

Mössbauer Spectroscopy in the Studies of Iron Phases From the Slags After Zinc and Lead Production

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Abstract

Upper Silesia District is one of the most polluted areas in the country. Rich deposits of metal ores and hard coal have contributed to the extensive development of metallurgy and mine industry which started as early as in the Middle Ages. The ecological hazard can be illustrated by an over 100-year-old waste dump of Zn-Pb ores in one of the Silesian cities – in Ruda Śląska. Despite the long storage period, the wastes, represented mainly by weathered slags as also vitrified waste material, contain a lot of heavy metals in varied their chemical forms. The following metals have been found in wastes: Cd, Pb, Zn, As, Cu, Ti and other, and also a lot of amounts of iron. In the article the results Mössbauer spectroscopy are presented, as a preliminary stage of mineralogical studies of Zn-Pb wastes. Depending on the type of tested waste material different iron phases have been shown: in the weathered slag four different products of the iron oxidation were detected: divalent Fe(OH)_2 , mixed valence magnetite, Fe_3O_4 and three valence Fe(OH)_3 , $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ compounds, in the vitrified material metallic forms of iron are dominated.

Keywords: Mössbauer spectroscopy, Phase composition, Slag after zinc and lead production

1. Introduction

Smelter wastes and slags in particular, are a subject of an increasing interest as a material which may be reused. This mostly concerns iron slag, which – due to favorable parameters of technical properties and their chemical composition – find their application in construction and road building industries [4, 5, 6, 10]. Presently, many of the Upper-Silesian iron slag dumps are under liquidation and the material from current operation of steel plants is directly transferred to aggregate manufacturing plants. The Zn-Pb dumps are, however, an unsolved problem [3]. Their

presence is related to the expansive mining and steel-production activity in the past century which covered the area of many Silesian cities e.g. Ruda Śląska, Świętochłowice, Bytom and Tarnowskie Góry. Many of the dumps are over 100 years old and the accumulated material is highly weathered. Thus, the methods for the pro-ecological management of the Zn-Pb slag are intensively sought. Waste dumps from zinc and lead works are extremely toxic for the environment. The wastes contain a lot of heavy metals and sulphur, which are released from components of wastes in the weathering process. Their compounds are soluble, becoming a source of pollution for superficial water, soil and flora [3, 4]. The efficient solution of these problems requires

knowledge concerning the mechanical properties and chemical composition of the material.

2. Samples

Zn-Pb wastes deposited for over 100 years at one of the Upper-Silesian waste dumps were studied. The material was composed of a highly weathered slag (red-brown color, medium-grained structure and they are porous) (Fig. 1a) as well as a vitrified hard material which was relatively well-preserved and characteristically green-colored (Fig. 1b).

Researches of chemical composition have indicated that the analyzed material contain a significant amount of heavy metals: Cd (32-262 ppm), Pb (5340-29385 ppm), Zn (6270-83700 ppm), As (2560-17400 ppm), Cu (166-1859 ppm), Ti (0,14-0,33 Mass%) and others, accompanied by large amounts of Fe (13,40-20,60 Mass%) – especially in the Zn-Pb slag.

The metals are present in glaze, they form their own minerals (magnetite, hematite, franklinite, and olivine) and metallic aggregates and they are also present in the structure of other minerals (barite, augite, monticellite). The metals can form inclusions in other minerals.

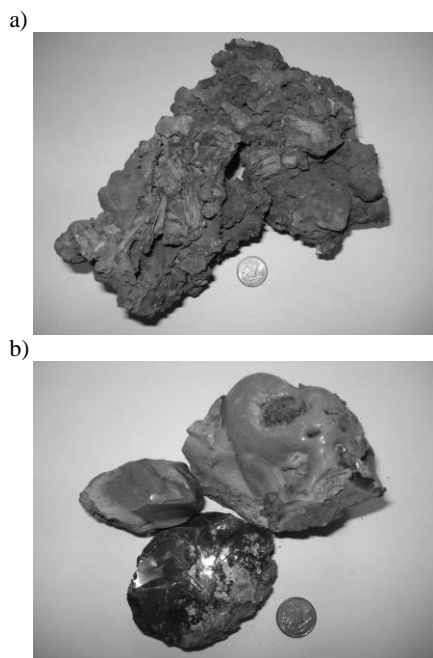


Fig. 1. a, b. The studied Zn-Pb waste material: a) – weathered slag; b) – vitrified wastes

The presence of the metals in the waste materials often raises business owners' interest as these may be reused. The chemical form of the metals, however, and the way these are bonded with the waste components, is important. Most of the heavy metals are dispersed in the glaze or occur as a substitution in structures of silicate phases and rarely constitute own minerals. The situation is

different as far as iron is concerned which, occurs mainly in the form of own oxide and hydroxides phases. Microscopic examination in transmitted and reflected light demonstrated the presence of magnetite and hematite in the slag, while the determination of other iron forms (e.g. hydroxides) was hindered due to their microcrystalline structure and high dispersion. Due to the above, to provide a full characteristic of the iron phases present in the tested Zn-Pb wastes, Mössbauer spectroscopy has been applied. The fruitfulness of this method has been demonstrated in our previous studies concerning steelmaking slags [4].

