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Accompanying Elements in Sphalerite in Pyrometallurgical Process of Zinc and Lead Production

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Abstract - The primary raw materials used in the Imperial Smelting Process (ISP) for zinc and lead production are Zn and Pb concentrates. Dust generated in the course of ISP is recycled as secondary raw material. The examined samples, taken from particular technological sections (Sinter Plant, Shaft Furnace Unit, Lead Refining Plant) showed presence of sphalerite grains. The identified sphalerite grains indicate the presence of Pb sulphides, Fe sulphides, Cd sulphide, Fe and Zn oxides, as well as accompanying elements such as Ca, Mn, Cu, As, Se, Ag, Sn and Sb. The tests performed have demonstrated the differentiation in the content of the various accompanying elements in sphalerite grains present in both charge mixture as well as in dusts from various stages of the process. This differentiation may be an indication of migration of the accompanying elements from sphalerite grains to the products of the process (zinc, lead) or to waste products during the pyrometallurgical process.

***Keywords*:** Pyrometallurgy, Zinc, Lead, Imperial Smelting Process, Sphalerite, Accompanying elements.

1. Introduction

The "Miasteczko Śląskie" Zinc Smelting Plant is the only zinc and lead manufacturer in Europe that uses the ISP (Imperial Smelting Process) pyrometallurgical process.

The basic manufacturing line at Miasteczko Śląskie is concentrated around the shaft furnace and comprises (Pozzi M. Nowińska K, 2006; Zinc and lead… 2000)

1. Sinter Plant, which also includes the Sulphuric Acid Plant and the Cadmium Plant.
2. The Shaft Furnace Unit (reduction of zinc and lead compounds),
3. Lead Refining and Zinc Rectification Units (pyrometallurgical removal of contaminants from the shaft furnace products).

The charges for the pyrometallurgical zinc and lead production process comprise appropriately proportioned blends of primary raw materials (zinc blende and galena concentrates), intermediates (Zn-Pb sinter) and waste products (dust, dross, recycles, slag) and process products (crude zinc and crude lead) (Pozzi M. Nowińska K, 2006; Zinc and lead… 2000) .

The primary raw materials, intermediates and waste products contain a number of accompanying elements.

In view of the growing interest in the winning of accompanying elements in the pyrometallurgical production of zinc and lead, it was reasonable to conduct research on the identification of the forms in which these elements occur at the various stages of the process. Moreover, the identification of the phase composition (main phases of Zn, Pb and accompanying elements) of dusts and slags forms grounds for determining the environmental impact of wastes from ISP.

The aim of this study was to demonstrate the diversity of the content of accompanying elements in sphalerite derived from the charge mixture and from dusts generated at the various stages of the pyrometallurgical production process of zinc and lead.

This research is a continuation of the research on the determination of the mineralogical composition of raw materials (charge mixture) and waste products (dust) of ISP to identify the main phases of Zn and Pb and admixtures of accompanying elements. Previous research allowed to determine the variability of the content of accompanying elements in galena grains contained in the charge mixture and dusts from ISP (Adamczyk Z., Nowińska K, Melaniuk- Wolny E.– in review).

2. Experimental Setup and Procedure

Test samples were taken from the charge mixture for the Sinter Plant (Raw Materials Stores 1 and 2, labelled as MS1 and MS2, respectively) and from dusts from the various process stages, including dust from fabric filters in the Sinter Plant (FT12 and FT 24, labelled as PR2 and PR3, respectively), dust from the grinding mill in the Sinter Plant (FT12R, labelled as PR5). Samples were used to make specimens for investigating the chemical composition within micro-areas using an X-ray microanalyser.

Chemical composition was determined by means of a Joel JCXA 733 X-ray microanalyser, equipped with an ISIS 300 energy-dispersive spectrometer from Oxford Instruments, to obtain information on qualitative and quantitative chemical composition of the microarea of the grain under study (analysis conditions: focused beam (diameter: 1-2 µm, accelerating voltage 20 kV, current $3 \cdot 10^{-9}$ A). Additionally, measurements of the mean chemical composition in a given microarea of fine-grained samples were made using a beam defocused to ca. 30 µm or a beam scanning a maximum area of 30×30 µm.

