Proceedings of the 3rd World Congress on Mechanical, Chemical, and Material Engineering (MCM'17)
Rome, Italy – June 8 – 10, 2017
Paper No. MMME 136
ISSN: 2369-8136
DOI: 10.11159/mmme17.136

Chemical Composition of Iron Sulphides Contained In Dust from the Pyrometallurgical Zn and Pb Production

Zdzisław Adamczyk, Katarzyna Nowińska
Institute of Applied Geology, Silesian University of Technology
Akademicka 2, Gliwice, Poland
katarzyna.nowinska@polsl.pl; zdzislaw.adamczyk@polsl.pl

Abstract **–** The paper presents results of investigations of chemical composition of iron sulphides contained in dust from the pyrometallurgical production process of zinc and lead. The main mineral components of these dusts are oxides of lead and zinc, sulphides of lead and zinc and sulphides of iron. The tests performed have demonstrated that the chemical composition of iron sulphide grains was not close to stoichiometric, the grains were non-uniform in terms of phase composition, and they always included admixtures in the form of inclusions of other sulphides, i.e. zinc sulphide and lead sulphide, and accompanying elements (Ca, Mn, Se, As, Ag, Cu, Cd, Se).

Keywords**:** Pyrometallurgy, Zinc, Lead, Iron Suplhide, Dust, Imperial Smelting Process

1. Introduction

The "Miasteczko Śląskie" Zinc Smelting Plant is the only zinc and lead manufacturer in Europe that uses the Imperial Smelting Process (ISP) pyrometallurgical process. Dusts emitted by the plant are much diversified in terms of chemical and mineral composition. The main mineral components of these dusts are oxides of lead and zinc, sulphides of lead and zinc and sulphides of iron. These constituents contain, in addition to main elements, a number of accompanying elements, such as [1, 2, 3, 4, 5]. The mineral constituents emitted with the dusts may undergo decomposition and may release the elements contained therein into the hypergenic environment.

The aim of this study was to demonstrate the diversity of the content of accompanying elements in iron sulphides present in the dusts emitted from the ISP process.

2. Characteristics of dusts from the ISP process

The basic production departments of the zinc smelting plant include the Sinter Unit, the Shaft Furnace Unit, the Lead Refining Unit and the Zinc Refining Unit. 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). The following types of dust are generated in the production process [6]:

Dust no. 1 – from the sinter grinding unit (12-chamber filter),
Dust no. 2 – from the sinter unit (12-chamber filter),
Dust no. 3 – from the sinter unit (24-chamber filter),
Dust no. 4 – from electrostatic precipitator,
Dust no. 5 – from the shaft furnace (12-chamber filter),
Dust no. 6– from lead refining (10-chamber filter),
Dust no. 7 – from sinter unit storage yard.

These dusts contain mainly fine particles, smaller than 20 μm, whereas the percentage of the particular grain fractions depends chiefly on the conditions of running the production processes and on the properties of the processed raw materials. In the case of dusts from high-temperature processes (dusts nos. 2, 3, 4 and 5), particles of less than 2.5 μm are predominant, while dusts from units where dust generation results from mechanical comminution of raw materials (dusts nos. 1 and 7) contain larger amounts of particles of the 10-63 μm fractions [3].

The mineral composition of the dusts listed above is diverse, with the main constituents including: sulphides (ZnS, PbS, FeS2), oxides (ZnO, PbO, FeO) and sulphates (Pb, Zn, Fe). These constituents rarely occur in the form of individual grains. In most cases they form complex multiphase systems, being the result of phase transformations occurring in the course of the pyrometallurgical process.

The presence of iron sulphides was established in dusts from high-temperature processes, that is in those from the roast sintering process (1200°C) (dusts nos. 2 and 3) and from the shaft furnace process (1000°C) (dust no. 5). Earlier research has shown that iron sulphides present in the analysed dusts were derived from the MS-1 charge mixture in the ISP process [7].

3. Experimental setup and procedure

Dust samples were taken for testing from fabric filters of the Sinter Unit (FT12 - sample PR-2, FT24 - sample PR-3) and of the Shaft Furnace Unit (FT12 - sample PR-5). 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 [8], and the measurements were performed under the following conditions: focused beam (diameter: 1-2 μm, accelerating voltage 20 kV, current 3·10-9 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 iron) and accompanying elements (the remaining elements). The average of 10 measurements was taken as the final result.

