

Phase composition of metallurgical slag studied by Mössbauer spectroscopy

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Abstract. The iron bearing phase composition of metallurgical slag currently produced in a tub, converter and electrical furnaces were determined from the Mössbauer spectra and compared with the composition of the slag stored for decades on the dump.

Key words: metallurgical slag • Mössbauer spectroscopy • phase composition

Introduction

Metallurgical industry supplies huge amount of wastes, mainly in the form of slag, which is being stored for decades on dumps. Nowadays, there are attempts to utilize this material in some sectors of the economy [5, 9], mainly in the construction of roads. However, the metallurgical slag frequently contains significant amount of heavy metals which, during long storage, may lead to the environmental pollution. In the long-term plan these wastes may be treated as raw materials. Therefore, the determination of their physical and chemical properties, mainly their phase composition is the subject of many studies of applied character [1].

The obtained results are, as well, very interesting from the point of view of the fundamental research. The crystallization in a blast furnace may be compared with natural magma processes, but the initial composition of the batch and applied supplements may lead to the synthesis of materials never appearing in the nature. The time evolution of the formed phases in relation to the conditions of the slag storing appears interesting as well.

The metallurgical slag was studied in the past by many authors, for example: Kucha and Jędrzejczyk [6], Puziewicz, Zainoun, Bril [8], Jonczy [2] – slag after Zn-Pb production, slag after Cu production Muszer [7], slag after steel production Jonczy [3, 4].

In practice, each particular type of slag is unique, which requires application of many different research techniques. Especially, in the case where the slag is rich in the iron bearing phases the application of routine analytical methods as optical microscopy, scanning microscopy or X-ray diffraction not always leads to unam-

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Table 1. Concentration of Fe in the studied samples (at.%) (researches using mass spectroscopy were made in Activation Laboratories Ltd. – ACTLABS in Canada)

G1	0.34
G2	0.38
G3	0.53
G4	0.21
G5	31.80
G6	31.60
G7	33.00
G8	14.40
G9	19.80
G10	17.60
G11	2.46
G12	0.74
G13	17.90
G14	20.00
G15	19.30
G16	3.00
G17	11.00
G18	11.00
G19	9.00
G20	9.00

biguous results. In particular, the relative concentration of the particular phases is difficult for the estimation. Therefore, these results should be correlated with the spectroscopic analysis data, as, for example, Mössbauer spectroscopy.

Samples

The studied samples were divided into four groups.

Group I, samples G1, G2, G3 and G4 were slag from a tub furnace. They were light grey, greenish shade powders with a minimal concentration of iron, see Table 1.

Group II (G8–G14), samples of black converter slag. The results of X-ray diffraction studies pointed out to the presence of wustite, magnetite, fayalite and solid solution of brownmillerite-srebrodolskite $\text{Ca}_2(\text{Fe,Al})\text{O}_5$ and iron rich metallic precipitations.

Group III (G5–G7) represented slag from current production of the electrical furnace. They were black and fragile. The iron content was about 30%, appearing mainly in the form of magnetite and wustite.

Finally, the most diverse, group IV (G15–G20) included samples of slag stored for decades on waste

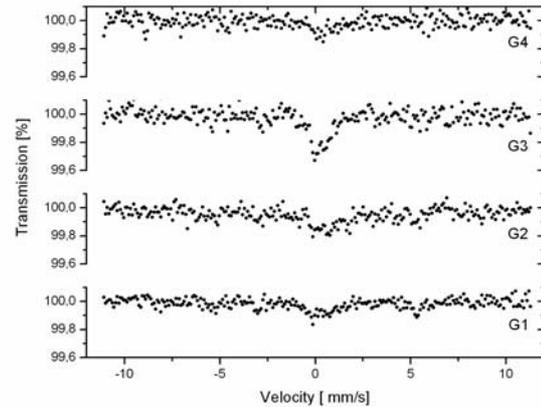


Fig. 1. The Mössbauer spectra of G1–G4 samples.

dump. They differ in the color, fragility and porosity. The atomic concentration of Fe in the studied samples is collected in Table 1.

Results of the Mössbauer study

For the Mössbauer study, 60 mg of the powder samples and 100 mg of lucid were pressed into pellets, 12 mm in diameter, identical for each specimen. The Mössbauer spectra were recorded at room temperature with a Wissel spectrometer using a $^{57}\text{Co}/\text{Rh}$ source of 0.9 GBq activity. The spectra were collected usually for 24 h; for samples with low iron content, the measuring time was extended to few days. The numerical analysis of the multicomponent spectra was performed with the use of MOSMOD program, assuming Gaussian distribution of the hyperfine fields for the magnetic fractions.

