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APPLICATION OF MÖSSBAUER SPECTROSCOPY IN PYRITIC AND COPPER CALCINES STUDIES

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ABSTRACT

In the present study, Mössbauer spectroscopy is applied to the qualitative and quantitative investigation of pyritic and copper calcines prepared by the roasting of untreated concentrates and those which have received a preliminary treatment in a magnetic field. It was established that there are no significant differences in phase content between those calcines which have received a preliminary treatment and those which have not.

New phases were found in copper calcines depending on the intensifying factor applied.

INTRODUCTION

The reactivity of solid substances depends on the conditions under which they are prepared, the thermal processing used, and the presence of microimpurities, as well as on the treatment (mechanical, radiation, etc.) applied. In the majority of instances, the increase in the activity of solid substances results in the appearance of defects, the concentration and nature of which determines the behaviour of reagents in the different solid phase processes [1].

Recently, investigators have been attempting to increase the rate or degree of a given reaction by the application of magnetic, electric, or high-frequency electromagnetic fields [2—5]. Roasting of metal sulphides in a fluidized bed, a typical heterogeneous process of the solid + gas type, may be intensified by the methods described in refs. 6—9.

Having in mind the mechanism of metal sulphide oxidation, it may be expected that any factor that increases the number of defects, activates and makes a larger number of defects active for the respective reaction centre [7—10], will have a favourable influence on the oxidation process. In our previous work [10,11], it was stated that the preliminary treatment of

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pyritic and copper concentrates in a magnetic field of a determined type and intensity exerts an influence on their reactivities. A relationship between the sulphur contents of the calcines and their specific surface areas was established.

It is also interesting to discover whether preliminary treatment in a magnetic field influences the number and type of phases in the products obtained. A quantitative comparison of the products, namely the iron-containing phase (Tables 1 and 2) is difficult and inadequate by the conventional methods of investigation (chemical and X-ray structural analysis, infrared spectroscopy).

The application of Mössbauer spectroscopy as a new method of qualitative and quantitative analysis [12—14] has aroused interest. This interest is based on the Mössbauer spectra specificity as well as on the relationship between the quantity of the studied phase and the intensity of the resonance absorption or scattering and high susceptibility towards the magnetic state of the samples.

EXPERIMENTAL

In the present study, Mössbauer spectroscopy is applied in the qualitative and quantitative investigation of pyritic and copper calcines prepared by the roasting of untreated concentrates and those which have received a preliminary processing in a magnetic field.

Investigations were carried out with a spectrometer working in a constant

TABLE 1

Materials investigated with details of laboratory treatment

Sample no.	Material	Treatment
1	Pyritic concentrate	None
2	Pyritic calcine	Industrial
3	Pyritic calcine	Concentrate treated for 5 min in 16 × 10^{-2} T non-homogeneous magnetic field then roasted in air at 760°C
3a	Pyritic calcine	Untreated concentrate roasted in air at 760°C
3b	Pyritic calcine	Concentrate treated for 1 min in 16 × 10^{-2} T non-homogeneous magnetic field then roasted in air at 760°C
3c	Pyritic calcine	Concentrate treated for 5 min in 16 × 10^{-2} T non-homogeneous magnetic field then roasted in air at 760°C
4	Copper concentrate	None
5	Copper calcine	Industrial
6	Copper calcine	Untreated concentrate roasted in air at 820°C
7	Copper calcine	Untreated concentrate roasted in air +30% O_2 at 800°C
8	Copper calcine	Concentrate treated for 5 min in 16 × 10^{-2} T non-homogeneous magnetic field then roasted in air at 820°C
9	Copper calcine	Concentrate treated for 1 min in 16 × 10^{-2} T non-homogeneous magnetic field then roasted in air +30% O_2 at 800°C

TABLE 2

Phases established in the studied pyritic and copper calcines by X-ray structural analysis and infrared spectroscopy