For every sample a series of microanalyses, comprising a dozen to several dozen measurements of the chemical composition of characteristic (prevailing) particles of dust, were performed in order to determine the dominating form of occurrence of individual elements, principally the main elements, and to associate the information obtained on chemical composition with the morphology of dust particles (Sokołowski J., Nosiła M., Pluta B. 1980). About 10 chemical composition measurements were made in the microarea of any single dust particle and the average was taken as the final result. The areas for analysis were selected on the basis of microscope scanning images obtained by detecting secondary electrons as well as backscattered electrons. Images obtained by detecting secondary electrons were used mainly for observing the morphology of dust particles, whereas the signals originating from backscattered electrons enabled, after appropriate processing, obtaining scanning images, the contrast of which depended exclusively on differences in chemical composition, which significantly facilitated the selection of points for analysis.

3. Results

The tests performed have demonstrated the presence of sphalerite grains both in the charge mixture, as well as in dusts from ISP. These grains contain numerous accompanying elements.

3.1. Sphalerite Grains in the Charge Mixture

The sphalerite grains present in the charge mixture always contain inclusions of other sulphides, including, among others, zinc sulphide and iron sulphides. This is evidenced by the chemical composition of sphalerite grains. The stoichiometric formula of this mineral indicates that sphalerite theoretically contains 67.09 wt% Zn and 32.91 wt% S. It may, however, contain admixtures of various accompanying elements, such as: Cd, In, Ge, Ga and Fe, Mn, Co, Cu, As (Furdyna 1988; Twardowski 1990; Pattrick et al. 1993, 1998; Axelsson and Rodushkin 2001; Lentz 2002; Nitta et al. 2008).

Yet, of the 19 sphalerite grains identified in the charge mixture (Tables 1 and 2), only one (MS-4) had its chemical composition close to stoichiometric. The other grains had either a large deficit of zinc content (ca. 59 wt% on the average) when sulphur fraction was close to stoichiometric in grains from MS1 (ca. 33 wt% on the average, Table 1), or a significant deficit of sulphur in grains from MS2 (ca. 29 wt% on the average, Table 2). Zinc deficit in the sphalerite structure is made up by accompanying elements. Some of these elements are so abundant, that they most probably form their own phases in the form of inclusions in sphalerite grains. The highest concentrations of accompanying elements, among those studied, are those of iron (average for MS1 and MS2, 4.86 and 7.31 wt%, respectively) and lead (average for MS1 and MS2, 1.29 and 2.08 wt%, respectively). Iron in sphalerite grains in MS1 forms mainly sulphides (ca. 7 wt% on the average) and small amounts of oxides (1.52 wt% on the average), whereas iron in sphalerite grains in MS2 is predominantly in the form of oxides (more than 7 wt% on the average), with no occurrence of iron sulphides (Tables 1 and 2). Lead, on the other hand, occurs only in the form of sulphide in average amounts ranging from ca. 1.50 to ca. 2.50 wt%.

Table 1. Chemical and phase composition of selected sphalerite grains in charge mixture MS1 (raw material).

Element	Analysis (grain) number							Min	Max	Average
	MS1-3	MS1-4	MS1-5	MS1-6	MS1-13	MS1-16	MS1-17			
S	32.234	32.487	30.405	32.009	35.435	36.639	32.929	30.405	36.639	33.229
Ca	0.000	0.128	0.000	0.000	0.000	0.000	0.039	0.000	0.130	0.029
Mn	0.129	0.059	0.000	0.010	0.010	0.093	0.000	0.000	0.155	0.061
Fe	0.298	0.128	5.655	0.519	7.355	9.155	6.783	0.128	9.155	4.859
Cu	0.089	0.000	0.000	0.303	0.000	0.000	3.904	0.000	3.904	0.293
Zn	65.580	66.184	61.711	65.006	54.584	53.214	51.060	51.060	66.184	59.316
As	0.288	0.030	0.059	0.636	0.000	0.158	0.315	0.000	0.636	0.140
Se	0.000	0.010	0.030	0.000	0.129	0.000	0.128	0.000	0.129	0.022
Ag	0.109	0.030	0.000	0.157	0.248	0.102	0.227	0.000	0.264	0.089
Cd	0.447	0.345	0.337	0.235	0.436	0.167	0.148	0.000	0.447	0.197
Sn	0.119	0.000	0.317	0.039	0.000	0.297	3.953	0.000	3.953	0.361
Sb	0.199	0.000	0.584	0.000	0.297	0.000	0.000	0.000	0.584	0.119
Pb	0.507	0.601	0.901	1.087	1.507	0.176	0.513	0.000	7.592	1.285
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	No. of samples: 17		
Phase	Phase fraction									
PbS	0.590	0.695	1.051	1.269	1.751	0.205	0.585	0.000	8.841	1.492
ZnS	98.629	98.810	92.876	97.954	81.878	79.819	75.226	75.226	99.098	88.570
FeS_2+FeS	0.000	0.000	0.000	0.000	15.904	19.797	9.587	0.000	19.797	7.396
CdS	0.480	0.367	0.362	0.253	0.467	0.179	0.155	0.000	0.480	0.210
Cu_2FeSnS_4	0.000	0.000	0.000	0.000	0.000	0.000	13.830	0.000	13.830	0.814
Fe oxide	0.301	0.128	5.712	0.525	0.000	0.000	0.616	0.000	5.975	1.519
Total	100,0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	Data from 17 analyses		