4. Results

Most likely, the iron sulphide FeS2 grains present in PR-2, PR-3 and PR-5 dusts contain inclusions of zinc sulphide and lead sulphide. This is indicated by the chemical composition of the examined grains of iron sulphides which, in theory, should contain 53.50 wt.% S and 46.50 wt.% Fe in the case of FeS2, or 36.47 wt.%. S and 63.53 wt.% Fe in the case of FeS.

A large deficit of sulphur content and deficit of iron is usually observed in all iron sulphide grains, with large amount of zinc and relatively high percentage of lead determined at the same time.

In the PR-2 dust the zinc content in iron sulphide FeS2 varied between ca. 1.05 and ca. 1.73 wt.%., caused by the presence of zinc sulphide inclusions within the range of ca. 1.62 to ca. 2.6 wt.%.

Lead content, on the other hand, varied between 0.58 and ca. 2.04 wt.%, indicating the presence of lead sulphides in amounts of 0.68 to 2.39 wt.% (Table 1).

Table 1: Chemical and phase composition of iron sulphide grains in sample PR-2 (dust from the Sinter Unit) (wt. %).

Element	Analysis (grain) number						Average
	1	2	3	4	5	6	
S	51.5857	51.6671	51.3658	50.9791	51.4558	51.0557	51.3515
Ca	0.0000	0.0696	0.0000	0.0000	0.0000	0.2934	0.0605
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.1815	0.0302
Fe	44.1209	44.3043	43.7380	43.8374	43.9830	43.8465	43.9717
Cu	0.0592	0.0597	0.0000	0.4497	0.0000	0.4158	0.1851
Zn	1.4656	1.4423	1.7281	1.0523	1.3808	1.0765	1.3576
As	0.7548	1.2232	0.3377	0.8500	0.4300	1.0409	0.7517
Se	0.0628	0.1789	0.0099	0.2130	0.0699	0.2130	0.1246
Ag	0.2877	0.0000	0.1986	0.7563	0.2300	0.2244	0.2828
Cd	0.0000	0.0000	0.0000	0.4821	0.0000	0.0000	0.0804
Sn	0.0000	0.0000	0.1490	0.0596	0.0265	0.0000	0.0392
Sb	0.3869	0.4777	0.4271	0.5277	0.6327	0.5340	0.4977
Pb	1.2763	0.5770	2.0459	0.7927	1.7913	1.1184	1.2669
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	
Phase fraction							
FeS_2	96.2841	97.1266	95.0073	97.4305	95.8158	97.0175	96.2841
ZnS	2.2188	2.1935	2.6040	1.6225	2.0867	1.6523	2.2188
PbS	1.4971	0.6800	2.3887	0.9470	2.0975	1.3302	1.4971
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	

In order to demonstrate the association between the various accompanying elements determined in pyrite grains and the phases present in the form of inclusions in the examined dust grains PR-2, PR-3 and PR-5, the values of the coefficient of correlation between them were determined (Tables 2, 5, 6).

Table 2: The values of the correlation coefficient between the content of the various phases in iron sulphide grains and the content of accompanying elements in the PR-2 dust (significant correlation for $p<0.05$ is indicated in bold).

Phase	Ca	Mn	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Pb
FeS_2	0.40	0.30	0.34	0.70	**-0.82**	**0.85**	**0.95**	0.34	0.52	-0.64	0.18	**-0.95**
ZnS	-0.51	-0.54	0.13	**-0.95**	**1.00**	-0.48	**-0.86**	-0.57	-0.58	0.50	-0.51	0.58
PbS	-0.27	-0.12	-0.55	-0.44	0.58	**-0.93**	**-0.84**	-0.15	-0.41	0.61	0.04	**1.00**

The values of the correlation coefficient listed in Table 2 show a significant positive correlation between iron sulphide FeS_2 and elements such as As and Se, which may be an indication that these elements are constituents of this phase.

The values of the correlation coefficients of the various accompanying elements in the iron sulphide FeS_2 grains in the PR-2 dust indicate (Table 3) that there are significant correlations ($p<0.05$) between them:

- positive: Ca and Mn; As and Se;
- negative: S and Cu; Zn and Cu; Ca and Mn; Fe and Cu, As, Ag; As and Se; Se and Ag, Pb.

Table 3: The values of the correlation coefficient between accompanying elements in iron sulphide grains in PR-2 dust (significant values of correlation coefficients at $p<0.05$ shown in bold).