Sample no.	Phases established by	
	X-Ray structural analysis	Infrared spectroscopy
1	FeS_2, α-quartz	FeS_2, SiO_2
2	Fe_2O_3 (traces), α-quartz, Fe_3O_4	Fe_2O_3, Fe_3O_4, SiO_2
3	Fe_2O_3, Fe_3O_4, α-quartz	Fe_2O_3, SiO_2
4	$CuFeS_2$, FeS_2, α-quartz	FeS_2, $CuFeS_2$, Cu_2S, ZnS, SiO_2, Al_2O_3
5	$CuFeS_2$, Fe_3O_4, Fe_2O_3 (traces), α-quartz	$CuFeS_2$, Cu_2O, Fe_3O_4, Fe_2O_3
6	$CuFeS_2$, Fe_2O_3 (traces), Fe_3O_4, α-quartz	$CuFeS_2$, Fe_2O_3, Fe_3O_4, Cu_2O
7	Fe_3O_4, Fe_2O_3, α-quartz	$CuFeS_2$, CuS, Cu_2O, Fe_2O_3, Fe_3O_4, α-quartz
8	Fe_3O_4, Fe_2O_3, α-quartz	$CuFeS_2$, Fe_3O_4, Fe_2O_4, CuO
9	$CuFeS_2$ (traces), Fe_2O_3, α-quartz	$CuFeS_2$, Fe_2O_3, Fe_3O_4, Cu_2O, SiO_2

acceleration mode (a saw-tooth form of the velocity) [15]. ^{57}Co in a palladium matrix of 20 mCi activity was used as a γ-ray source. All measurements were carried out at room temperature using pellets with a density of 20 mg Fe cm^{-2} made from compressed powder of the samples studied.

Calibration of the velocity scale was performed using the metallic iron spectrum and the cited isomeric shifts are in relation to the centre of gravity of the iron six-line pattern.

Figure 1 shows the experimental Mössbauer spectra. The complicated character of these is a result of the superposition of the separate phase spectra due to the complex content of the samples studied.

The pyritic calcines prepared under laboratory conditions (Table 1) are of the same quality and, for this reason, the spectrum of only one of them is shown. The difference can be seen only by comparing them with the initial industrial calcine.

RESULTS

The spectrum parameters (position of the spectral lines, their intensity and width) obtained by the treatment of the spectrum by the least-squares method, may be used to obtain information about the quantitative ratios of the resultant phases.

Spectra decomposition was carried out with the help of the "Mosgam" program using an ICL computer [16].

The quantitative determination of the iron-containing phases was carried out assuming that the absorbers were sufficiently thin and the individual phases had the same Debay—Waller factor. The results from the investigations are presented in Table 3.