3. Results

For the Mössbauer study 150 mg of the powder samples with 100 mg of plexiglass powder were pressed into pellets, 12 mm in diameter, identical for each specimen. The Mössbauer spectra were recorded at room temperature with the Wissel spectrometer using $^{57}\text{Co/Rh}$ source of 0.7 GBq activities. The spectra of the slags were collected usually for 24 h; for samples of Zn-Pb vitrified waste material with residual iron content, the measuring time was extended for few days. The numerical analysis of the complicated, multicomponent spectra was performed with the use of MOSMOD program. The identification of the fraction, see Table 1, were based from the known from the literature hyperfine parameters [1, 7, 8, 9, 11], and their percentage content was concluded from the areas of the corresponding subspectra with the thin absorber approximation, see Table 2. No correction for the differences in the recoil free fraction for different compounds was included.

Slag: The spectra of 5 samples are shown in Fig. 2. Four different products of the iron oxidation were detected: divalent $\text{Fe}(\text{OH})_2$, mixed valence magnetite, Fe_3O_4 and three valence $\text{Fe}(\text{OH})_3$, $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ compounds. The contributions of each fraction are provided in Table. 2. It turns out that the studied samples exhibit chemical in homogeneity, which may depend on the sampling. Nevertheless, for the simple, technologically clear parameter of the slag, we estimated the average oxidation state of iron in each sample, defined as the mean weighted valence. These average oxidation states of Fe ions vary from 2.4 to 2.8 for nearly fully oxidized sample no. 5, see Table 2.

Zn-Pb vitrified waste material: Only four samples contained enough iron to obtain some reasonable, but still weak spectra (Fig. 3). The unambiguous identification of the iron bearing fraction is doubtful. However, considering the isomer shift values, it may be concluded that in contrary to the slag samples in these specimen metallic forms of iron dominate. In particular, in three samples the contribution of austenite, ferrites and martensite could be recognized, accompanied with some content of Fe_2O_3 . The sample no. 6 is quite different. The dominating fractions are metallic iron and its initial corrosion product, FeO . The composition of Zn-Pb vitrified waste samples are given in Table 3.

Table 1.

Hyperfine parameters, IS, QS and H, of the different iron compounds in Zn-Pb slag samples (1-5), and in Zn-Pb vitrified waste material samples (6-9). In last column the literature data are given [7-10]. * - parameter fixed in the fitting

		sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8	sample 9	Ref.
Fe(OH) ₂	IS	1.03(2)	1.130(4)	1.05(5)	1.06 (2)	1.07(1)	-	-	-	-	1.18
	QS	2.12(4)	2.32 (2)	2.1(1)	2.10(4)	2.70(2)	-	-	-	-	2.28-2.61
	H	0*	0*	0*	0*	0*	-	-	-	-	0
Fe(OH) ₃	IS	0.40(4)	0.42(1)	0.3(2)	0.39(4)	0.37(1)	-	0.37*	0.37*	0.37 *	0.37
	QS	0.76(8)	0.66(2)	0.6(4)	0.80(8)	0.74(2)	-	0.7(1)	0.70*	0.6(2)	0.70
	H	0*	0*	0*	0*	0*	-	0*	0*	0*	0
Fe ₃ O ₄ (A)	IS	0.32(1)	0.32(2)	0.31(1)	0.301(8)	-	-	-	-	-	0.28
	QS	0.12(2)	-0.04(4)	-0.10(2)	-0.70(16)	-	-	-	-	-	0
	H	487FIX	489(2)	487(1)	490.6(6)	-	-	-	-	-	487
Fe ₃ O ₄ (B)	IS	0.72(2)	0.63(5)	0.70(3)	0.64(2)	-	-	-	-	-	0.65
	QS	-1.2(4)	0.06(6)	-0.18(6)	-0.10(4)	-	-	-	-	-	0
	H	455.225	449(3)	459.(2)	460(1)	-	-	-	-	-	455
γ-Fe ₂ O ₃	IS	-	-	-	-	0.327(2)	-	-	-	-	0.33
	QS	-	-	-	-	0*	-	-	-	-	0
	H	-	-	-	-	482(2)	-	-	-	-	497
Fe ₂ O ₃	IS	0.368(6)	0.351(7)	0.359(6)	0.376(3)	0.337(3)	0.37*	0.37*	0.37*	0.37*	0.37
	QS	-0.2*	-0.20(1)	-0.2*	-0.2*	-0.2*	-0.2*	-0.2*	-0.2*	-0.2*	-0.2
	H	512.2(6)	515.5(5)	511.5(5)	513.9(3)	513.2(2)	511*	510(2)	510(2)	512(3)	511
Austenite	IS	-	-	-	-	-	-	-0.12(3)	0.02(3)	-0.12(3)	-0.13
	QS	-	-	-	-	-	-	0*	0*	0*	0
	H	-	-	-	-	-	-	0*	0*	0*	0
Ferrite	IS	-	-	-	-	-	-	-0.09(2)	-0.09(2)	-0.09(2)	0
	QS	-	-	-	-	-	-	0*	0*	0*	0
	H1	-	-	-	-	-	-	330(1)	331(1)	333(1)	335-270
Martensite	H2	-	-	-	-	-	-	307(2)	294(2)	303(2)	
	H3	-	-	-	-	-	-	275(3)	230(3)	265(3)	
	H	-	-	-	-	-	-	-	-	-	
FeO + small particles	IS	-	-	-	-	-	0.75(5)	-	-	-	
	QS	-	-	-	-	-	1.62(12)	-	-	-	
	H	-	-	-	-	-	0*	-	-	-	
Fe	IS	-	-	-	-	-	-0.00(1)	-	-	-	
	QS	-	-	-	-	-	0*	-	-	-	
	H	-	-	-	-	-	328.7(4)	-	-	-	

