

Environmental mobility of trace elements present in dusts emitted from Zn–Pb metallurgical processes

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Abstract The paper presents results of investigations into possibility of migration to the soil and water environment of trace elements present in one of the main phases, zinc sulphide, emitted in dusts from various operations of pyrometallurgical extraction of Zn and Pb at the Miasteczko Śląskie Zinc Smelting Plant. The quantity of elements was estimated on the basis of: (1) dust fall, (2) zinc sulphide content in dust, (3) element content in zinc sulphide and (4) mobility of zinc sulphide under the hypergenic conditions of the soil and water environment of the Smelting Plant area. Among the elements considered, arsenic emitted with zinc sulphide contained in dusts from the Sintering Machine will pose a potential hazard for the soil and water environment of the Miasteczko Śląskie Zinc Smelting Plant area.

Keywords Lead · Zinc · Pyrometallurgy · Trace elements · Dust · Environment

Introduction

The Miasteczko Śląskie Zinc Smelting Plant is the only facility in Poland using the ISP (Imperial Smelting Process) pyrometallurgical process for simultaneous production of zinc and lead. The plant has been in operation since 1966. The production line at the Smelting Plant consists of Sintering Unit (Sintering Machine) with Sulphuric Acid

Plant, Shaft Furnace Unit, Lead Refining Plant and Zinc Rectification Unit (Zhao 2013).

During the production process dusts from various points of the production line are emitted into the environment. These dusts are much varied in terms of mineral composition (Lentz 2012; Nitta et al. 2008; Patrick et al. 1993, Patrick et al. 1998) which gives rise to diverse forms of metals present in the soils of the region. Soils in the area of Miasteczko Śląskie are mainly of sandy (podzolic) type with occasional occurrence of silty and boggy soils, alluvial soils and rendzinas. Most of the soils are classified as slightly acid or acid, which results in high mobility of metals in the soil and increased metal uptake by plants. The area of the Miasteczko Śląskie Zinc Smelting Plant is highly contaminated with heavy metals, particularly with zinc (84.7–630.9 mg/kg) and lead (853.7–9427.0 mg/kg), and slightly less with cadmium (36.4–1036.5 mg/kg), copper (32.2–500.0 mg/kg) and arsenic (83.0–768.0 mg/kg). Other heavy metals are present in concentrations lower than the limits defined for group C industrial areas. Zinc concentrations in underground water of the Zinc Smelting Plant area are relatively low, less than 10.00 mg/L, occasionally exceeding 300.00 mg/L. Maximum lead concentrations in underground water taken from monitoring wells located within the plant area reach ca. 1.00 mg/L. Such low lead concentrations in water show that lead leaching is very slow. Noteworthy is the high content of arsenic in underground water at the plant site. It reaches 350.00 mg/L and indicates that this element is highly mobile (Smelting plant study—soil quality in the area 2010).

The area around the smelting plant consists mainly of farmland and forests. Scotch pine is the prevailing species with admixture of fir and birch. Elements present in dusts emitted by the Miasteczko Śląskie Smelting Plant are characterised by high bioavailability (Kicińska 2011). A

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small portion of them is bound in the crystalline lattice of minerals, and large portion is found in the exchange (mobile) positions. For this reason, the results of metal determinations in the wood of pines, birches and firs growing near the smelting plant have proved a statistical relationship between dust fall and metal accumulation in vegetation. This allows us to state that the vegetation growing in the vicinity of the smelting plant site limits the mobility of elements in the soil and water environment (Gerold-Śmietańska 2007).

Studies of the migration possibility of chemical elements contained in the dust emitted to the soil and water environment by the Miasteczko Śląskie Zinc Smelting Plant form a basis for determining the mechanisms of pollutant transformations in that environment. The subject of investigations was dusts emitted to air from the stack of the Sintering Machine.

As it was proved, the main phase constituents of investigated dust emitted to the environment were (Adamczyk et al. 2010, 2013, 2015):

- sulphides—ZnS and PbS,
- sulphate—PbSO₄,
- oxides—zincite (ZnO), wustite (FeO) and minium (PbO),

with substantial content of zinc sulphide.

The chemical composition of zinc sulphide from selected points of this process line was investigated (Adamczyk et al., 2010, 2015).

