Variation of the content of accompanying elements in galena in pyrometallurgical process of zinc and lead production

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Concentrates of zinc and lead are primary raw materials in the pyrometallurgical process (Imperial Smelting Process) of lead and zinc production. During the studies it was found that Zn (sphalerite) and Pb (galena) sulphides were the main minerals in the raw material. The examined samples, taken from particular technological sections showed presence of galena. After detailed chemical studies it was found that this mineral showed high variation of concentration of accompanying elements, such as: Ca, Mn, Cu, As, Se, Ag, Cd, Sn, Sb. The results of these studies may make, in addition to providing a better understanding of accompanying elements circulation in the ISP technological process, a valuable contribution to the identification of the forms of occurrence of the accompanying elements in the various technological wastes. The form of elements occurrence in wastes is the basic factor in the development of optimal metals recovery method.

Keywords: *Imperial Smelting Process, pyrometallurgical process, zinc, lead, galena, accompanying elements*

Introduction

The growing interest in the winning of accompanying elements in the pyrometallurgical production of zinc and lead creates the need to identify the forms in which these elements occur at the various stages of the process. This is dictated by both environmental as well as economic requirements. The identification of these forms includes detailed examination of mineral components present in the raw material, in the dust and in waste products (Pozzi M., Nowińska K., 2006).

The aim of this study was to demonstrate the diversity of the content of accompanying elements in galena derived from galena concentrate (the raw material) and from dusts generated at the various stages of the pyrometallurgical production process of zinc and lead. These dusts are recycled in the process and included in the raw material charge (Zinc and Lead Production Process in "Miasteczko Śląskie" Zinc Smelting Plant, 2000).

Experimental setup and procedure

Test samples were taken from the charge mixture for the sinter plant (Raw Materials Store 1) and from dusts from the various process stages, including dust from fabric filters in the sinter plant (FT12- sample PR2 and FT 24- sample PR3), dust from the grinding mill in the sinter plant (FT12R- sample PR5) and from the lead refinery (FT10-sample PR7). Samples were used to make specimens for investigating the chemical composition within micro-areas using an X-ray microanalyser.

The chemical composition (qualitative and quantitative) of the separate grains was determined by means of a Joel JCXA 733 X-ray microanalyser. The microanalyser was equipped with an ISIS 300 energy-dispersive spectrometer from Oxford Instruments (Sokołowski J., Nosiła M., Pluta B., 1980; Szummer A., 1994) and the measurements were performed under the following conditions: focused beam (diameter: 1-2 µm, accelerating voltage 20 kV, current $3 \cdot 10^{-9}$ A).

A series of microanalyses was conducted for each of the grains studied, such series comprising up to ten chemical composition measurements carried out to determine the main chemical components (sulphur and lead) and accompanying elements (the remaining elements). The average of 10 measurements was taken as the final result.

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Results

The charges for the pyrometallurgical zinc and lead production process comprise appropriately proportioned blends of raw materials (sphalerite and galena concentrates), intermediates (Zn-Pb sinter) and waste products (dust, dross, recycles, slag) and process products (crude zinc and crude lead). The primary raw materials for the process are concentrates of sphalerite and galena, and therefore the starting point of pondering over the occurrence and possible migration of the various accompanying elements in galena was the galena concentrate (Melaniuk-Wolny E., 2001).

The galena grains present in this concentrate always contain inclusions of other sulphides, including zinc and iron sulphides. This is indicated by the chemical composition of the examined galena grains. The theoretical composition of galena is 86.60 wt. % Pb and 13.40 wt. % S, whereas out of 10 grains examined, only one (designated MS-1) had its chemical composition close to stoichiometric. The remaining grains contained excess amount of sulphur and were deficient in lead, and also contained such high amount of zinc, and lesser amount of iron, that most probably these metals formed separate sulphide phases (Tab. 1).

Tab. 1. Chemical and phase composition of galena grains in galena concentrate (raw material).