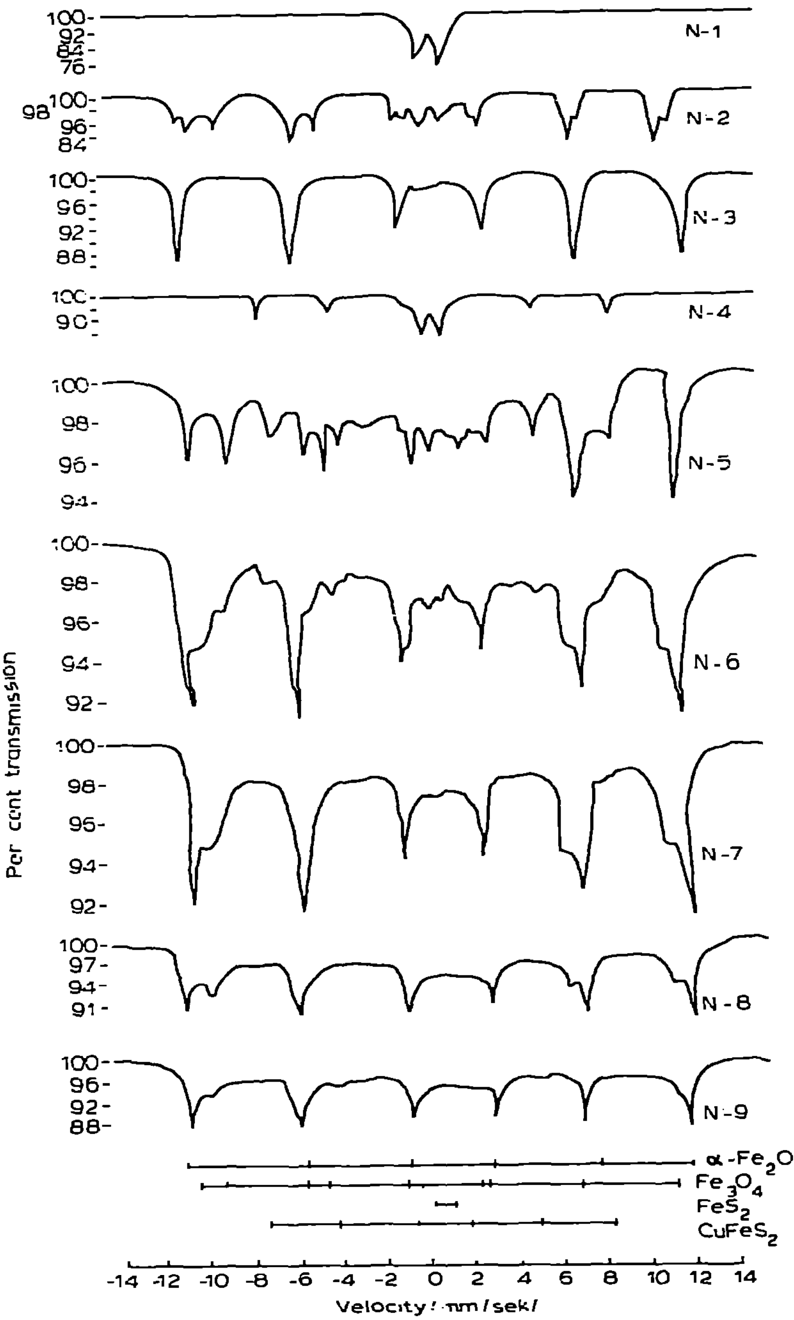

Fig. 1. Experimental Mössbauer spectra of pyritic and copper calcines at room temperature.

The identification of the following phases is certain: pyrite (FeS_2), haematite (α-Fe_2O_3), chalcopyrite ($CuFeS_2$) and magnetite (Fe_3O_4). Other phases, designated C, D, E, and F, were also observed.

The resultant magnetite differs from the standard one in the intensities of the patterns, which correspond to the octahedral (B) and tetrahedral (A) sites of iron atoms in the close-packed oxygen lattice. This magnetite was

TABLE 3

Quantitative Mössbauer spectra of pyritic and copper calcines

Sample no.	IS_{Fe} (mm s^{-1})	QS (mm s^{-1})	*H* (kOe)	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Γ_3 (mm s^{-1})	Established phases (%)
1a	0.305	0.616	0	0.30			100 pyrite
2a	0.356	0.634	0	0.42			11.2 pyrite
2c	0.374	—0.09	514.7	0.31	0.27	0.28	20.4 haematite
2d	0.285	0	491	0.36	0.38	0.33	33.1 $A_{magnetite}$
	0.664	0	458	0.44	0.35	0.31	35.2 $B_{V=0.08}$ $Fe^{2+}:Fe^{3+} = 0.35$
3a	0.303	0.619	0	0.29			2.2 pyrite
3c	0.377	—0.09	515	0.33	0.29	0.27	86.9 haematite
3d	0.266	0	492	0.28	0.29	0.23	6.4 $A_{magnetite}$
	0.642	0	456	0.39	0.31	0.29	4.4 B
4a	0.305	0.616	0	0.29			68.4 pyrite
4b	0.247	0	353	0.28	0.27	0.26	31.6 chalcopyrite
5a	0.430	0.760	0	0.83			14.4 C
5b	0.270	0	343	0.48	0.48	0.48	20.4 D
5c	0.409	—0.09	516	0.41	0.41	0.41	6.5 haematite
5d	0.286	0	490	0.41	0.41	0.41	20.1 $A_{magnetite}$
	0.671	0	459	0.47	0.47	0.47	31.4 $B_{V=0.03}$ $Fe^{2+}:Fe^{3+} = 0.04$
5e	0.5	5.0	0	0.80			7.1 badly treated
6a	0.345	0.595	0	0.6			4.7 pyrite + C
6b	0.250	0	348	0.43	0.64	0.20	6.8 D
6c	0.380	—0.09	515	0.35	0.31	0.23	31.1 haematite
6d	0.30	0	481	0.63	0.52	0.51	38.7 $A_{phase\ F}$
	0.64	0	460	0.85	0.59	0.78	18.6 B
7a	0.310	0.630		0.53			3.1 pyrite + C
7b	0.255	0	346	0.31	0.62	0.55	4.1 D
7c	0.380	—0.09	515	0.34	0.30	0.25	39.3 haematite
7d	0.289	0	417	0.56	0.50	0.49	38.1 $A_{phase\ F}$
	0.632	0	461	0.98	0.66	0.58	15.0 B
8a	0.302	0.620	0	0.29			1.6 pyrite
8c	0.383	—0.09	515	0.33	0.29	0.25	33.7 haematite
8d	0.313	—0.01	474	0.85	0.76	0.61	64.7 E
9a	0.314	0.755	0	0.8			3.6 pyrite + C
9b	0.383	—0.09	515	0.33	0.29	0.24	44.6 haematite
9c	0.306	0	481	0.68	0.66	0.51	51.7 E + magnetite impurities
	0.507	0	455	1.26	1.28	1.38	51.7 E + magnetite impurities
Standards							
a	0.303	0.616	0	0.30			Pyrite
b	0.247	0.002	353	0.29	0.28	0.27	Chalcopyrite
c	0.381	—0.09	515	0.33	0.29	0.25	Haematite
d	0.280	0.005	490	0.28	0.27	0.24	$A_{magnetite}$
	0.671	0.005	459	0.40	0.32	0.30	$B_{V=0}$
e	Velocity scale calibration by α-Fe, non-linearity 0.13%						