	S	Ca	Mn	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Sb
Ca	-0.39											
Mn	-0.52	**0.97**										
Fe	0.76	-0.11	-0.29									
Cu	**-0.89**	0.51	0.58	-0.40								
Zn	0.71	-0.51	-0.54	0.13	**-0.95**							
As	-0.05	0.54	0.38	0.51	0.37	-0.49						
Se	-0.52	0.58	0.49	0.13	0.80	**-0.87**	**0.81**					
Ag	-0.72	-0.25	-0.11	-0.49	0.67	-0.57	-0.10	0.30				
Cd	-0.65	-0.25	-0.20	-0.31	0.66	-0.58	0.13	0.49	**0.92**			
Sn	-0.21	-0.41	-0.33	-0.69	-0.23	0.50	-0.62	-0.51	0.19	0.17		
Sb	-0.34	0.18	0.20	-0.15	0.44	-0.50	-0.17	0.32	0.15	0.17	-0.20	
Pb	0.09	-0.28	-0.13	-0.54	-0.45	0.59	**-0.93**	**-0.85**	-0.16	-0.41	0.61	0.04

The chemical composition of iron sulphide FeS2 grains identified in PR-3 dust, like those in PR-2 dust, is not close to stoichiometric, wherein these are accompanied by FeS inclusions in an amount of ca. 4.7 to ca. 13.9 wt.%. The FeS2 grains contain, in addition to iron sulphide FeS, admixtures of ZnS (ca. 0.58 to ca. 3.57 wt.%) and of PbS (0.0000 to ca. 1.82 wt.%) (Table 4).

Table 4: Chemical and phase composition of iron sulphide grains in sample PR-3 (dust from the Sinter Unit) (wt. %).

Element	Analysis (grain) number						Average
	1	2	3	4	5	6	
S	50.8264	50.6725	50.1040	50.0045	49.9716	49.1105	50.1149
Ca	0.1784	0.1495	0.1594	0.1768	0.1263	0.1410	0.1552
Mn	0.0209	0.0000	0.0598	0.0098	0.0320	0.0368	0.0266
Fe	44.7661	46.7968	45.8009	45.7163	46.7168	46.3059	46.0171
Cu	0.4077	0.0000	0.1594	0.0255	0.2209	0.3662	0.1966
Zn	2.0838	0.3886	1.5141	2.3550	1.1214	1.3972	1.4767
As	0.0000	0.3179	0.2891	0.2678	0.0731	0.2094	0.1929
Se	0.1361	0.0409	0.4194	0.0144	0.2647	0.3675	0.2071
Ag	0.7107	0.0000	0.0996	0.4532	0.0430	0.3563	0.2771
Cd	0.1057	0.0000	0.6079	0.2100	0.2465	0.0968	0.2111
Sn	0.2198	0.0000	0.7078	0.3109	0.1562	0.3435	0.2897
Sb	0.0000	0.0697	0.0787	0.0240	0.0000	0.0000	0.0287
Pb	0.5443	1.5642	0.0000	0.4318	1.0275	1.2689	0.8061
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	
Phase fraction							
FeS_2	91.4696	87.9255	88.5864	85.3223	84.9568	82.5307	86.7985
FeS	4.7283	9.6751	9.0974	10.6048	12.1519	13.8521	10.0183
ZnS	3.1621	0.5825	2.3163	3.5662	1.6909	2.1232	2.2402
PbS	0.6399	1.8169	0.0000	0.5067	1.2004	1.4941	0.9430
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	

The values of the correlation coefficients of the various accompanying elements in the iron sulphide grains in the PR-3 dust indicate (Table 5) that there are no significant correlations ($p<0.05$) between them.

Table 5: The values of the correlation coefficient between the content of the various phases in iron sulphide grains and the content of accompanying elements in the PR-3 dust (significant correlation for $p<0.05$ is indicated in bold).

Phase	Ca	Mn	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Sb	Pb
FeS_2	0.59	-0.08	-0.62	0.07	0.12	-0.27	-0.24	0.28	0.12	0.02	0.32	-0.39
FeS	-0.72	0.15	0.76	-0.16	-0.31	0.37	0.33	-0.49	-0.03	0.0000	-0.14	0.43
ZnS	0.71	0.13	-0.81	0.29	1.00	-0.31	-0.09	0.81	0.24	0.43	-0.40	-0.72
PbS	-0.59	-0.53	0.67	-0.05	-0.71	0.05	-0.24	-0.32	-0.80	-0.79	-0.19	1.00

Correlation coefficients presented in Table 6 indicate the existence of significant correlations ($p<0.05$) between accompanying elements:

- positive: Mn and Se, Cd; Cd and Sn;
- negative: Ca and Fe; Fe and Ag.