Element	**Analysis (grain) designation**									
	MS1-1	**MS1-2**	**MS1-3**	**MS1-4**	**MS1-5**	**MS1-6**	**MS1-7**	**MS1-8**	**MS1-9**	**MS1-10**
	Chemical composition [wt. %]									
S	12.9652	15.3793	13.2939	14.8141	14.1384	14.3714	14.6559	14.6825	15.1486	16.2205
Ca	0.0792	0.0099	0.2207	0.0396	0.0785	0.0600	0.2085	0.0000	0.0684	0.0398
Mn	0.2672	0.0000	0.2910	0.0000	0.1865	0.0600	0.0397	0.4762	0.2248	0.1493
Fe	0.0000	0.2667	0.0000	0.0890	0.4320	0.2399	0.4468	0.0694	0.2248	0.0597
Cu	0.0000	0.2371	0.2408	0.0297	0.0098	0.2598	0.1489	0.0794	0.0391	0.1493
Zn	0.5344	1.0766	0.5017	2.3042	2.9553	3.8777	4.8059	5.1786	7.2713	9.9811
As	0.5839	0.0000	0.5920	0.0396	0.0000	0.1999	0.0000	0.0000	0.0000	0.2985
Se	0.2276	0.6124	0.4916	0.1681	0.3436	0.0200	0.1589	0.3671	0.1271	0.0000
Ag	0.0000	0.0395	0.4515	0.0494	0.0000	0.0000	0.0000	0.6151	0.3421	0.2189
Cd	0.1188	0.8495	1.6555	0.0000	0.0196	0.2399	0.0000	0.1389	0.4593	0.0000
Sn	0.2177	0.0000	1.6354	0.0000	0.0000	0.1799	0.1887	0.0000	0.2052	0.0000
Sb	0.7522	0.0000	1.5050	0.0000	0.0589	0.3298	0.0000	0.0000	0.4984	0.2189
Pb	84.2538	81.5290	79.1211	82.4664	81.7771	80.1619	79.3466	78.3929	75.3909	72.6639
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Phase	**Phase composition**									
PbS	99.1880	94.2075	97.5917	94.8568	95.5438	94.1238	92.0838	92.1442	88.9304	84.9419
ZnS	0.8120	1.6056	0.7986	3.4206	4.4562	5.8762	7.1981	7.8558	11.0696	15.0581
FeS_2+ Fe_xS_{2-x}	0.0000	4.1869	1.6098	1.7226	0.0000	0.0000	0.7182	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

Zinc content in galena varied between 0.50 and 9.98 wt. %., caused by the presence of zinc sulphide inclusions within the range of ca. 0.80 to 15.00 wt. %. Iron content, on the other hand, varied between 0.00 and 0.44 wt. %, indicating the presence of iron sulphides (FeS_2 and Fe_xS_{2-x}) in amounts of 0.00 to 4.18 wt. %.

The differentiation between the content of the main elements, and particularly the accompanying elements in galena grains of the galena concentrate cannot be made “directly” due to the presence of zinc and iron sulphide inclusions. These sulphides may also contain accompanying elements, and the amounts determined are the overall quantities of these elements present in all phases of the grain, i.e. in galena, zinc and iron sulphides. In order to demonstrate the association between the various accompanying elements and the phases present in the examined galena concentrate grains, the values of the coefficient of correlation between them were determined (Tab. 2).

These values showed positive correlation between galena and elements such as Ca, Mn, As, Se, Cd, Sn and Sb, which may be an indication that these elements are constituents of this phase. Some of these elements show positive correlation with zinc or iron sulphide (Mn, Se, Cd and Sn), whereas Ag correlated positively only with zinc sulphide, and Cu only with iron sulphide.

Among the examined galena grains in galena concentrate of particular interest was grain MS-3, wherein the content of Cd, Sn and Sb is more than 1.50 wt. % (Tab. 1) of each of these elements. This grain presumably contains a sulphide phase (or phases) of these metals.

Tab. 2. The values of the coefficient of correlation between the content of the various phases in galena grains and the content of accompanying elements in galena concentrate (raw material).

Phase	Ca	Mn	Cu	As	Se	Ag	Cd	Sn	Sb
PbS	0.28	0.06	-0.06	0.40	0.50	-0.25	0.32	0.39	0.39
ZnS	-0.23	0.08	-0.08	-0.32	-0.65	0.27	-0.44	-0.38	-0.33
FeS_2+ Fe_xS_{2-x}	-0.05	-0.48	0.44	-0.13	0.69	-0.16	0.51	0.13	-0.06

Galena present in the dust added to the raw material charge always contains inclusions of other sulphides, including, as was also in the case of galena concentrate, zinc and iron sulphides (Tab. 3). In this case none of the galena grains examined had its chemical composition close to stoichiometric.