interpreted as non-stoichiometric $Fe_{3-V}O_4$, where V represents the vacancies. From the ratios of the areas of the patterns A and B (S_A/S_B), information can be derived about the number of vacancies [17] and the ratio of ferrous and ferric iron ($Fe^{2+} : Fe^{3+}$). Equations (1) and (2) are derived for non-stoichiometric magnetite, but in some cases, they may also be used when the vacancies are occupied by small amounts of impurity.

$$V = \frac{2 - (S_A/S_B)}{6 + 5(S_A/S_B)} \tag{1}$$

$$Fe^{2+} : Fe^{3+} = \frac{S_A/S_B}{2 + (S_B/S_A)} \tag{2}$$

The values of V and $Fe^{2+} : Fe^{3+}$ for samples 2 and 5, in which the magnetite content is higher, are given in Table 3.

The parameters of the unidentified phase C (samples 5—7, 9) are close to those of pyrite and, for this reason, it is represented quantitatively by the available pyrite.

The presence of a phase, designated D and having parameters close to those of chalcopyrite, is observed in samples 5—7. This phase can be determined with some degree of uncertainty as chalcopyrite which has undergone thermal dissociation [18].

Phase E was identified in samples 8 and 9 and is characterized by rather wide lines. It may be a type of copper ferrite.

In samples 6 and 7, the identified phase F has parameters close to those of magnetite. It is apparent from Table 3 that, compared with the industrial plant calcines, the pyritic calcines obtained under our conditions do not differ in phase content. The difference is only in the phases obtained: the pyritic calcine obtained under laboratory conditions and characterized by an increase in rate and degree of oxidation contains 76.5% more haematite, 57.5% more magnetite and 9.0% less pyrite compared with the industrial calcine, which in itself speaks of a better and more complete oxidation process [19,20].

Copper calcines obtained under laboratory conditions with different intensifying factors (temperature, O_2, magnetic field) differ in phase from the initial industrial calcine. They contain the new phases E, F, C and pyrite.

Thus, the amount of haematite is 8% higher in sample 7 than in sample 6 and 5% higher than in sample 8, but it is 5% less than the amount in sample 9, i.e. the different thermal factors, oxygen and magnetic field used influence not only the rate and degree of completion of the process, but also the type and quantity of the phases obtained.

CONCLUSIONS

Mössbauer spectroscopy is used as a new method of quantitative and qualitative phase analysis of pyritic and copper calcines prepared by the application of different factors intensifying the oxidation process.

It was established that pyritic calcines which have received a preliminary treatment are not significantly different in phase content from the untreated calcines.

New phases were found in copper calcines depending on the applied intensifying factor.

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