Table 6: The values of the correlation coefficient between accompanying elements in iron sulphide grains in PR-3 dust (significant values of correlation coefficients at $p<0.05$ shown in bold).

	S	Ca	Mn	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Sb
Ca	0.47											
Mn	-0.44	-0.23										
Fe	-0.35	**-0.84**	-0.11									
Cu	-0.22	-0.05	0.42	-0.45								
Zn	-0.07	0.71	0.12	-0.81	0.28							
As	-0.20	0.00	-0.06	0.44	-0.75	-0.32						
Se	-0.57	-0.46	**0.95**	0.09	0.50	-0.10	-0.05					
Ag	0.11	0.71	-0.15	**-0.86**	0.55	0.81	-0.52	-0.24				
Cd	-0.13	0.05	**0.81**	-0.16	-0.08	0.24	0.19	0.61	-0.25			
Sn	-0.35	0.22	**0.85**	-0.35	0.14	0.42	0.23	0.69	0.05	**0.88**		
Sb	0.32	0.12	0.09	0.22	-0.67	-0.40	0.77	0.02	-0.57	0.42	0.30	
Pb	-0.12	-0.58	-0.54	0.68	-0.05	-0.71	0.06	-0.24	-0.32	-0.80	-0.79	-0.18

The iron sulphide FeS grains identified in the PR-5 dust are characterised by high content of both zinc (ca. 1.01 to ca. 2.58 wt.%) and lead (ca. 0.07 to ca. 4.58 wt.%), caused by the presence of zinc sulphide inclusions within the range of ca. 1.51 to ca. 3.85 wt.% and of lead sulphide inclusions within the range of ca. 0.09 to ca. 5.80 wt.%. In grain 1 of iron sulphide FeS the presence of metallic Cu in an amount of ca. 4.21 wt.% was determined, while in grains 3 and 5 CuS was found in the amounts of ca. 3.27 wt.% and ca. 2.98 wt.%, respectively (Table 7).

Table 7: Chemical and phase composition of iron sulphide grains in sample PR-5 (dust from the Shaft Furnace) (wt. %).

Element	Analysis (grain) number					Average
	1	2	3	4	5	
S	33.4887	36.0880	34.8538	36.0946	36.2482	35.3547
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Fe	54.9309	61.7090	55.6056	61.3298	60.4143	58.7979
Cu	4.2026	0.0406	2.1679	0.2196	1.9781	1.7218
Zn	2.5759	1.0111	2.1452	1.6783	1.1254	1.7072
As	0.0000	0.2401	0.0199	0.1539	0.1600	0.1148
Se	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ag	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cd	0.2254	0.0000	0.1951	0.0670	0.0000	0.0975
Sn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sb	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pb	4.5764	0.9112	5.0125	0.4568	0.0740	2.2062
Total	100.0000	100.0000	100.0000	100.0000	100.0000	
Phase fraction						
FeS	86.6466	97.4332	87.7258	96.9583	95.2534	92.8035
ZnS	3.8467	1.5114	3.2041	2.5119	1.6799	2.5508
PbS	5.2954	1.0553	5.8010	0.5298	0.0856	2.5534
Cu met.	4.2112	0.0000	0.0000	0.0000	0.0000	0.8422
Covelline	0.0000	0.0000	3.2692	0.0000	2.9811	1.2501
Total	100.0000	100.0000	100.0000	100.0000	100.0000	

Table 8: The values of the correlation coefficient between the content of the various phases in iron sulphide grains and the content of accompanying elements in the PR-5 dust (significant correlation for $p<0.05$ is indicated in bold).

Phase	Fe	Cu	Zn	As	Cd	Pb
FeS	**1.00**	-0.88	**-0.89**	**0.96**	**-0.94**	**-0.95**
ZnS	**-0.90**	0.76	**1.00**	**-0.94**	**0.98**	0.86
PbS	**-0.96**	0.70	0.86	**-0.89**	**0.94**	**1.00**

The correlation coefficients (Table 8) indicate that As occurs in the form of substitutions in the crystal lattice of FeS, whereas Cd occurs in the form of substitutions in ZnS and PbS. This is primarily due to the fact that the PR-5 dust is derived from the shaft furnace where reducing conditions prevail, as well as due to the geochemical affinity of As and Fe and of Cd and Zn and Pb.