Mobility of zinc sulphide in the soil and water environment was assessed in relation to conditions prevailing in that environment (pH, Eh, temperature). In an environment with a pH of 4.5–7.5 zinc sulphide may break down into ionic or solid forms. In the case of ionic forms, all accompanying elements present in zinc sulphide migrate along with the main ions (of zinc and sulphur) to ground water.

The aim of the study outlined in this paper was to determine the possibility of migration of trace elements from zinc sulphide emitted by the Sintering Machine (as the main emission source of arsenic and tin) to ground waters.

Methodology

Investigations were conducted by the authors in the years 2005–2010. Dust samples from the current production of the smelting plant were taken in 12 series (120 samples in total). Chemical and mineral composition of the samples was determined.

Chemical composition was determined by means of X-ray fluorescence (XRF) using a Rigaku ZSX Primus wavelength-dispersive X-ray fluorescence spectrometer.

The spectrometer was fitted with a rhodium X-ray tube with variable voltage adjustment between 20 and 60 kV, and LiF, Ge and several synthetic analysing crystals.

Mineral constituents were identified using polarised light optical microscopy and chemical composition determined in micro-areas. A Zeiss Axioplan microscope was used. Chemical composition was determined in micro-areas using a JEOL X-ray micro-analyser (EPMA) with wavelength- and energy-dispersive spectrometers (WDS, EDS) and with an electron backscatter diffraction accessory from Oxford Instruments. Ten measurements were made for each grain, and average was taken as the final result.

The estimation of the load of trace elements introduced into ground waters as a consequence of zinc sulphide decomposition was made for the scenario least favourable to the environment: all of the zinc sulphide from dust fallout from the Sintering Machine into the soil and water environment is decomposed.

To ensure correctness of these estimates, additional considerations must be taken into account. Dust emissions from the Zinc Smelting Plant amount to 48 Mg/year, of which the emissions from the Smelting Machine constitute more than 7 %. The adopted value of annual dust fall was based on a detailed analysis of dust fall measurements in 25 points around the Smelting Plant. This analysis indicates that the average dust fall is 59 g/(m² × year) (median equal to 58 g/(m² × year) (Adamczyk et al. 2010).

In order to determine the mobility of the elements present in zinc sulphide, geochemical modelling based on Eh–pH diagrams was applied. These diagrams were plotted for conditions characteristic of the soil and water environment in the Smelting Plant area.

For this reason the following values were adopted: mean precipitation 700 mm/year, mean temperature in winter season –5 °C, maximum temperature in summer season +30 °C. Studies were performed within the water stability region, within Eh range of –0.8... +1.4 V and pH range of 0...14 (pH of the soil and water environment under study is within the range 4.5...7.5). The diagrams show the stability regions of the forms of occurrence of trace elements contained in zinc sulphide at extreme seasonal temperatures, i.e. –5 °C and +30 °C.

Results

Based on the data on the mean chemical composition of the dust from the Sintering Machine (Table 1) and results of dust phase composition determination made by the authors (Adamczyk et al. 2010, 2015), the fractions of zinc sulphide and other phase components (lead sulphide, lead sulphate, zinc oxide, iron oxide and lead oxide) were calculated (Table 1).

Table 1 Chemical and phase composition of dust from the Sintering Machine (dust emitted to the air)

Element	Content (wt%)	Phase	Content (wt%)
Si	0.69	PbS	14.9
Al	0.14	ZnS	25.6
Fe	5.40	PbSO ₄	22.4
Mn	0.12	ZnO	4.3
Mg	0.15	FeO	5.4
Ca	1.55	PbO	18.0
K	0.46	Total	90.6
Pb	50.32		
Zn	21.24		
S	13.61		
Ag	1.08		
As	0.55		
Cd	3.89		
Cu	0.18		
Se	0.22		
Sb	0.16		
Sn	0.24		
Total	100.0000		

Average of 12 measurements. Analytical error 0.01 %

Calculations were made based on data related to: (1) content of the elements determined in defined points of the micro-area, (2) stoichiometric ratios, taking into account atomic masses of the elements contained in the identified phase constituent.