Group I. Samples, G1, G2, G3 and G4, contained only a minimal amount of iron. Thus, in spite of the fact that the spectra were recorded with good statistics, see Fig. 1, the analysis of the local states of Fe impurities is not possible. Qualitatively, the broad absorption peak at zero velocity may be assigned to the non-magnetic Fe^{3+} state in the form of tiny particles, not visible in the X-ray study. In some cases some traces of crystalline hematite may not be excluded.

Group II. The spectra of the samples G8, G9, G10, G12, G13 and G14 samples looked very similar, see Fig. 2, Table 2. The dominating fraction, about 65% of iron, cf. Table 1, is the non-magnetic Fe^{2+} state, probably in the form of some silicates. Results of X-ray investigations pointed out to the presence of fayalite

Table 2. Mössbauer parameters of converter slag. G8, G9, G10, G11, G12, G13 and G14 samples. IS – isomer shift, QS – quadrupole splitting (or quadrupole shift in the case of magnetic spectra), H – hyperfine magnetic field, f – area fraction of subspectra. In the case of sample G11, additional paramagnetic fraction (14%) of Fe^{3+} with IS = 0.42 mm/s, QS = 0.33 mm/s was concluded (not listed in the Table)

	IS1 (mm/s)	QS1 (mm/s)	f_1 (%)	IS2 (mm/s)	H_2 (T)	QS2 (mm/s)	f_2 (%)	IS3 (mm/s)	H_3 (T)	QS3 (mm/s)	f_3 (%)
G8	1.04	1.38	63	0.12	35.3	0.34	20	0.32	44.6	-0.16	17
G9	1.04	1.50	68	0.11	37.5	0.33	17	0.26	46.9	-0.20	15
G10	1.04	1.45	66	0.04	38.3	0.31	19	0.25	46.7	-0.21	15
G11	0.94	1.86	86	–	–	–	–	–	–	–	–
G12	1.04	1.44	66	0.02	37.7	0.26	19	0.25	46.9	-0.22	15
G13	1.05	1.42	63	0.09	38.1	0.36	15	0.29	46.1	-0.18	22
G14	1.05	1.46	63	0.11	39.6	0.35	17	0.27	48.0	-0.20	20

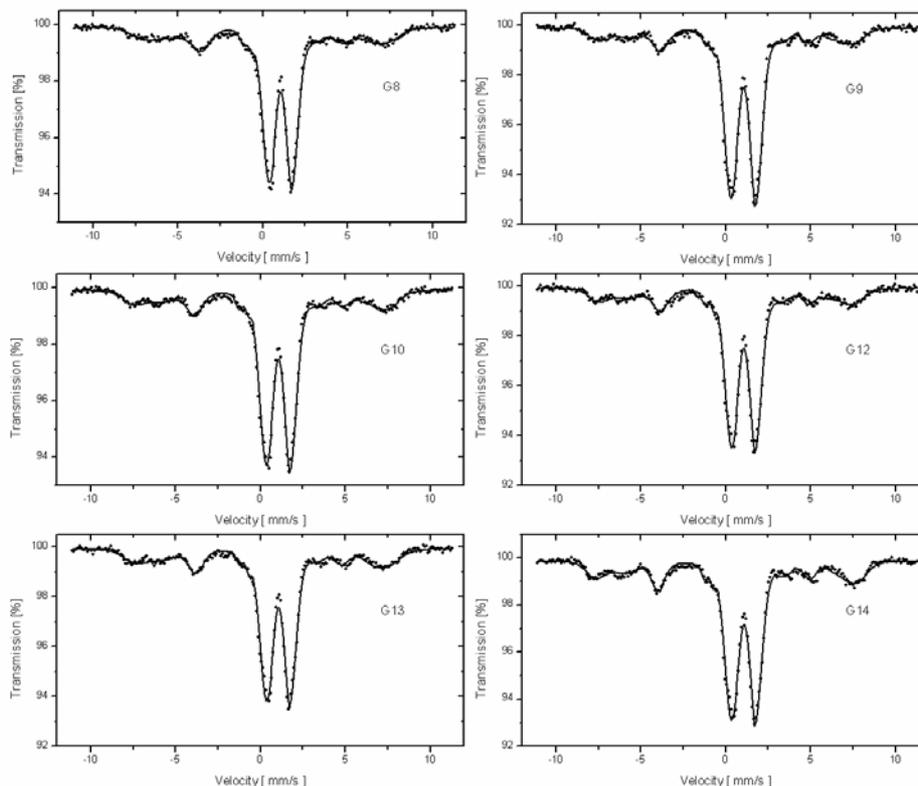


Fig. 2. The Mössbauer spectra of the samples of converter slag.

in these samples. The suggested appearance of the wustite is less probable because of the rather big value of the quadrupole splitting. The rest of iron appears in the form of magnetic phases. One of them, with the low isomer shift, 0–0.1 mm/s and a magnetic field in the range of 35–40 T was assigned to the metallic precipitations, probably iron-rich alloys, again in the agreement with the X-ray data. The second magnetic fraction with rather broad distribution of hyperfine magnetic field and isomer shift, cf. Table 2, should be assigned to a variety of the Fe^{3+} magnetic phases. One sample from this series, G11, which contained a rather low concentration of iron, exhibits totally different pattern, see Fig. 3. In this sample the Fe^{2+} fraction dominates (86%). The rest is a paramagnetic fraction of Fe^{3+} .

