carried out certain actions during the measurement, which changed every minute. Those actions were: normal breathing, deep breathing, movements of head from side to side, up and down, speaking including faces, bending at the waist, normal breathing (according to OSHA 29CFR1910.134).

3. Results and Discussions

3.1. Results from FIT Factor and Efficiency Measurement of Respirator

The respirators were tested randomly during working cycles such as lead solidification in moulds, tapping of molten lead out of the trap into the moulds (see Fig. 2) and during continuous removal of molten lead out of the blast furnace into the trap (see Fig. 1). Unlike the distribution measurement of aerosol particles (see below), the efficiency measurement of the respirator was performed randomly,
without concentration on technological process. Nevertheless, Fig. 4 and 6 show the results of measurement, when the tapping of raw lead out of the trap into the moulds was carried out during the measurement (see Fig. 2). In this case, the number of particles in cm$^3$ reached the values of 70 – 115 thousands. During the raw lead solidification cycle, the concentration reached the order of 20 – 40 thousands of particles, for values see Fig. 5.

The results of measurement for efficiency testing of respirators, as in the previous experiments in the joinery works, steel works, rolling plant and during uranium ore mining, showed that even standard respirators protect workers against the penetration of nano-particles to a certain extent. It is also important to put the respirator on the face of the worker correctly (insufficient fixing – see first part of the measurement, see Fig. 6).

<table>
<thead>
<tr>
<th>activity in time</th>
<th>n-particles near the respirator</th>
<th>n-particles in the breathing zone under the respirator</th>
<th>efficiency S (%)</th>
<th>FIT Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal breathing 0-60</td>
<td>38,500</td>
<td>347</td>
<td>99</td>
<td>111</td>
</tr>
<tr>
<td>Deep breathing 60-120</td>
<td>78,100</td>
<td>a) 463</td>
<td>99</td>
<td>169</td>
</tr>
<tr>
<td>Head from side to side 120-180</td>
<td>40,200</td>
<td>a) 137</td>
<td>99.6</td>
<td>293</td>
</tr>
<tr>
<td>Head up and down 180-240</td>
<td>23,100</td>
<td>372</td>
<td>98</td>
<td>62</td>
</tr>
<tr>
<td>Speaking 240 – 300</td>
<td>38,000</td>
<td>1623</td>
<td>95</td>
<td>23</td>
</tr>
<tr>
<td>Bending at the waist 300 – 360</td>
<td>24,500</td>
<td>413</td>
<td>98</td>
<td>59</td>
</tr>
<tr>
<td>Normal breathing 360 – 420</td>
<td>25,400</td>
<td>165</td>
<td>99</td>
<td>154</td>
</tr>
<tr>
<td><strong>Total efficiency and FIT FACTOR</strong></td>
<td>b) 38,257</td>
<td>b) 503*</td>
<td>98</td>
<td>124</td>
</tr>
</tbody>
</table>

Figure 3. Values of measured aerosol particles, FIT factor, respirator efficiency and graphic representation of the number of particles in front of and under the REFIL 530 FFP2 respirator (the tapping of raw lead into the moulds completed, averaged values of n-particles during the measuring cycle)

Figure 4. Values of measured aerosol particles, FIT factor, respirator efficiency and graphic representation of the number of particles in front of and under the REFIL 530 FFP2 respirator (during the tapping of raw lead into the moulds, averaged values of n-particles during the measuring cycle)

<table>
<thead>
<tr>
<th>activity in time</th>
<th>n-particles near the respirator</th>
<th>n-particles in the breathing zone under the respirator</th>
<th>efficiency S (%)</th>
<th>FIT Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal breathing 0-60</td>
<td>87,900</td>
<td>a) 505</td>
<td>99</td>
<td>174</td>
</tr>
<tr>
<td>Deep breathing 60-120</td>
<td>115,000</td>
<td>a) 1440</td>
<td>98</td>
<td>80</td>
</tr>
<tr>
<td>Head from side to side 120-180</td>
<td>175,000</td>
<td>a) 1450</td>
<td>99</td>
<td>121</td>
</tr>
<tr>
<td>Head up and down 180-240</td>
<td>87,600</td>
<td>a) 696</td>
<td>99</td>
<td>126</td>
</tr>
<tr>
<td>Speaking 240-300</td>
<td>72,400</td>
<td>705</td>
<td>99</td>
<td>102</td>
</tr>
<tr>
<td>Bending at the waist 300-360</td>
<td>44,900</td>
<td>374</td>
<td>99</td>
<td>120</td>
</tr>
<tr>
<td>Normal breathing 360-420</td>
<td>29,500</td>
<td>245</td>
<td>99</td>
<td>120</td>
</tr>
<tr>
<td>Total efficiency and FIT FACTOR</td>
<td>b) 87,471</td>
<td>b) 773</td>
<td>99</td>
<td>120</td>
</tr>
</tbody>
</table>
### Table of Measured Aerosol Particles and Efficiency