The list above indicates that the abundant phase in the dust studied is zinc sulphide (25.6 wt%). A significant constituent of the dust is also lead sulphate—second most voluminous phase (22.4 wt%). Percentage of all phases amounts to 90.4 wt%, and the remaining elements, i.e. Si, Al, Mn, Mg, Ca, K, Ag, As, Cd, Cu, Se, Sb and Sn, are presumably substituents of the main elements in these phases, and percentage thereof is 9.6 wt%.

Zinc sulphide will decompose in the water and soil environment, and trace elements will be released along with it. In the average chemical composition of zinc sulphide coming from the Sintering Machine, Fe and Pb occur in concentrations exceeding 1 wt%; and also Cd is present in the amount of approximately 1 wt%. These elements most probably constitute separate phases in the form of inclusions in zinc sulphide. Concentrations of other elements, i.e. As, Se, Mn, Sn, Sb, Cu, Ag, Ca, are below 0.4 wt% (Table 2). These elements may form admixtures

Table 2 Chemical composition of zinc sulphide in dust from the Sintering Machine: dusts PR1 and PR2 (in wt%)

Element	Measurement point			Average PR2 (Nowinska and Adamczyk 2015)	Average PR3 (Adamczyk et al. 2010)	Average chemical composition of sphalerite PR2 and PR3
	PR2-6	PR2-7	PR2-8			
S	32.33	31.87	35.63	33.43	33.05	33.28
Ca	0.00	0.05	0.00	0.02	0.03	0.02
Mn	0.10	1.31	0.00	0.18	0.25	0.21
Fe	0.61	1.68	6.79	2.87	4.41	3.50
Cu	0.01	0.25	0.00	0.12	0.09	0.11
Zn	64.50	60.33	56.76	61.23	57.79	59.81
As	0.50	0.79	0.43	0.34	0.25	0.31
Se	0.00	0.00	0.00	0.07	0.47	0.24
Ag	0.00	0.00	0.00	0.06	0.11	0.08
Cd	1.95	1.02	0.11	0.71	1.23	0.92
Sn	0.00	0.12	0.28	0.10	0.36	0.20
Sb	0.00	0.26	0.00	0.09	0.32	0.19
Pb	0.00	2.32	0.00	0.78	1.64	1.13
Total	100.00	100.00	100.00	Average of 10 tests	Average of 7 tests	Average of 17 tests
<i>Phase percentage</i>						
PbS	0.00	2.76	0.00	0.91	1.92	1.33
ZnS	96.59	92.41	85.20	92.11	87.70	90.30
FeS-FeS ₂	1.32	3.71	14.68	6.21	8.54	7.17
CdS	2.09	1.12	0.12	0.76	1.33	1.00
Total	100.00	100.00	100.00			

Analytical error 0.01 %

both in zinc sulphide and in the phases that constitute inclusions therein.

Therefore, when considering the possibility of migration of these elements into the environment after the decomposition of zinc sulphide, content of these elements in inclusions, i.e. in PbS, FeS-FeS₂, CdS, should be indicated. In order to determine the migration of elements into the environment, only two of them were considered, namely As and Sn. Discussion of all potential migrating elements would require a much broader study. Furthermore, these two elements may be hazardous to the environment due to their toxicity.

As stated in previous publications of the authors (Adamczyk et al. 2010), the average content of As and Sn is as follows:

- in PbS—0.0977 wt% As and 0.0622 wt% Sn,
- in FeS-FeS₂—0.3598 wt% As and 0.0442 wt% Sn,

and taking the average content of these phases in zinc sulphide (PbS—1.326 wt%, FeS-FeS₂—7.173 wt%), the weighted average for these phases is as follows:

- As—0.0013 wt% in PbS and 0.0258 wt% in FeS-FeS₂, and
- Sn—0.0008 wt% in PbS and 0.0131 wt% in FeS-FeS₂.

Thus, the average content of As in zinc sulphide is 0.2778 wt% and that of Sn is 0.1846 wt%.

Dust emission from the Sintering Machine, when considering annual emissions from the Plant, is 3.36 Mg, whereas the dust fall from that emission point is 4.13 g/(m² × year). Fraction of zinc sulphide in the dust is calculated at 25.6 wt%; therefore, the amount of this phase emitted annually from the stack of the Sintering Machine is 0.8602 Mg, which translates into 1.0573 g/(m² × year) in fallen dust (Table 3). Along with zinc

sulphide, trace elements are discharged into the environment, among them As and Sn, in amounts of 0.0093 Mg/year and 0.0062 Mg/year, respectively, and 0.0115 g/(m² × year) As and 0.0076 g/(m² × year) Sn in fallen dust.