The average fractions of other elements rarely exceed 0.35 wt%, with slightly higher content in sphalerite grains of MS2 than of MS1 (Table 2). Of particular interest is grain identified as MS1-17, where the highest content of copper and tin has been determined. The composition of this grain includes, in addition to sphalerite and iron sulphides, Cu and Sn sulphide, which in stoichiometric terms corresponds to stannine, the content of which is close to 14 wt%.

The differentiation between the content of the main elements, and particularly of the accompanying elements in sphalerite grains of the charge mixture samples, cannot be made “directly”, due to the presence of inclusions, mainly of iron sulphides and oxides and of lead sulphide. These phases may also contain accompanying elements, and the amounts determined are the overall quantities of these elements present in all phases of the sphalerite grains.

In order to demonstrate the association between the various accompanying elements and the phases present in the examined grains of the charge mixture (MS1 and MS2), the values of the correlation coefficient were determined (Table 3).

Accompanying elements show low values of the correlation coefficient with sphalerite and with identified phases found in inclusions in sphalerite grains. One exception is the high correlation between iron oxide and manganese (0.78). Poor positive correlation was observed between:

- sphalerite and Sb,

- Pb sulphide and Ca, Mn, As, Ag, Cd,
- Fe sulphides and Ag,
- Cd sulphide and Ca, As, Se, Ag, Sb,
- Cu, Fe and Sn sulphide and As, Se, Ag,
- Fe oxide and Ca, As, Se, Sb,

which may be an indication that these elements are constituents of the given phase.

Table 2. Chemical and phase composition of sphalerite grains in charge mixture MS2 (raw material).

Element	Analysis (grain) number		Average
	MS2-18	MS2-19	
S	26.638	30.995	28.817
Ca	0.171	0.039	0.105
Mn	0.805	0.109	0.457
Fe	13.047	1.569	7.308
Cu	0.735	0.256	0.496
Zn	54.062	64.487	59.274
As	0.574	0.592	0.583
Se	0.141	0.178	0.159
Ag	0.040	0.039	0.040
Cd	0.413	0.099	0.256
Sn	0.221	0.118	0.170
Sb	0.342	0.178	0.260
Pb	2.809	1.342	2.075
Total	100.0000	100.0000	
Phase	Phase fraction		
PbS	3.334	1.574	2.454
ZnS	82.804	96.726	89.765
CdS	0.451	0.107	0.279
Fe oxide	13.411	1.594	7.502
Total	100.0000	100.0000	

Table 3. The values of the correlation coefficient between the content of the various phases in sphalerite grains and the content of accompanying elements in the charge mixture (raw material).