<table>
<thead>
<tr>
<th>Activity In Time</th>
<th>n-particles Around the Respirator</th>
<th>n-particles in the Breathing Zone Under the Respirator</th>
<th>Efficiency $S$ (%)</th>
<th>FIT Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal breathing 0-60</td>
<td>31,800</td>
<td>271</td>
<td>99</td>
<td>117</td>
</tr>
<tr>
<td>Deep breathing 60-120</td>
<td>19,400</td>
<td>359</td>
<td>98</td>
<td>54</td>
</tr>
<tr>
<td>Head from side to side 120 - 180</td>
<td>24,100</td>
<td>140</td>
<td>99</td>
<td>172</td>
</tr>
<tr>
<td>Head up and down 180 - 240</td>
<td>18,000</td>
<td>145</td>
<td>99</td>
<td>124</td>
</tr>
<tr>
<td>Speaking 240 – 300</td>
<td>23,400</td>
<td>331</td>
<td>98</td>
<td>71</td>
</tr>
<tr>
<td>Bending at the waist 300 – 360</td>
<td>20,200</td>
<td>197</td>
<td>99</td>
<td>102</td>
</tr>
<tr>
<td>Normal breathing 360 – 420</td>
<td>21,300</td>
<td>127</td>
<td>99</td>
<td>167</td>
</tr>
<tr>
<td>Total efficiency and FIT Factor</td>
<td>b) 22,600</td>
<td>b) 224</td>
<td>99</td>
<td>115</td>
</tr>
</tbody>
</table>

**Figure 5.** Values of measured aerosol particles, FIT factor, respirator efficiency and graphic representation of the number of particles in front of and under the SEGREG FFP3 respirator (averaged values of n-particles during the measuring cycle)
Figure 6. Values of measured aerosol particles, FIT factor, respirator efficiency and graphic representation of the number of particles in front of and under the SEGREG FFP3 respirator (during the tapping of raw lead into the moulds, averaged values of n-particles during the measuring cycle)

3.2. Distribution Measurement of Nano- and Micro-Particles Depending on the Course of Technological Operations Related to Raw Lead Melting at the Blast Furnace

During this measurement, the technological processes running in melting of lead waste for the production of raw lead were accurately recorded. Therefore, the measured spectrum is assigned to individual technological processes in Table 1 as well as in other graphs (Fig. 7, 8 - 11). Thus we obtain the dependence of the total concentration of aerosol nano- and micro-particles during individual processes, distribution of nano-particles, their surface, volume and weight.
Table 1. Measured surface, volume and weight of nano-particles during running technological processes