Table 2.

Percentage contribution of iron in the different compounds in Zn-Pb slag samples. The uncertainty is $\pm 2\%$. In the last column the weighted average oxidation state, with the 0.1 uncertainty

Sample	Fe(OH) ₃	Fe(OH) ₂	Fe ₃ O ₄ (A)	Fe ₃ O ₄ (B)	γ-Fe ₂ O ₃	α-Fe ₂ O ₃	Oxidation state
1	16	48	9	17	0	10	2.4
2	14	51	5	10	0	20	2.4
3	14	49	6	12	0	19	2.5
4	14	33	10	19	0	24	2.6
5	16	20	0	0	19	45	2.8

Table 3.

Percentage contribution of the different iron compounds in samples of Zn-Pb vitrified waste material samples

Sample	Metallic states [%]			Oxides [%]		
	Austenite	Ferrite/Martensite	α-Fe	Fe(OH) ₃	FeO	Fe ₂ O ₃
6	-	-	55(3)	-	44(4)	0,8(2)
7	8(2)	69(7)	-	11(1)	-	13(2)
8	24(4)	55(6)	-	4(1)	-	17(2)
9	25	38(7)	-	10(2)	-	7(1)

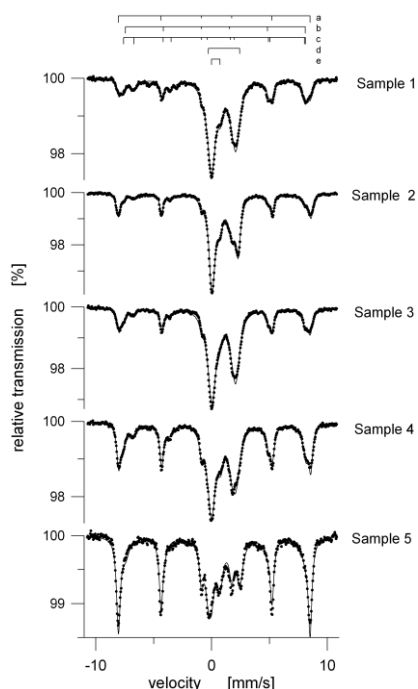


Fig. 2. The room temperature Mössbauer spectra of five samples of Zn-Pb slags, displayed in the sequence increasing oxidation state of iron. At the top the line positions of α -Fe₂O₃ (a), γ -Fe₂O₃ (b), Fe₃O₄ (c), Fe(OH)₂ (d); Fe(OH)₃ (e) are marked

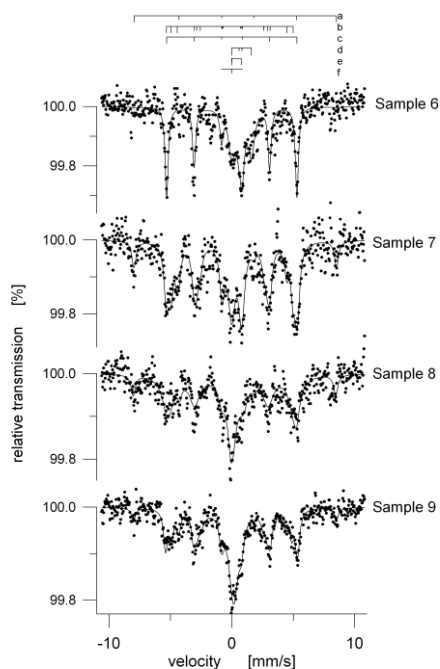


Fig. 3. The room temperature Mössbauer spectra of Zn-Pb vitrified waste samples. At the top the line positions of α -Fe₂O₃ (a), ferrite/martensite steels (b), Fe (c), FeO (d); Fe(OH)₃ (e) austenite (f)

4. Conclusions

Mineralogical studies of slags require the use of a multidirectional research methodology. Due to the varied and changeable mineralization and chemical composition metallurgical slags are one of the most diverse groups of wastes. Due to the complicated microcrystalline structure of the slag components, particularly in the weathered slags, the microscopic and X-ray studies could not resolve all doubts concerning with determination of iron rich phases. The application of the Mössbauer spectroscopy provided a unique, clear and consistent characterization of the iron bearing compounds and their relative abundances.

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