Phase	Ca	Mn	Cu	As	Se	Ag	Cd	Sn	Sb
ZnS	-0.08	-0.06	-0.40	0.06	-0.17	-0.48	0.09	-0.39	0.16
PbS	0.39	0.23	-0.09	0.17	0.02	0.39	0.17	-0.16	0.08
FeS_2+FeS	-0.23	-0.31	0.01	-0.30	-0.11	0.44	-0.18	0.07	-0.24
CdS	0.26	0.30	-0.07	0.15	0.20	0.29	-	-0.13	0.26
Cu_2FeSnS_4	0.01	-0.14	-	0.14	0.38	0.37	-0.08	-	-0.17
Fe oxide	0.45	0.78	0.04	0.28	0.26	-0.43	0.11	-0.07	0.26

At the same time some of the accompanying elements show similar correlation coefficients for several phases, especially Ag in relation to PbS, FeS_2–FeS, CdS and Cu_2FeSnS_4. This is further evidence showing that the accompanying elements are included in all phases of sphalerite grains of the charge mixture. However, it is difficult to state which of the phases is the main carrier of a given element.

Similar observations were made in the case of phases present in galena grains which contained inclusions of zinc sulphide or iron sulphides in the charge mixture for the process (Adamczyk Z., Nowińska K, Melaniuk- Wolny E., Szewczenko J. – in review).

3.2. Sphalerite Grains in Dusts from the Pyrometallurgical Process

Sphalerite grains present in dusts from the various process stages (PR2, PR3 and PR5), which supplement the raw materials charge, also contain inclusions of other phases, among them, as in the case of the charge mixture, lead sulphide and iron sulphides. In addition, inclusions in sphalerite grains in PR3 dust may be formed of Fe oxide, and in PR5 dust – of Zn oxide (Tables 4 to 6). Also in this case none of the sphalerite grains examined had its chemical composition close to stoichiometric.

Table 4. Chemical and phase composition of sphalerite grains in PR2 dust.

Element	PR2-1	PR2-2	PR2-3	PR2-4	PR2-5	PR2-9	PR2-10	Min	Max	x
S	32.375	31.972	32.448	32.470	34.395	35.505	35.384	31.866	35.622	33.436
Ca	0.000	0.000	0.019	0.049	0.000	0.000	0.056	0.000	0.056	0.017
Mn	0.048	0.000	0.000	0.165	0.000	0.000	0.130	0.000	1.307	0.175
Fe	0.192	0.130	0.531	0.835	3.591	6.616	7.703	0.130	7.703	2.867
Cu	0.029	0.050	0.300	0.000	0.115	0.000	0.435	0.000	0.435	0.119
Zn	65.342	64.912	64.577	63.762	61.668	56.676	53.830	53.830	65.342	61.236
As	0.000	0.869	0.058	0.010	0.000	0.420	0.324	0.000	0.869	0.340
Se	0.000	0.659	0.000	0.039	0.000	0.000	0.000	0.000	0.659	0.070
Ag	0.000	0.250	0.242	0.078	0.000	0.000	0.046	0.000	0.250	0.062
Cd	1.257	1.019	0.676	0.719	0.000	0.000	0.333	0.000	1.950	0.709
Sn	0.000	0.000	0.010	0.078	0.000	0.000	0.472	0.000	0.472	0.096
Sb	0.000	0.140	0.000	0.185	0.000	0.000	0.343	0.000	0.343	0.093
Pb	0.758	0.000	1.140	1.612	0.230	0.784	0.944	0.000	2.321	0.779
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000	Data from 17 analyses		
Phase fraction										
PbS	0.875	0.000	1.324	1.872	0.266	0.909	1.110	0.000	2.755	0.911
ZnS	97.377	98.686	96.804	95.555	92.009	84.818	81.678	81.678	98.686	92.114
FeS_2+FeS	0.412	0.208	1.148	1.804	7.725	14.273	16.851	0.208	16.851	6.213
CdS	1.336	1.105	0.723	0.768	0.000	0.000	0.361	0.000	2.084	0.762
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000	Data from 10 analyses		

The average lead content in sphalerite grains in the examined dust varied between ca. 0.39 and ca. 1.64 wt%, caused by the presence of Pb sulphide inclusions within the range of average values of ca. 0.45 to 1.92 wt% On the other hand, the average content of iron in these dusts varied from ca. 0.40 to ca. 4.41 wt%, the highest content occurring in PR2 and PR3 (several percent by weight), indicating the presence of iron sulphides in sphalerite grains in average amounts of 6.21 to 8.54 wt% or smaller amounts of Fe oxide (Tables 4 to 6).