Tab. 3. Chemical and phase composition of galena grains in dust derived from various process stages.

Element	Analysis (grain) designation									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
	Chemical composition [wt. %]									
S	14.2813	14.0112	14.5191	14.4279	14.2492	14.2799	14.2969	14.8270	16.8042	13.8190
Ca	0.0000	0.0885	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0298	0.0691
Mn	0.0000	0.1180	0.0875	0.0000	0.0197	0.0000	0.0000	0.0000	0.1491	0.0000
Fe	0.2994	0.2105	0.3793	0.0000	0.0393	0.1626	0.0000	0.5413	0.3480	0.1974
Cu	0.0000	0.2459	0.0875	0.0000	0.0000	0.0000	0.0000	0.2223	0.1591	0.1086
Zn	2.1754	2.6458	2.9563	3.7910	3.3805	3.2422	4.1156	4.2045	11.5939	1.5694
As	0.0599	0.4229	0.0778	0.1393	0.0000	0.1829	0.0805	0.2706	0.0000	0.0000
Se	0.0000	0.2557	0.0972	0.0995	0.1179	0.0000	0.1107	0.0000	0.1491	0.1875
Ag	0.0000	0.0000	0.0000	0.1493	0.1474	0.6505	0.4327	0.4350	0.2486	0.0000
Cd	0.0000	0.0000	0.0000	0.1791	0.2653	0.6606	0.7446	1.0246	1.1833	0.0000
Sn	0.0000	0.0885	0.0000	0.0000	0.4226	0.0000	0.3723	0.0000	0.0000	0.0000
Sb	0.0000	0.0000	0.1361	0.0000	0.2457	0.0000	0.4931	0.0000	0.0000	0.0000
Pb	83.1841	81.9129	81.6590	81.2139	81.1124	80.8212	79.3536	78.4748	69.3348	84.0490
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Phase	**Phase composition**									
PbS	96.1127	95.6572	94.7556	94.3126	94.8216	94.7437	93.7251	92.4203	81.6352	97.5648
ZnS	3.2439	3.9877	4.4274	5.6818	5.1002	4.9052	6.2735	6.3906	17.6176	2.3512
FeS_2+ Fe_xS_{2-x}	0.6434	0.3551	0.8170	0.0055	0.0782	0.3511	0.0014	1.1891	0.7472	0.0839
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

Zinc content in galena in dust varied between 1.57 and 11.59 wt. %, caused by the presence of zinc sulphide inclusions within the range of ca. 2.32 to 17.61 wt. %. Iron content, on the other hand, varied between 0.00 and 0.54 wt. %, indicating the presence of iron sulphides in amounts of 0.00 to 3.24 wt. %.

The determined content of the main elements, and particularly of accompanying elements in galena grains derived from the dust, as was also in the case of galena concentrate, is the overall quantity of these elements present in all phases of the grain, i.e. in galena, zinc and iron sulphides. In order to demonstrate the association between the various accompanying elements and the phases present in the dust grains examined, the values of the coefficient of correlation between them were determined (Tab. 4).

Tab. 3. (contd.)