The worst case scenario may be that (it may be assumed that in the least favourable conditions) all of the zinc sulphide in fallen dust (1.0573 g/(m² × year)) will be decomposed in the soil and water environment. In such a case all trace elements bound into that phase will migrate into that environment. Under such assumptions, the maximum concentration of zinc in ground water may reach 9.52 mg Zn/L (with annual precipitation of 700 mm). Concentrations of arsenic and tin in ground water will, under these conditions, reach 0.16 mg As/L and 0.11 mg Sn/L, respectively.

According to the latest studies (Nowinska and Adamczyk 2015), zinc sulphide will decompose in the soil and water environment within the entire range of pH values, forming, among others, Zn²⁺ and Zn(OH)⁺ ions, which are mobile in the environment. As and Sn released during such decomposition create the following forms:

- As—ionic: HAsO³⁻, AsO₄³⁻, HAsO₄²⁻, H₂AsO₄⁻, solid: As,
- Sn—ionic: Sn(OH)₆²⁻, solid: SnO₂ and Sn(SO₄)O₂,

irrespective of seasonal temperature changes (−5... +30 °C). Within the pH range characteristic of the soil and water environment in the area covered by the study, pH = 4.5...7.5, only the following ions will be present: HAsO³⁻, HAsO₄²⁻, H₂AsO₄⁻. Therefore, only ions of arsenic will be mobile in the environment, with no tin ions present. Tin in the pH range of 4.5 to 7.5 forms stable SnO₂ (Fig. 1).

Table 3 Content of Zn, As, and Sn in dust emissions and fallen dust from the stack of the Sintering Machine (E3) with zinc sulphide amount taken into account

Emission (Mg/year)	Amount of ZnS in dust emissions from E3	0.8602
	Zn fraction in emissions from E3	0.5419
	Fraction of As contained in ZnS in emissions from E3	0.0093
	Fraction of Sn contained in ZnS in emissions from E3	0.0062
Dust fall (g/(m ² × year))	Amount of ZnS in fallen dust from E3	1.0573
	Fraction of Zn in fallen dust from E3	0.6661
	Fraction of As contained in ZnS in fallen dust from E3	0.0115
	Fraction of Sn contained in ZnS in fallen dust from E3	0.0076