One important element present in the examined sphalerite grains is cadmium, the average content of which in dust grains varied from ca. 0.71 to ca. 2.58 wt%. The highest amounts of cadmium were found in one of the sphalerite grains in PR5 dust (8.69 wt%) (Tables 4 to 6).

The average contents of other elements rarely exceed 0.35 wt%, except for Se and Sn in PR3 dust slightly exceeding 0.35 wt%. Selenium, the content of which in one of the sphalerite grains in PR3 dust was determined at nearly 2 wt% (PR3-3), has probably substituted sulphur in sphalerite or in inclusions of lead sulphide or of iron sulphides. The sphalerite grain PR3-6 is also of interest, as the content of Sn and Sb therein exceeds 1 wt% for each of these elements. Both of these elements may be included in Pb sulphides or in sphalerite. However, considering the process applied at the plant, they may form alloy inclusions in sphalerite grains (Tables 4 to 6).

Table 5. Chemical and phase composition of sphalerite grains in PR3 dust.

Element	PR3-1	PR3-2	PR3-3	PR3-4	PR3-5	PR3-6	PR3-7	Min	Max	x
S	31.580	30.577	31.332	35.322	29.672	35.412	37.483	29.672	37.483	33.054
Ca	0.079	0.000	0.010	0.000	0.087	0.000	0.000	0.000	0.087	0.025
Mn	0.000	0.000	0.000	0.300	0.076	0.246	1.105	0.000	1.105	0.247
Fe	1.885	1.096	0.522	7.092	0.217	8.386	11.670	0.217	11.670	4.410
Cu	0.000	0.000	0.083	0.263	0.260	0.000	0.000	0.000	0.263	0.087
Zn	64.147	62.318	63.660	55.407	57.199	52.839	48.936	48.936	64.147	57.787
As	0.000	0.000	0.000	0.917	0.000	0.529	0.335	0.000	0.917	0.254
Se	0.237	0.474	1.909	0.000	0.693	0.000	0.000	0.000	1.909	0.473
Ag	0.227	0.495	0.031	0.000	0.043	0.000	0.000	0.000	0.495	0.114
Cd	0.375	3.362	0.386	0.699	3.467	0.310	0.000	0.000	3.467	1.228
Sn	0.296	0.938	0.261	0.000	0.000	1.012	0.000	0.000	1.012	0.358
Sb	0.395	0.179	0.428	0.000	0.000	1.267	0.000	0.000	1.267	0.324
Pb	0.780	0.559	1.377	0.000	8.287	0.000	0.471	0.000	8.287	1.639
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000			
Phase fraction										
PbS	0.911	0.657	1.633	0.000	9.683	0.000	0.552	0.000	9.683	1.919
ZnS	96.776	94.585	97.410	83.785	86.242	81.104	74.005	74.005	97.410	87.701
FeS_2+FeS	0.000	0.000	0.000	15.460	0.345	18.556	25.444	0.000	25.444	8.544
CdS	0.404	3.641	0.421	0.754	3.730	0.339	0.000	0.000	3.730	1.327
Fe oxide	1.908	1.117	0.536	0.000	0.000	0.000	0.000	0.000	1.908	0.509
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000			

Table 6. Chemical and phase composition of sphalerite grains in PR5 dust.

Element	PR5-1	PR5-2	PR5-3	PR5-4	Min	Max	x
S	28.057	28.353	31.500	30.036	28.057	31.500	29.486
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.201	0.201	0.000	1.210	0.000	1.210	0.403
Cu	0.000	0.000	0.075	0.000	0.000	0.075	0.019
Zn	70.107	70.803	67.305	58.952	58.952	70.803	66.792
As	0.000	0.000	0.011	0.000	0.000	0.011	0.003
Se	0.201	0.000	0.032	0.000	0.000	0.201	0.058
Ag	0.000	0.000	0.398	0.180	0.000	0.398	0.145
Cd	0.642	0.643	0.323	8.692	0.323	8.692	2.575
Sn	0.000	0.000	0.334	0.000	0.000	0.334	0.083
Sb	0.160	0.000	0.022	0.000	0.000	0.160	0.046
Pb	0.632	0.000	0.000	0.930	0.000	0.930	0.391
Total	100.000	100.000	100.000	100.000			
Phase fraction							
PbS	0.734	0.000	0.000	1.063	0.000	1.063	0.449
ZnS	85.301	84.848	96.670	82.013	82.013	96.670	87.208
FeS_2+FeS	0.000	0.747	0.000	4.459	0.000	4.459	1.301
CdS	0.687	0.682	0.346	9.148	0.346	9.148	2.716
Zn oxide	13.278	13.723	2.984	3.316	2.984	13.723	8.325
Total	100.000	100.000	100.000	100.000			