Element	Analysis (grain) designation						
	PR3-2	**PR3-3**	**PR5-6***	**PR5-7***	**PR5-8***	**PR7-32***	**PR7-33***
	Chemical composition						
S	14.7062	14.4029	13.3287	14.8595	13.1238	14.2552	13.4194
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mn	0.1114	0.0391	0.0000	0.0399	0.0000	0.0196	0.0000
Fe	0.5104	0.1172	0.1800	0.0000	0.3213	0.0587	0.0702
Cu	0.3434	0.3613	0.0000	0.0000	0.3012	0.6846	0.3911
Zn	3.3873	3.7203	3.1297	1.5846	4.6892	3.4130	1.8251
As	0.0000	0.0976	0.4200	0.0000	0.0904	0.0000	0.4011
Se	0.4176	0.0781	0.0000	0.0000	0.1004	0.0000	0.0000
Ag	0.0000	0.0000	0.0000	0.0997	0.0000	0.0000	0.0000
Cd	0.0000	0.0000	0.0000	0.0000	0.0000	0.0293	0.9125
Sn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.4841
Sb	0.0000	0.0000	0.0000	0.1894	0.0000	0,0000	0.3109
Pb	80.5238	81.1835	82.9417	83.2270	81.3736	81.5396	81.1856
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Phase	**Phase composition**						
PbS	93.8015	94.3851	95.3563	94.4336	93.0777	94.8614	97.1723
ZnS	5.0924	5.5822	4.6437	2.3205	6.9223	5.1386	2.8277
FeS_2+ Fe_xS_{2-x}	1.1061	0.0327	0.0000	3.2460	0.0000	0.0000	0.0000
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

*Explanation: * - PR5-6; PR5-7; PR5-8 – sample of dust from fabric filter FT- 12R;*
PR7-32; PR7-33 – sample of dust from fabric filter FT-10; analysis results according to (Adamczyk Z., Melaniuk-Wolny E., Nowińska K., 2010)

Tab. 4. The values of the coefficient of correlation between the content of the various phases in galena grains and the content of trace elements in dust.

Phase	Ca	Mn	Cu	As	Se	Ag	Cd	Sn	Sb
PbS	0.01	-0.57	-0.32	0.00	-0.97	0.27	-0.13	-0.30	-0.55
ZnS	0.01	0.51	0.28	0.05	1.00	-0.21	0.14	0.29	0.57
FeS_2+ Fe_xS_{2-x}	-0.10	0.28	0.17	-0.21	-0.08	-0.25	-0.03	0.06	-0.03

These values showed positive correlation between galena and only such elements as Ca and Ag, which may be an indication that these elements are constituents of this phase. Ca also showed positive correlation with zinc sulphides. The remaining elements, such as Mn, Cu, As, Se, Cd, Sn and Sb, correlated positively with zinc sulphides, while Mn, Cu and Sn correlated positively with iron sulphides.

Among the examined galena grains in dust, of particular interest were these where Cd content was more than 1 wt. % (grains P-8 and P-9) or where Sn content was close to 1.50 wt. % (grain P-17) (Tab. 3). Presumably the elements formed separate sulphide phases in these grains.

Comparison between basic statistical data (Tab. 5) demonstrates the difference of chemical and phase compositions of galena grains derived from galena concentrate and from dust. This is manifested mainly in:

- lower content of most of the accompanying elements (Ca, Mn, As, Se, Ag, Cd, Sn and Sb) in galena grains in dust as compared to that in grains in galena concentrate (the exceptions being Fe and Cu),
- increased galena content in galena grains in dust at the expense of zinc and iron sulphides as compared to initial content in galena grains in galena concentrate.

This may be an indication of migration of these elements from galena grains to the products of the process (crude zinc, crude lead) or to waste products at the various stages of the pyrometallurgical process. Therefore, specific purification of the galena grains must take place during the production process, resulting in the reduction of the content of accompanying elements (Fig. 1) by even more than 60 wt. % (Ca, Mn, Se and Sb).

Tab. 5. Basic statistical data on the chemical and phase composition of examined galena grains derived from galena concentrate (MS) and from dust (P).