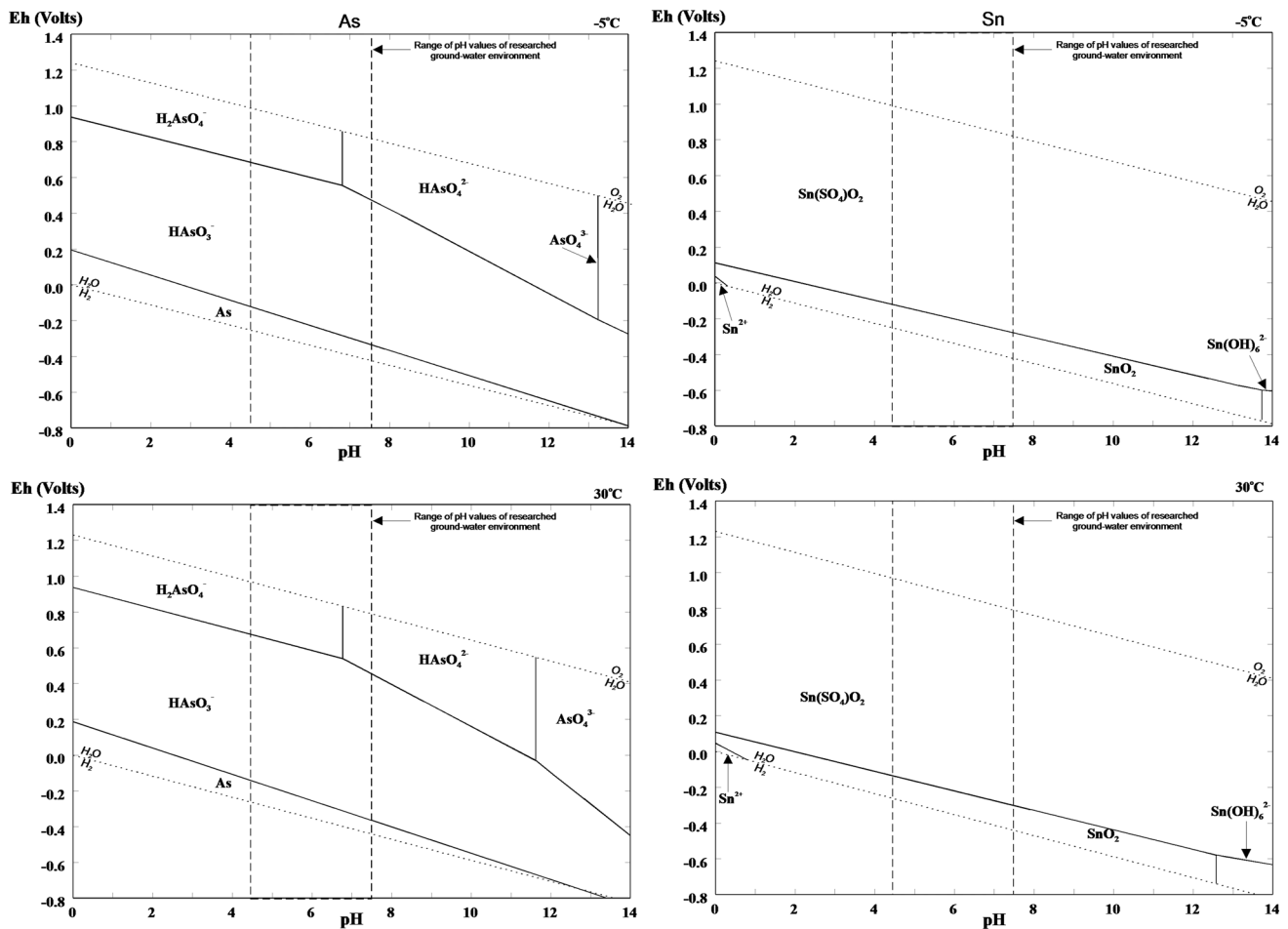


Fig. 1 Mobility of As and Sn from zinc sulphide emitted by the Sintering Machine (emission point E3) to the soil and water environment at -5 and 30 °C

Conclusions

Zinc sulphide is one of the main forms present in the dust discharged from the stack of the Miasteczko Śląskie Zinc Smelting Plant. Along with zinc sulphide, trace elements are discharged into the environment, among them As and Sn, in amounts of 0.0093 Mg/year and 0.0062 Mg/year, respectively, and 0.0115 g/(m² × year) As and 0.0076 g/(m² × year) Sn in fallen dust.

Zinc sulphide will decompose into mobile forms Zn²⁺ and Zn(OH)⁺ in the soil and water environment over the whole pH range, and thereby trace elements As and Sn contained in zinc sulphide will be released to the environment. Movement of metals into other environmental compartments, i.e. ground water, surface water, or the atmosphere, is expected to be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of metal in the soil system is closely related to the solution and surface chemistry of the soil and to the specific properties of metal and associated waste matrix.

Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes may also enhance metal mobility (ground water issue). Biogeochemical redox processes strongly influence also mobility of metalloids such as arsenic (As) and antimony (Sb). Environmental As chemistry has received great attention during the last two decades due to the worldwide health impacts of As-contaminated water and soils. Arsenic in natural waters and soils is closely related to the presence of iron (hydr)oxides being arsenate and arsenite strongly sorbed onto the surfaces of Fe oxides, forming inner-sphere complexes. The simultaneous presence of high dissolved As and Fe(II) concentrations in anoxic groundwater has led to the conclusion that reductive dissolution of As rich Fe(III) (hydr)oxides mobilises geogenic As (Borch et al. 2010, Voliante et al. 2010)

The plotted Eh and pH diagrams indicate that within the pH range of 4.5–7.5, which is characteristic of the soil and

water environment of the area under study, the mobile forms of arsenic in this environment include HAsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- . Under these conditions tin occurs in the stable form of SnO_2 .

It may therefore be assumed that among the elements considered, arsenic emitted with zinc sulphide contained in dusts from the Sintering Machine will create a potential hazard for the soil and water environment of the Miasieczko Śląskie Zinc Smelting Plant area.

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