3.3. Accompanying Elements vs. Phase Composition of Sphalerite Grains

In order to demonstrate the association between the various accompanying elements and the phases present in sphalerite grains in the examined dusts, the values of the coefficient of correlation between the elements and the phases were determined (Table 7). Some of the elements show considerably high value of this coefficient (0.69), either positive or negative, which may be an indication that:

- Pb sulphide may contain Ca, and sometimes Mn (PR2) or Cd (PR5),
- Zn sulphide may contain Cd (PR2) and Cu, As, Ag, Sn (PR5), whereas the process of formation of PR2 - and PR3 probably excludes the presence in Zn sulphide of Sn and Mn, respectively,
- Fe sulphides may contain Sn (PR2) and Mn and As (PR3) and Cd (PR5), whereas the process of formation of PR2 probably excludes the presence of Cd,
- Fe oxide may contain Ag (PR3),
- Zn oxide – Ag is probably not included in this oxide in the process of formation of PR5 dust.

Table 7. The values of the correlation coefficient between the content of the various phases in sphalerite grains in dusts and the content of accompanying elements.

Dust	Phase	Ca	Mn	Cu	As	Se	Ag	Cd	Sn	Sb
PR2	PbS	0.79	0.76	0.43	-0.03	-0.33	-0.05	0.01	0.10	0.56
	ZnS	-0.23	0.02	-0.30	-0.05	0.39	0.46	0.69	-0.74	-0.27
	FeS_2+FeS	0.11	-0.14	0.23	0.03	-0.33	-0.43	-0.74	0.70	0.17
	CdS	-0.04	0.24	-0.14	0.26	0.18	0.10	1.00	-0.34	0.01
PR3	PbS	0.72	-0.24	0.58	-0.43	0.28	-0.14	0.65	-0.38	-0.34
	ZnS	0.33	-0.85	-0.09	-0.61	0.63	0.57	0.25	0.21	0.03
	FeS_2+FeS	-0.57	0.86	-0.13	0.73	-0.62	-0.55	-0.56	-0.09	0.14
	CdS	0.33	-0.44	0.33	-0.42	0.12	0.56	1.00	0.15	-0.36
	Fe oxide	0.37	-0.49	-0.48	-0.56	0.10	0.71	0.04	0.24	0.01
PR5	PbS	-	-	-0.56	-0.56	0.28	-0.22	0.77	-0.56	0.29
	ZnS	-	-	0.97	0.97	-0.04	0.77	-0.57	0.97	-0.07
	FeS_2+FeS	-	-	-0.41	-0.41	-0.49	0.04	0.99	-0.41	-0.48
	CdS	-	-	-0.37	-0.37	-0.39	0.09	1.00	-0.37	-0.38
	Zn oxide	-	-	-0.60	-0.60	0.48	-0.89	-0.53	-0.60	0.49

The set of basic statistical data (Table 8) demonstrates the differentiation of chemical and phase compositions of sphalerite grains derived from the charge mixture (MS) and from dust (PR). This is manifested mainly in:

- lower average content of such accompanying elements as Ca, Cu and Sn in sphalerite grains in dust as compared to that in grains in charge mixture,
- higher average content of such accompanying elements as Mn, As, Se, Ag and Sb in sphalerite grains in dust as compared to that in grains in charge mixture,

In the first case this may be an indication of migration of these elements from sphalerite grains and from inclusions of other phases contained therein to the products of the process (metallic zinc and metallic lead) or to waste products generated at the various stages of the pyrometallurgical process. The second case indicates that these elements are poorly mobile when it comes to migration to the main and waste products of the process, and on the other hand they show a tendency to move to sphalerite and to new phases formed during the process (Fe oxide and Zn oxide).