<table>
<thead>
<tr>
<th>Spectrum No.</th>
<th>Technological process</th>
<th>Surface (nm²/cm³)</th>
<th>Volume (nm³/cm³)</th>
<th>Weight (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>test</td>
<td>3.16E+09</td>
<td>1.13E+11</td>
<td>135</td>
</tr>
<tr>
<td>2</td>
<td>background before the tapping</td>
<td>9.99E+08</td>
<td>2.39E+10</td>
<td>28.6</td>
</tr>
<tr>
<td>3</td>
<td>passage of VZV a)</td>
<td>9.89E+09</td>
<td>3.83E+11</td>
<td>459.4</td>
</tr>
<tr>
<td>4</td>
<td>tapping</td>
<td>2.11E+09</td>
<td>4.70E+10</td>
<td>56.4</td>
</tr>
<tr>
<td>5</td>
<td>pouring lead into the mould</td>
<td>4.64E+09</td>
<td>6.88E+10</td>
<td>82.6</td>
</tr>
<tr>
<td>6</td>
<td>lead solidification</td>
<td>2.40E+09</td>
<td>7.13E+10</td>
<td>85.6</td>
</tr>
<tr>
<td>7</td>
<td>lead solidification</td>
<td>1.53E+09</td>
<td>4.56E+10</td>
<td>54.7</td>
</tr>
<tr>
<td>8</td>
<td>lead solidification</td>
<td>2.17E+09</td>
<td>4.01E+10</td>
<td>48.2</td>
</tr>
<tr>
<td>9</td>
<td>opening of 2nd gate, causing draught</td>
<td>1.03E+09</td>
<td>1.96E+10</td>
<td>23.5</td>
</tr>
<tr>
<td>10</td>
<td>still solidification</td>
<td>1.15E+09</td>
<td>2.05E+10</td>
<td>24.6</td>
</tr>
<tr>
<td>11</td>
<td>slag tapping (approximately 10 m from instruments)</td>
<td>6.99E+08</td>
<td>1.51E+10</td>
<td>18.1</td>
</tr>
<tr>
<td>12</td>
<td>slag tapping (approximately 10 m from instruments)</td>
<td>7.37E+08</td>
<td>2.29E+10</td>
<td>27.5</td>
</tr>
<tr>
<td>13</td>
<td>lead solidification</td>
<td>5.73E+08</td>
<td>1.66E+10</td>
<td>20</td>
</tr>
<tr>
<td>14</td>
<td>lead solidification</td>
<td>6.05E+08</td>
<td>1.73E+10</td>
<td>20.7</td>
</tr>
<tr>
<td>15</td>
<td>lead solidification</td>
<td>4.98E+08</td>
<td>1.30E+10</td>
<td>15.6</td>
</tr>
<tr>
<td>16</td>
<td>lead solidification</td>
<td>3.28E+08</td>
<td>8.38E+09</td>
<td>10.1</td>
</tr>
<tr>
<td>17</td>
<td>another slag tapping</td>
<td>6.12E+08</td>
<td>1.68E+10</td>
<td>20.2</td>
</tr>
<tr>
<td>18</td>
<td>removal of the casting out of the mould - passing VZV a)</td>
<td>6.91E+09</td>
<td>3.08E+11</td>
<td>370</td>
</tr>
<tr>
<td>19</td>
<td>removal of the casting out of the mould - passage of VZV a)</td>
<td>1.51E+09</td>
<td>3.21E+10</td>
<td>38.5</td>
</tr>
<tr>
<td>20</td>
<td>2nd tapping</td>
<td>3.89E+09</td>
<td>8.40E+10</td>
<td>100.8</td>
</tr>
<tr>
<td>21</td>
<td>pouring lead into the mould</td>
<td>1.56E+09</td>
<td>3.43E+10</td>
<td>41.2</td>
</tr>
</tbody>
</table>

a) VZV – forklift truck

Figure 7. Total concentration of aerosol nano-particles in size range from 15.1 to 685 nm
Figure 8. Total concentration of aerosol micro-particles in size range from 0.542 to 19.81 µm

Figure 9. Average size distribution of nano-particles during the “raw lead tapping” process, determined on the basis of four measurements

Figure 10. Average size distribution of nano-particles during the “lead solidification” process, determined on the basis of seven measurements

Figure 11. Concentration and size distribution of aerosol nano-particles during particular technological processes of lead waste melting. (Marks and numbers on the chart corresponding with technological processes in the Table 1)
Based on the results, we can conclude that:

- the assumption that the maximum concentration of aerosol nano-particles was during the tapping of raw lead out of the trap into the mould (see spectrum 4 – 6, 20 -21, Fig. 7, 11) was confirmed,
- during solidification depending on time and drop in lead temperature, the decrease in concentration of aerosol nano-particles to basically constant concentration is registered (see spectra 11 -17, Fig. 7),
- the size of nano-particles at their maximum concentration was most frequently 20 – 30 nm,
- bubbling through solidifying melting - probably deaeration of CO₂ (carbon identified, see Fig. 14),
- the role of draught took probably its effect for spectrum 8 (see Fig. 7) (lead was still bubbling melting),
- the comparison of sizes of the nano-particles occurred between two tapping processes shows that two groups of nano-particles can be identified, the first group 20 -30 nm and the second group 60 -80 nm occurring in the spectra in pouring into the moulds,
- the size of the main group of nano-particles identified during all technological processes was 20 – 40 nm – the size of a quite significant group of particles was 50 – 60 nm and this was in the early stage of solidification; the strong group of particles with the size of 60 - 80 nm was identified during the tapping, when the outdoor temperature dropped sharply by 4°C (see spectrum 20, Fig. 11), thus cooling the surrounding of the moulds,
- more detailed distribution in relation to technological processes is indicated by graph shown in Fig. 11,
- the maximum concentration of aerosol micro-particles corresponds approximately in relation to technological processes as in the case of nano-particles,
- a relatively small quantity of aerosol micro-particles identified in the point of measurement (4 m from the tapping) is attributable to the effect of gravitation,
- the differences in the concentration of measured nano-particles during respirator testing and distribution measurement are due to the effect of different distance and direction of technology location from the expected source.