The values of the correlation coefficients of the various accompanying elements in the iron sulphide FeS grains in the PR-5 dust indicate (Table 9) that there are significant correlations ($p<0.05$) between them:

- positive: As and Fe; Cd and Zn, Pb;
- negative: S and Zn; Fe and Zn; Cd and Pb; Zn and As; As and Cd, Pb.

Table 9: The values of the correlation coefficient between accompanying elements in iron sulphide grains in PR-5 dust (significant values of correlation coefficients at $p<0.05$ shown in bold).

	S	Fe	Cu	Zn	As	Cd
Fe	**0.92**					
Cu	-0.87	-0.87				
Zn	**-0.92**	**-0.90**	0.76			
As	0.88	**0.97**	-0.85	**-0.94**		
Cd	**-0.92**	**-0.95**	0.75	**0.98**	**-0.96**	
Pb	**-0.88**	**-0.96**	0.70	0.86	**-0.89**	**0.94**

5. Conclusions

Iron sulphides, in addition to zinc sulphide and lead sulphide, are one of the main constituents in dusts PR-2, PR-3 and PR-5 that are generated in the pyrometallurgical process of zinc and lead production at the "Miasteczko Śląskie" Smelting Plant.

These dusts have a complex mineral composition, resulting from the diversity of raw materials used and from the conditions of the production process (oxidation and reduction).

The tests performed have demonstrated that the chemical composition of iron sulphide grains was not close to stoichiometric, the grains were non-uniform in terms of phase composition, and they always included admixtures in the form of inclusions of other sulphides, i.e. zinc sulphide and lead sulphide, and accompanying elements (Ca, Mn, Se, As, Ag, Cu, Cd, Se). The calculated correlation coefficients indicate that As is present mainly in iron sulphides, while Cd is present mainly in lead sulphide.

Arsenic and cadmium are typochemical elements of MVT deposits, wherein they rarely form separate phases, often constituting substitutions in the crystalline lattice of Zn-Pb-Fe sulphides [9, 10].

Accompanying elements, after entering the ISP process in a charge mixture, are released during the decomposition of pyrite in a high-temperature process, and may accumulate in materials formed at various steps of the process, including the dust discharged into the environment.

References

[1] Z. Adamczyk, K. Nowińska, E. Melaniuk-Wolny, J. Szewczenko, "Variation of the content of accompanying elements in galena in pyrometallurgical process of zinc and lead production," *Acta Montanistica Slovaca*, vol. 18, no. 3, pp. 158-163, 2013.

[2] Z. Adamczyk, K. Nowińska, E. Melaniuk-Wolny, "The mineralogical and chemical study of feedstock mixtures and by-products from pyrometallurgical process of zinc and lead production," *Wydawnictwo Politechniki Śląskiej*, Gliwice.

[3] E. Melaniuk-Wolny, „Właściwości pyłu emitowanego w hutnictwie cynku i ołowiu," Doctoral Thesis, Gliwice, 2001, 235 pp.

[4] M. Pozzi, K. Nowińska, „Dystrybucja wybranych pierwiastków towarzyszących koncentratom Zn - Pb w technologii Imperial Smelting Process," Gliwice: Wydawnictwo Politechniki Śląskiej, 172 pp, 2006.

[5] K. Nowińska, Z. Adamczyk, E. Melaniuk-Wolny, "Accompanying elements in sphalerite in pyrometallurgical process of zinc and lead production," *Materials and Manufacturing Processes*, vol. 30, no. 12, pp. 1457-1464, 2015.

[6] Technologia otrzymywania cynku i ołowiu w Hucie Cynku „Miasteczko Śląskie". Technical documentation (unpublished), Miasteczko Śląskie, 2010.

[7] Z. Adamczyk, K. Nowińska, "Skład chemiczny pirytu w mieszance wsadowej do pirometalurgicznego procesu otrzymywania cynku i ołowiu," *Systemy Wspomagania Inżynierii Produkcji*, vol. 5, no. 17, pp. 38-47, 2016.

[8] Szummer (red.), Podstawy ilościowej mikroanalizy rentgenowskiej. Warszawa: Wydawnictwo Naukowo-Techniczne, 1994.

[9] J. Cabała, "Koncentracje pierwiastków śladowych w rudach Zn-Pb i możliwość przechodzenia ich do odpadów," *Prace Naukowe GIG, ser. Konferencje*, 13, pp. 17-32, 1996.

[10] B. B. Rachel, „Geochemia Tl, As, Cd, Pb w rudach oraz odpadach hutniczych Zn-Pb Górnego Śląska," Doctoral Thesis, Kraków, 2008.