The list in Table 8 also demonstrates the differentiation of the average phase fraction of sphalerite grains derived from the charge mixture to dusts, which is manifested by:

- increased sphalerite content in sphalerite grains in dust (PR) at the expense of Pb sulphide, Fe sulphides and Zn oxide as compared to initial content in sphalerite grains in charge mixture (MS),
- increased content of Cd sulphide and Zn oxide.

Thus, a specific geochemical differentiation of accompanying elements present in sphalerite grains (Fig. 1) takes place during the process, including:

- purification of sphalerite grains - reduction of the content of accompanying elements Ca, Cu and Sn (even up to 43 wt% for Ca),
- enrichment of sphalerite grains with accompanying elements Mn, As, Se, Ag and Sb (even up to 530 wt% for Se).

Table 8. Basic statistical data on the chemical and phase composition of examined sphalerite grains derived from charge mixture (MS) and from dust (PR). Explanation: Min-minimum, Max-maximum, Me-median, x-arithmetic mean, σ-standard deviation, V-variation coefficient.

Element	Min		Max		x		Me		σ		V	
	MS	PR	MS	PR	MS	PR	MS	PR	MS	PR	MS	PR
S	26.64	28.06	36.64	37.48	32.76	32.49	32.49	32.15	2.45	2.51	0.07	0.08
Ca	0.00	0.00	0.17	0.09	0.04	0.02	0.00	0.00	0.06	0.03	1.51	1.77
Mn	0.00	0.00	0.81	1.31	0.10	0.16	0.06	0.00	0.18	0.35	1.73	2.18
Fe	0.13	0.00	13.05	11.67	5.12	2.79	5.66	0.97	3.51	3.51	0.69	1.26
Cu	0.00	0.00	3.90	1.00	0.31	0.13	0.04	0.02	0.89	0.23	2.83	1.78
Zn	51.06	48.94	66.18	70.80	59.31	61.22	57.30	62.54	5.12	5.60	0.09	0.09
As	0.00	0.00	0.64	0.92	0.19	0.24	0.11	0.01	0.22	0.32	1.17	1.34
Se	0.00	0.00	0.18	1.91	0.04	0.19	0.00	0.00	0.06	0.44	1.62	2.28
Ag	0.00	0.00	0.26	0.50	0.08	0.09	0.04	0.00	0.09	0.14	1.11	1.60
Cd	0.00	0.00	0.45	8.69	0.20	1.31	0.20	0.66	0.16	1.94	0.80	1.49
Sn	0.00	0.00	3.95	1.01	0.34	0.17	0.12	0.00	0.89	0.30	2.60	1.71
Sb	0.00	0.00	0.58	1.27	0.13	0.15	0.00	0.00	0.19	0.29	1.39	1.86
Pb	0.00	0.00	7.59	8.29	1.37	1.05	0.90	0.69	1.67	1.76	1.22	1.68
Phase fraction												
PbS	0.00	0.00	8.84	9.68	1.59	1.22	1.05	0.80	1.95	2.06	1.23	1.68
ZnS	75.23	74.00	99.10	98.69	88.70	89.91	85.26	92.21	7.96	7.12	0.09	0.08
FeS_2+FeS	0.00	0.00	19.80	25.44	6.62	5.79	0.00	1.23	7.52	7.86	1.14	1.36
CdS	0.00	0.00	0.48	9.15	0.22	1.40	0.21	0.71	0.17	2.05	0.80	1.47
Cu_2FeSnS_4	0.00	0.00	13.83	0.00	0.73	0.00	0.00	0.00	3.17	0.00	4.36	-
Fe oxide	0.00	0.00	13.41	1.91	2.15	0.16	0.39	0.00	3.45	0.47	1.61	2.89
Zn oxide	0.00	0.00	0.00	13.72	0.00	1.51	0.00	0.00	0.00	3.99	-	2.64

Of interest is also decreased content of Fe and Pb in sphalerite grains derived from dust as compared to that content in sphalerite grains derived from the charge mixture (Fig. 1), the result of which is a drop in the content of phases that contain these elements – Pb sulphide and Fe sulphide (Fig. 2). An opposite case occurs with Cd, the content of which in dust, as compared to its content in the charge mixture, rises significantly to over 600 wt%, leading thereby to increased content of Cd sulphide in dusts (Figs. 1 and 2).