### 3.3. Taking Samples of Nano- and Micro-Particles from Air at the Blast Furnace in order to Determine their Morphology and Composition

A sample of aerosol in the range of size of 1 nm – 30 µm, divided into 12 fractions, was taken by means of samplers. The morphology of taken particles from fractions was determined by means of a scanning electron microscope. After the conditioning of samples by mineralization it was possible to determine, using the ICP - MS method, the individual metals, of which the taken particles are composed.

The particles of mainly spherical shape (see Fig. 12), which based on the atomic representation have the summary formula PbS 0.5Pb, are the main component present in the air. Our result corresponds with the published scheme Pb–S [4], which shows that those elements aremiscible in liquid condition.

In addition to spherical formations, there follow the crystalline forms of the shape of cube, cuboid, cylinder in different stage of agglomeration (aggregation) as well as amorphous particles mainly composed of silicates (slag). Such clusters, consisting of different crystals or spherical particles, are very stable and are mostly composed of primary crystals lesser than 300 nm. However, slightly spherical particles lesser than 100 nm are not an exception. The occurrence of spherical formations can be explained by rapid solidification of vapours, which was supported by relatively low temperature in the point of sampling. Similar phenomenon was observed in measurement of the pouring of molten pig iron into the ladle in the steel works [5].

Zinc (ZnO) and iron belong to other elements with the maximum concentration represented in nano- and micro-particles. Other identified metals from the sampling were: chrome, tin, manganese, nickel, iron, copper, arsenic, zinc, and cadmium. For graphic representation of distribution and volume concentration of metal nano- and micro-particles see Fig. 13 in partial graphs for the metal in question.
Figure 13. Distribution and concentration of individual metals in the area at the blast furnace.
The nano-particles to the size of 100 nm were not identified for Cr and As. The particles with the size of 10 – 900 nm were not measured for Cu and Ni. For most metals, the high concentrations of particles occurred in the range of 900 – 1100 nm. A certain exception was identified for Mn, where the maximum values ranges at the interval of 20 – 100 nm. The example of the results of point analysis from energy spectrum is shown in Fig. 14.

![Image](image1.png)

**Figure 14.** Example of the result of the application of energy dispersive spectroscopy

The lines of lead and sulphur in the energy spectrum are very close to each other so this is their superposition, thus affecting their resulting values of qualitative analysis to a certain extent.

The identification of carbon in the spectrum can be explained by presence of coke and plastics in melting process.

### 4. OSH Measures in Kovohutě

It can be noted that the company Kovohutě Příbram nástupnická a.s. seeks to promote the maximum level of personnel health protection and elimination of harmful effects of its activity on the environment.

After the involvement in the Society for Mining, Metallurgy, Materials and the Environment, new knowledge began to be applied consistently in Kovohutě [6 - 8] such as:

- personnel health monitoring including statistical evaluation of the development of plumbemia for workers as well as workplaces (close cooperation with the Occupational Disease Clinic of the First Faculty of Medicine of the Charles University in Prague) [7],
- a full eating prohibition outside the dedicated areas provided with basic hygiene conditions,
- a full smoking ban throughout the complex of the company,
- drinking possible only within the dedicated areas,
- maximum respiratory protection by introducing top quality Airstream AH4 helmets with air filtration,
- division of changing rooms into clean and dirty parts,
- daily exchange of work clothes for clean cloths at hazardous workplaces,
- improvement of working environment by changing the technology or intensifying the exhaustion,
- control of dust by moistening regularly the hazardous areas and the whole complex.

