Assessment of occupational risk connected with exposure to heavy and carcinogenic metals in chosen industrial processes

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Introduction

The aim of the study is to assess and reduce occupational risk connected with exposure of workers of heavy metals refining stations and anticorrosive coating stations (tin, nickel, chromium, zinc and cadmium plating). The measurements of chemical agents in the workplace air constitute the basis of the assessment.

People employed in heavy metals refining processes and anticorrosive coating processes are most of all exposed to metals and metalloids (arsenic, selenium) and metal compounds (MgO, CaO), some of which are very toxic (e.g. lead), other also carcinogenic (cadmium, nickel, arsenic, chromium VI compounds). Moreover the exposure to such agents as dusts (from 2 to 50% SiO_2), sulphuric acid (nickel production, copper electrorefining), cyanides (zinc coating in galvanizing bath), NaOH (tin coating, acid chromium plating) occurs.

In Poland, the problem of exposure to harmful chemical agents in heavy metals refining processes applies mostly to workers employed in big enterprises, whereas the coating processes are carried out in small and medium sized industrial enterprises.

Methodology

Methods of measurement:

Atomic absorption spectrometry with graphite tube and Zeeman background correction – As, Cd, Se, Sb, Ni, Cu, Pb, Ag, Cr, Sn, Zn

Atomic absorption spectrometry with air-acetylene flame – Zn, MgO (as Mg), iron oxides (as Fe) Fe, CaO (as Ca)

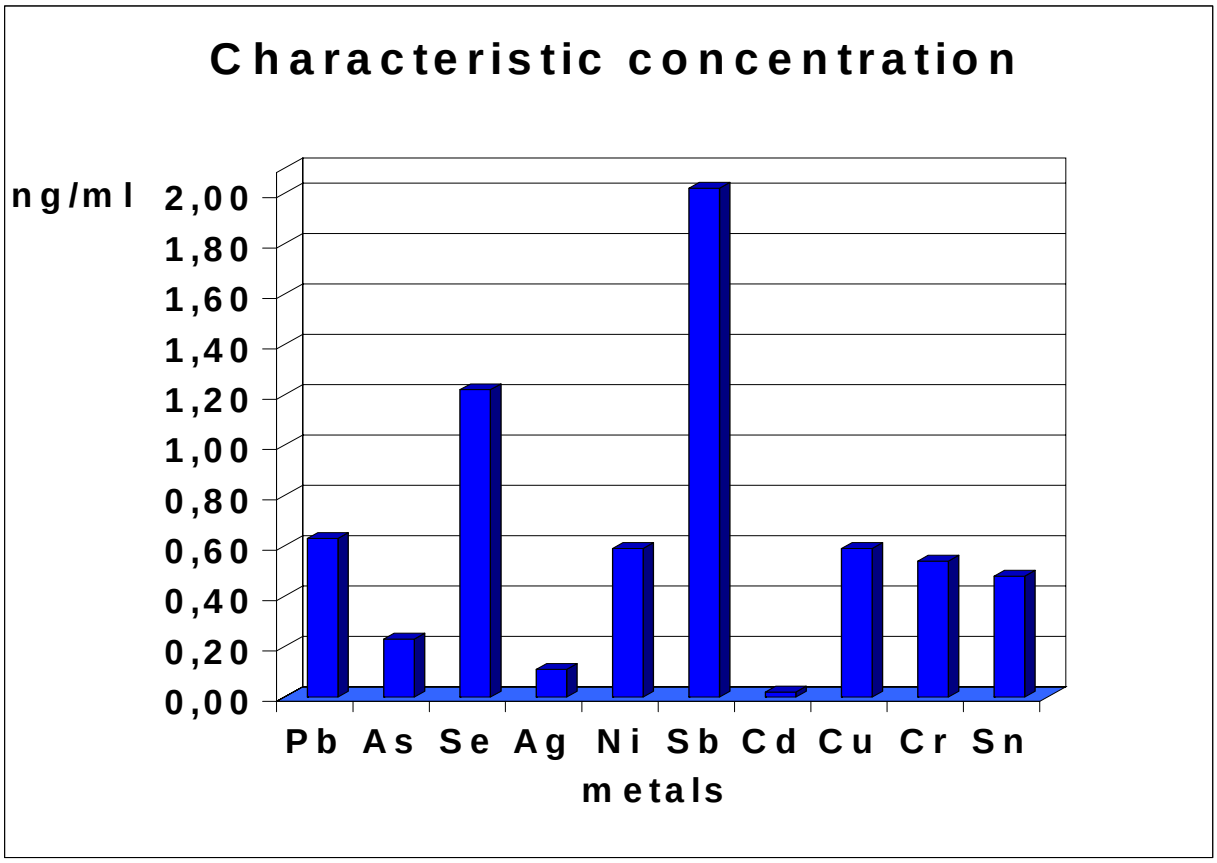
Air sampling

- personal sampling (flow rate – 1,5-1,8 l/min; sample collecting time: from 30 to 330 min)

Collection of air samples was performed according to principles enabling the assessment of agreement of working conditions with MAC and MAC-STEL values given in European and Polish Standards (EN 689: 1995; PN-04008-7: 2002).

The air samples collected on membrane filters (pore size – 0,85 μm) are treated with concentrated nitric acid (temperature – 140 ^{O}C) to ash the organic and inorganic matrix and to dissolve the metals present in the sample. The content of elements was determined in 0,1 mol/l HNO_3 solution.

Characteristic concentrations of elements for the applied methods are presented in table 1.