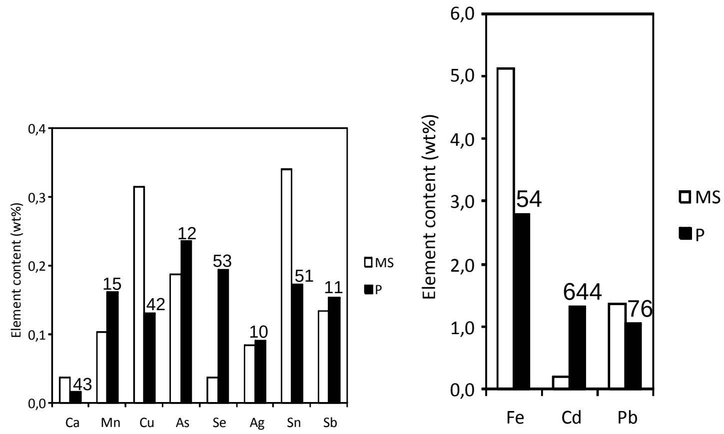

Fig. 1. Differentiation of the average content and percentage change of the average content of elements in sphalerite grains derived from dusts (PR) in relation to the charge mixture (MS)

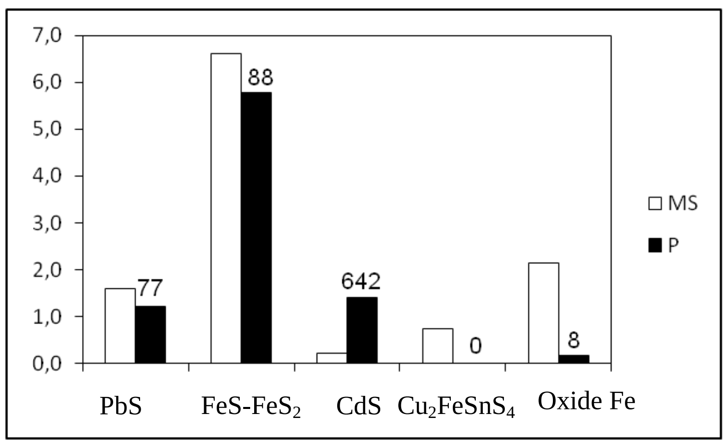

Fig. 2. Differentiation of the average fraction and percentage change of the average fraction of phases in sphalerite grains derived from dusts (PR) in relation to the charge mixture (MS).

4. Conclusions

The investigations carried out allow to draw the following conclusions:

1. Sphalerite grains, in both the charge mixture (raw material) and in dusts from the various stages of the pyrometallurgical zinc and lead production process, contain inclusions of Pb sulphide, Fe sulphides, Cd sulphide, Fe oxide and stannine in zinc blende concentrate and of Zn oxide in dusts.
2. Sphalerite grains derived from the charge mixture contain admixtures of such accompanying elements as Ca, Mn, Cu, As, Se, Ag, Sn and Sb. These elements are present both in the sphalerite of sphalerite grains, as well as in phases contained therein in the form of inclusions. Some of these elements form their own phases (e.g. Cu, Fe and Sn - stannine) or metallic alloys (e.g. Sn and Sb).
3. Differences in the content of the various accompanying elements in sphalerite grains in the charge mixture and in dust from the various process stages, may be an indication of migration of these elements during the pyrometallurgical process from sphalerite grains to the main products of the process (zinc, lead) and to waste products.
4. A specific geochemical differentiation of accompanying elements present in sphalerite grains takes place during the process, including:

– purification of sphalerite grains - reduction of the content of accompanying elements Ca, Cu and Sn,
– enrichment of sphalerite grains with accompanying elements Mn, As, Se, Ag and Sb.

5. A decrease is observed in the content of Fe and Pb in sphalerite grains derived from dust as compared to that content in sphalerite grains derived from the charge mixture, the result of which is a drop in the content of phases that contain these elements – Pb sulphide and Fe sulphide. An opposite case occurs with Cd, the content of which in dust, as compared to its content in the charge mixture, rises significantly to over 600 wt%, leading thereby to increased content of Cd sulphide in dust.

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