Group III. In this series (samples G5, G6 and G7) the dominating fraction was the paramagnetic Fe^{2+} state (80–90%), its hyperfine parameters indicated wustite

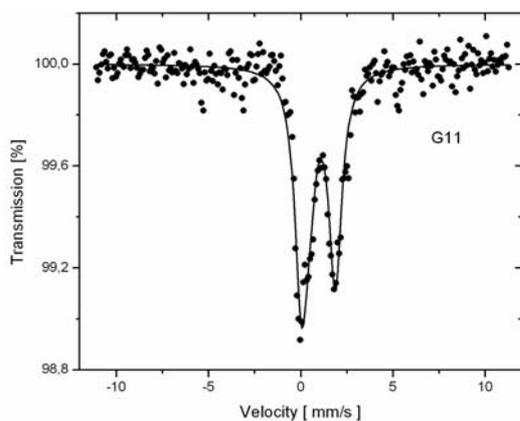


Fig. 3. The Mössbauer spectrum of sample G11 of converter slag.

in full agreement with the X-ray data. In the remaining samples, iron appears in the Fe^{3+} state, thought both in the paramagnetic and magnetic phase, see Fig. 4 and Table 3.

Group IV. Samples G15–G20, collected from the dump, differ strongly in their macroscopic properties. This is reflected in the recorded Mössbauer spectra, see Fig. 5, Table 4. In the iron poor sample G19 iron appears nearly exclusively in the form of Fe^{2+} state, probably wustite. On the other hand, the sample G16 contained only Fe^{3+} state, mainly in the form of well crystallized hematite (60%). The rest should be probably assigned to the tiny paramagnetic particles of hematite. The remaining samples reflected different