The above mentioned measures contributed to the fact that
the levels of plumbemia (blood lead level) for all workers did not exceed the limit of 400 μg/l of blood determined by the Government regulation.[5] This limit was abruptly introduced and in the first moment, it seems to be difficult to meet.[4]

5. Discussion of Lead Toxicity

Lead represents the longest toxicological story in human history. Lead poisoning is often classified as the oldest environmental disease. A number of historians attribute to lead the impact on the decline of the Roman Empire – water distribution in lead pipes, lead utensils and wine cups, jewellery, etc. In 18th-19th century, the bare reality was that persons working with lead will certainly loose their health.

The industry producing accumulators is currently the main lead processor. Another lead application is the lining on the transport container for sulphuric acid, shielding of workplaces with ionising radiation, glass work, ammunition, etc.

After the penetration into the organism (mainly by mouth and respiratory system), inorganic lead is firstly distributed into soft tissues, is bonded to erythrocytes, to plasma proteins, and inactivates specific enzymatic systems containing the groups – SH. Bones are the depot place – lead phosphate. Acute poisoning in clinical view is mainly manifested with neurotoxicity and haemolysis with subsequent renal impairment. Chronic lead intoxication affects a number of organ systems and biochemical processes.

Neurotoxic effects are serious.[9] Nano- and micro-particles of lead or its sulphides occur in the atmosphere during the tapping of molten lead. By passing through the alveolar sacs, they can enter blood and lymph, where there are assumptions for their distribution into other organs, where they can be adsorbed on the surface of important macromolecules, which can affect the regulatory mechanisms of enzymes and other proteins. They are probably able to penetrate biological membranes of cells, where there is a risk of damage to the genetic information of cell.[10]

It should also be noted the toxicity of other identified metals, which can be classified into the category of hazardous elements (metals harmful to the environment). For example, inhalation of ZnO vapours results in so-called metal fume fever; Ni – carcinogenic effects, chronic poisoning can cause damage to the heart muscle and CNS; As – high toxicity with the ability of cumulating in organs; Cd – damages kidneys, causes bone embrittlement and destruction of red blood cells [11], etc.

Heavy metals also slow down significantly the growth of plants, thus reducing the crop yield. Toxic effects on plants are related to the damage to the photosynthetic system, inhibition of the activity of key enzymes for plant metabolism. The great risk is their accumulation in the organism, e.g. for lead, the biological half-life is 1500 years.[12 - 14]

In general, the size of nano- and micro-particles is the key factor for determining their potential toxicity. However, this is not the only important factor. It should be noted the chemical composition, shape of particles, surface structure, surface charge, solubility, aggregation, etc. Nevertheless, it is very difficult to identify material properties, which are substantial and have a significant effect on the interaction between nano-particles and biological systems, and on the feedback of biological system. Therefore, it is essential to know the interrelations (connections) between the properties of nano-particles and their biological effects. In the context of the objectivity, we have admit that the results of published toxicity are very difficult to compare because most experiments were performed in vitro or on animal organs. For example, by identifying the toxicity in vitro for metal nano-particles the authors [15] concluded that stable metal particles have no significant cellular toxicity, while the nano-particles, which can be oxidized, reduced or dissolved, are cytotoxic and even genotoxic to cellular organisms. Overall, the consensus is that the nano-particles of metals such as Fe, Co, Mn, Ti, Pb, and others, induce oxidative stress and activate cells to induce inflammations. In addition, their catalytic activity increases their destruction effects on the cell.[16 - 18]

Only limited information is available about the toxicity of PbSnano-particles. Male rats were exposed to the effects of PbSnano-particles with the size of 30 – 60 nm. It was demonstrated that the PbSnano-particles induce oxidative damage and inflammation in lung tissue.[19]

Another study [20] in vivo on Danio rerio embryos demonstrated the effect on toxicity by type of surface ligand mercapatan basis bonded on the surface of PbS.

6. Conclusion

The measurements of efficiency of common respirators in the environment of lead waste melting have proved relatively high protection of workers against penetration of nanoparticles into the respiratory tract. It has been demonstrated that the distribution of nano- and microparticles depends on the performed technological operations during the melting. The maximum concentration of nanoparticle aerosols was found in the atmosphere during tapping of melted lead into the moulds, while the prevailing size of nanoparticles was in the risk area 20-30 nm. Apart from spherical shapes of nano- and microparticles in the aerosol (Pb x 0.5 PbS), the atmosphere also contained other crystalline shapes, e.g. cubes, cuboids and cylinders in various degrees of agglomeration. Apart from lead, the aerosol also contained nano- and microparticles of zinc and iron, as well as other identified metals, and their distributions are shown in Fig. 13.
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