Element		S	Ca	Mn	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Pb	PbS	ZnS	FeS_2+FeS
Min. [% wt.]	MS*	12.97	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.00	0.00	72.66	84.94	0.80	0.00
	P	13.12	0.00	0.00	0.00	0.00	1.57	0.00	0.00	0.00	0.00	0.00	0.00	69.33	81.64	2.32	0.00
Max. [% wt.]	MS*	16.22	0.22	0.48	0.45	0.26	9.98	0.59	0.61	0.62	1.66	1.64	1.50	84.25	99.19	15.06	4.19
	P	16.80	0.09	0.15	0.54	0.68	11.59	0.42	0.42	0.65	1.18	1.48	0.49	84.05	97.56	17.62	3.25
x [% wt.]	MS*	14.57	0.08	0.17	0.18	0.12	3.85	0.17	0.25	0.17	0.35	0.24	0.34	79.51	93.36	5.82	0.82
	P	14.33	0.01	0.03	0.20	0.17	3.61	0.13	0.09	0.13	0.29	0.14	0.08	80.77	94.05	5.44	0.51
Me [% wt.]	MS	14.67	0.06	0.17	0.16	0.11	3.42	0.02	0.20	0.04	0.13	0.09	0.14	79.75	94.17	5.17	0.00
	P	14.28	0.00	0.00	0.18	0.11	3.38	0.08	0.10	0.00	0.00	0.00	0.00	81.21	94.74	5.09	0.08
σ [% wt.]	MS	0.96	0.08	0.15	0.17	0.10	3.07	0.24	0.20	0.23	0.53	0.50	0.48	3.43	4.13	4.65	1.37
	P	0.81	0.03	0.05	0.17	0.20	2.25	0.15	0.11	0.20	0.43	0.37	0.15	3.25	3.46	3.42	0.82
V [%]	MS	0.07	0.94	0.90	0.91	0.85	0.80	1.41	0.79	1.31	1.53	2.06	1.44	0.04	0.04	0.80	1.66
	P	0.06	2.42	1.46	0.86	1.15	0.62	1.17	1.19	1.57	1.45	2.66	1.81	0.04	0.04	0.63	1.60

Explanation: Min-minimum, Max-maximum, Me-median, x-arithmetic mean, σ-standard deviation, V-variation coefficient Explanation:
** - MS – sample taken from raw materials store - data according to (Adamczyk Z., Melaniuk-Wolny E., Nowińska K., 2010)*

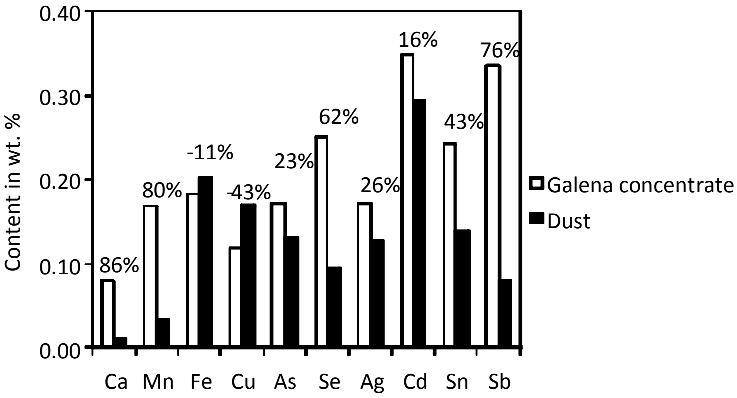

Fig. 1. Comparison of content of accompanying elements in galena grains in dust with that in galena concentrate and percentage of content change

Conclusions

The investigations carried out allow to draw the following conclusions:

1. Galena grains, in both the galena concentrate (raw material) and in dust from the various stages of the pyrometallurgical zinc and lead production process, contain inclusions of zinc and iron sulphides.
2. Inclusions of Cd, Sn and Sb sulphides may occur in galena of the galena concentrate, and inclusions of Cd and Sn sulphides may occur in galena in the dust.
3. Galena in the galena concentrate contains admixtures of such accompanying elements as Ca, Mn, As, Se, Cd, Sn and Sb, whereas galena in the dust contains Ca and Ag.
4. Zinc and iron sulphides, present in the form of inclusions in galena of the galena concentrate, contain accompanying elements, such as Mn, Se, Cd and Sn, whereas zinc sulphide additionally contains Ag, and iron sulphides additionally contain Cu.
5. Zinc sulphides, present in the form of inclusions in galena derived from dust, contain accompanying elements, such as Ca, Mn, Cu, As, Se, Cd, Sn and Sb, whereas iron sulphides contain Mn, Cu and Sn.
6. Differences in the content of the various accompanying elements in galena grains in galena concentrate and in galena grains derived from dust from the various process stages, may be an indication of migration of these elements during the pyrometallurgical process from galena grains to the main products of the process (crude zinc, crude lead) and to waste products. Specific purification of the galena grains takes place during the production process, resulting in the reduction of the content

of accompanying elements by even more than 60 wt. % (Ca, Mn, Se and Sb) in relation to galena present in the raw material.

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