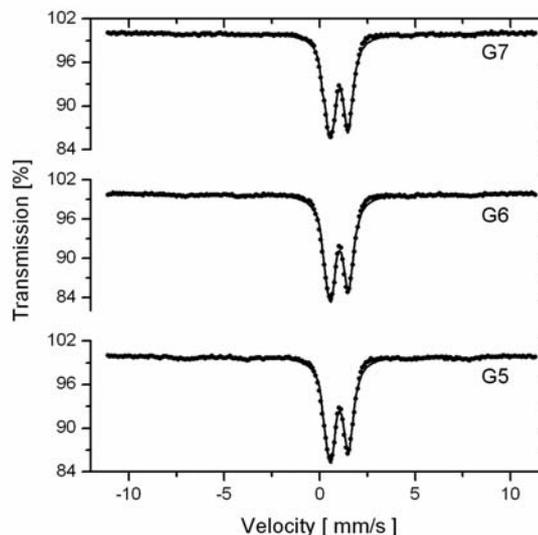


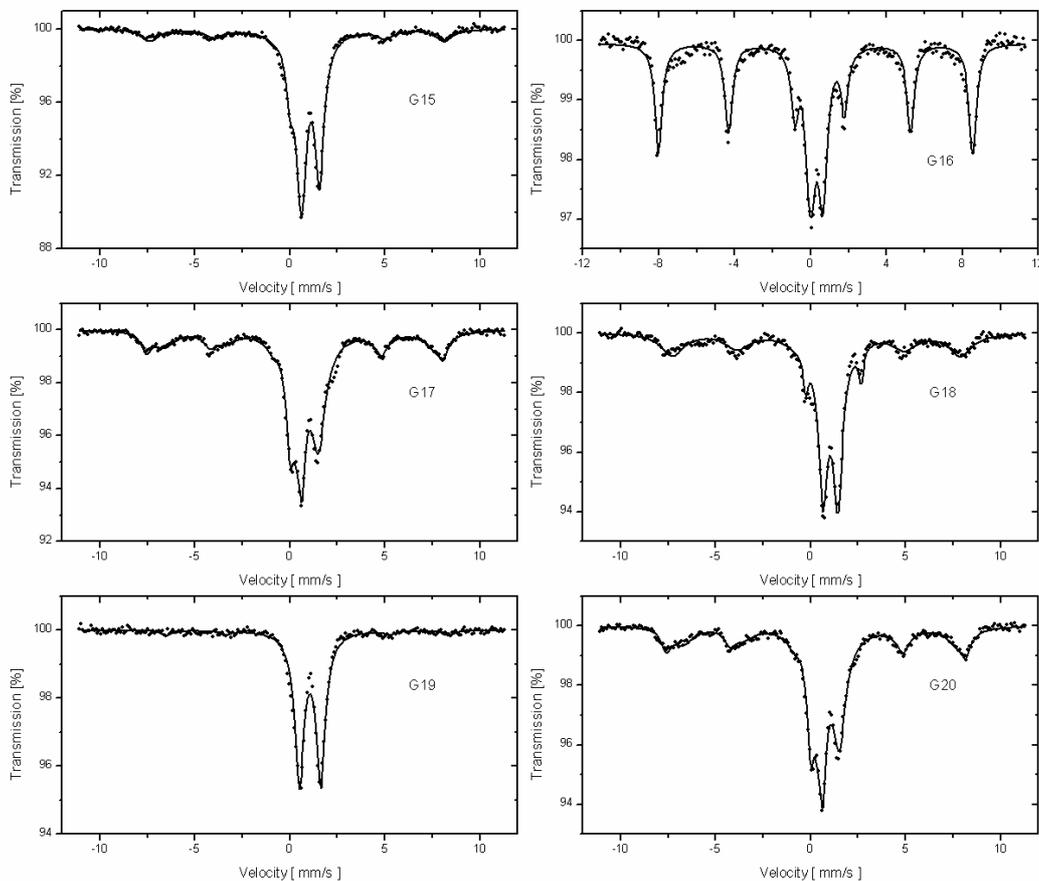
Fig. 4. The Mössbauer spectra of slag samples, G5, G6 and G7, from the electric furnace.

Table 3. The Mössbauer parameters of the samples G5, G6, G7

	IS1 (mm/s)	QS1 (mm/s)	f1 (%)	IS2 (mm/s)	QS2 (mm/s)	f2 (%)	IS3 (mm/s)	H3 (T)	QS3 (mm/s)	f3 (%)
G5	1.01	0.98	82	0.46	0.45	7	0.41	46.0	-0.06	11
G6	1.01	0.98	84	0.46	0.45	6	0.38	46.8	-0.01	10
G7	1.00	0.97	92	0.46	0.59	8	–	–	–	0

Table 4. The Mössbauer parameters of the samples G15–G20 from the dump

	IS1 (mm/s)	QS1 (mm/s)	f1 (%)	IS2 (mm/s)	QS2 (mm/s)	f2 (%)	IS3 (mm/s)	H3 (T)	QS3 (mm/s)	f3 (%)	IS4 (mm/s)	QS4 (mm/s)	H4 (T)	f3 (%)
G15	1.05	1.01	66	0.38	0.74	17	0.42	48.1	-0.06	17	–	–	–	–
G16	–	–	–	0.32	0.64	40	0.37	51.3	-0.11	60	–	–	–	–
G17	0.96	1.07	50	0.33	0.64	14	0.28	48.6	-0.02	12	0.58	-0.07	44.5	24
G18	1.04	0.77	55	1.20	2.90	6	0.42	47.2	-0.11	39	–	–	–	–
G19	1.06	1.13	94	–	–	–	–	–	–	–	0.94	46.3	0	6
G20	0.97	1.06	45	0.33	0.66	17	0.31	49.0	-0.01	14	0.55	-0.04	45.1	24

**Fig. 5.** The Mössbauer spectra of slag samples (G15–G20) from the dump.

stages of the progressing stages of oxidation, marked by the fraction of the Fe^{2+} fraction, decreasing from 66% in G15, through 55% and 50% in G18 and G17 samples, respectively, until 45% in G20 sample. The decrease of the wustite content is accompanied by a gradual increase in the magnetite fraction, both in magnetic and paramagnetic state.

In these samples still the wustite Fe^{2+} fraction dominates (~50%), the rest should be assigned to magnetic magnetite (~35%). The rest (~15%), is most probably, the tiny paramagnetic Fe_3O_4 particles, see Table 4.

Conclusions

The study of the metallurgical slag encounters serious problems caused by complicated composition of the studied specimen containing many poorly crystallized phases with diverse chemical compositions. In addition, any slag is not a uniform material and its samples differ from each other. In the studied case Mössbauer spectroscopy supplied quite reliable characteristic of the investigated slag.

Mössbauer spectra are quite different even within one series of samples, what was noted especially in the

case of samples taken from the dump. It is connected with the not uniform phase composition of the slag as well as the method of sampling.

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