Results of measurements

The results of determination of harmful chemical agents in air samples are presented in tables 1-3.

Table 1. Concentration level of chemical agents in air samples collected at Plant I workstations

Process	Post	Agent concentration [mg/m^3]								
		Pb	Cu	As	Ni	Ag	Se	Zn	Fe	Others
Cu refining	smelter operator	0,08-0,47	0,14-0,37	0,014-0,060	trace	0,005-0,008	n.d.	0,09-1,39	0,18-0,39	CaO <0,40
	refiner operator	0,07-0,26	0,12-0,28	0,046-0,062	<0,001	0,003-0,005	n.d.	n.d.	n.d.	CaO <0,33
Cu electrorefining	electrolyser operator	0,01-0,04	<0,04	<0,002	n.d.	<0,003	n.d.	n.d.	trace	H_2SO_4 0,12-0,31
Pb refining	furnace operator	0,23-0,52	0,02-0,09	0,009-0,042	n.d.	0,002-0,027	n.d.	0,02-0,19	trace	CaO <0,46
Silver production	anode slime leaching operator	0,04-0,14	0,04-0,11	0,021-0,047	0,015-0,040	0,047-0,050	<0,06	trace	trace	CaO 1,14-1,80 Sb <0,16
	furnace operator	0,060-0,082	0,01-0,04	0,008-0,011	trace	0,038-0,051	0,045-0,164	n.d.	n.d.	CaO <0,40
Ni sulphate production	apparatus operator	<0,03	<0,02	<0,002	<0,0025	n.d.	n.d.	trace	n.d.	CaO 0,40-1.23

n.d.-not detected

Table 2. Concentration level of chemical agents in air samples collected at Plant II workstations

Process	Post	Agent concentration [mg/m^3]								
		Pb	Cd	As	Zn	Ag	Se	Ni	Fe	Others
Zinc – lead ores roasting	smelter operator	0,05-0,12	0,003-0,008	n.d.	<0,04	n.d.	n.d.	n.d.	0,02-0,04	CaO 0,04-0,13 Sb trace
Zn and Pb production in a crude form	smelter operator	0,05-0,08	<0,003	0,002-0,008	0,24-0,86	trace	trace	n.d.	<0,05	CaO 0,03-0,20
Cadmium production	smelter-casting operator	0,20-0,50	0,008-0,013	<0,003	0,08-0,17	<0,001	n.d.	n.d.	<0,04	CaO 0,03-0,17
Pb refining	casting operator	0,03-0,08	0,002-0,005	<0,002	0,06-0,32	0,001-0,004	n.d.	n.d.	trace	CaO 0,07-0,16
Zn refining	refiner operator	0,01-0,05	<0,003	<0,002	0,05-0,80	trace	trace	n.d.	n.d.	MgO trace Cu trace

Table 3. Concentration level of chemical agents at Plant II workstations

Process	Post	Agent concentration [mg/m^3]			
		Zn and its compounds	Cr and its compounds	Sn and its compounds	Other agents
Acid zinc plating	Galvanic tube operator	0,02 - 0,06	0,002 - 0,010	n.d.	NaOH 0,17-0,22 H_2SO_4 n.d. HCN < 0,033
Acid chromium plating	Galvanic tube operator	0,01 - 0,02	0,002 - 0,028	n.d.	NaOH 0,10-0,34 H_2SO_4 <0,4
Acid tin plating	Galvanic tube operator	-	-	0,002 – 0,006	H_2SO_4 <0,4 other metals - Cu <0,002 **Pb <0,013**

Approximately 50 workstations in 4 Polish enterprises were examined (Plant I, II, III and IV).

Plant I – copper smelter (about 1500 workers employed in the production process)

Processes carried out: lead refining, copper refining, silver refining, nickel sulphate production, copper electrorefining

Plant II – non-ferrous metals smelter (about 500 workers employed in the production process)

Processes carried out: zinc refining, lead refining, cadmium refining

Plant III – shipping industry company

Processes carried out: galvanic tin coating in acid bath preceded by acid and alkaline etching

Plant IV – metal industry

Processes carried out:

- chromium electroplating in acid bath preceded by alkaline degreasing
- zinc coating in galvanising bath after preliminary degreasing in alkaline phosphate bath

Summary and conclusions

The examination leads to the conclusion that the risk created by metals and metalloids in the workstation air of the examined plants is diversified.

- It seems that lead constitutes the main problem in the heavy metal refining. Lead concentrations in the collected samples are often higher than Polish MAC (0,05 mg/m^3), both in Plant I and II.
- Cadmium presence in Plant I was not found, whereas cadmium concentrations in air samples from Plant II are quite high, but generally not higher than MAC (0,01 mg/m^3) and even if higher, not significantly.
- Arsenic concentrations examined in Plant II are very small. In one case only arsenic concentration is higher than ½ MAC value (0,01 mg/m^3). In Plant I arsenic occurs in all processes. Particularly high concentrations were found in the process of copper refining

(smelter and refiner operator posts). High concentrations of copper were found at these workstations.

- Quantities of other determined elements in Plants I and II are generally small (MAC fractions).
- Concentrations of chemical agents higher than hygienic standard values were not found at the galvanic metal coating, chromium plating, tinning and galvanising of the steel alloy surface workstations.
- The highest concentrations of aerosol containing metal compounds in the process of galvanisation were found during the insertion and removing of elements from the galvanisation tube.
- The analysis of the obtained results leads to the conclusion that even at the workplaces where the measured concentrations of given elements are small, the indicator of total exposure can be higher than 1 because of the great amount of present chemical agents.

The research continues.

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