

STUDYING PHASE STRUCTURE OF BURNED FERROUS MANGANESE ORES BY METHOD OF NUCLEAR GAMMA-RESONANCE SPECTROSCOPY

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Preliminary Note – Prethodno priopćenje

In the given article there are presented the results of studying the phase structure of burned ferrous manganese ores of Zhomart and Zapadny Kamys deposits of by the method of Mossbauer spectroscopy. There is established a variety of iron location forms in the studied materials and their quantitative content that allows to define the degree of completing regenerative processes at magnetizing roasting, and also the processes of formation of solid solutions $(Fe_{1-x}M_x)_3O_4$ and stabilization of $Fe_{1-x}O$ from eutectoid disintegration at cooling.

Key words: spectroscopy, concentrate, mineral

INTRODUCTION

At present at Zh. Abishev Chemical-Metallurgical Institute there is actively being studied the possibility of obtaining from ferrous manganese ores of Central Kazakhstan conditional manganese concentrates by the method of burning-magnetic division for smelting standard manganese ferrous alloys by the Mn/Fe ratio [1].

The objects of studying are first and foremost becoming ferrous manganese ores which at present are mined simultaneously with manganese ores, but due to the absence of the efficient technology of iron removal are not used in ferrous alloy processing and are stored in dumps.

The studies carried out before showed the possibility of iron removal by the burning magnetic method from ferrous manganese ores of Zhomart, Keregetas, Ushkatyn III and Zapadny Kamys deposits [1, 2]. In the presented work there are shown the results of studying the phase structure of the products obtained after the burning-magnetic processing the ferrous-manganese concentrate of Zhomart deposit with size 0-6 mm and ferrous manganese ore of Zapadny Kamys deposit with size 0-5 mm.

STATEMENT OF THE AIM OF THE STUDY

Studying and determining the laws of regenerative roasting of versions of iron and manganese ores and development on their basis of technology of burning-magnetic division of iron-and manganese containing minerals using the Shubarkols coal as a reducer.

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METHODOLOGY OF SOLVING THE TASKS OF THE STUDY

The results of the dry magnetic separation of the burned (in case of carbon redundancy in the charge) ferrous manganese materials in a magnetic separator for strong-magnetic materials 120-T are given in Tables 1 and 2. As it can be seen from the Tables, in both cases we managed to reduce iron content and to achieve in the non-magnetic fraction the Mn/Fe ratio no larger than 6, which satisfies the requirements when smelting ferromanganese silicon.

When studying complicated systems in which there is present redundant solid carbon, barren rock and manganese minerals, due to overlapping thermal effects of their interaction with each other, there is no possibility to define the form of iron presence and content based only on the widely used method of differential-thermal analysis.

One of the powerful methods of studying mineralogy of not only iron-containing but of practically all inorganic materials is nuclear gamma-resonance spectroscopy (Mossbauer spectroscopy). NGR spectroscopy takes a special place in a lot of fields of studies thanks to the unique possibilities of resonance absorption or emission of γ quanta emitted by separate radioactive isotopes (in our case Co_{57}) and interacting with corresponding crystal lattices in which there are compensated energy losses for the nuclear recoil. An energy narrow beam of recoilless γ quanta permits to study negligible changes in the superfine structure of nuclear levels caused by the nucleus interaction with in-crystal (magnetic and electric) fields of both static and dynamic origin (relaxation processes) [3].

From the analysis of Mossbauer spectra we can obtain the information of the charge density on the nucleus

Table 1 Products yield after magnetic separation of ferrous manganese ore of Zapadny Kamys deposit

Fraction and magnetic field direction	Magn. at 0,4kE	Magn. at 0,8kE	Magn. at 1,2kE	non-magn. at 1,2kE	Sum
Output, %	10,07	19,74	11,59	58,6	100
Content / %					
Mn _z	11,95	14,42	16,89	19,78	17,6
Fe _z	15,5	6,5	5	1,82	4,49
C	3,94	3,07	2,36	14,54	9,8
SiO ₂	39,4	45,52	46,29	40,1	41,8
Mn	0,77	2,22	3,38	10,87	3,92
Extraction ratio / %					
Mn	6,84	16,17	11,12	65,87	100
Fe	34,77	28,57	12,91	23,76	100
C	9,49	21,49	12,83	56,2	100
SiO ₂	4,05	6,19	2,79	86,97	100

Table 2 Products yield after magnetic separation of burned ferrous manganese concentrate of Zhomart deposit

Fraction and magnetic field direction	Magn. at 1,2kE	Non-magn. at 1,2kE	Sum
Output, %	18,58	81,42	100
Content / %			
Mn _z	8,5	39,1	33,41
Fe _z	53,2	1,63	11,2
SiO ₂	10,08	11,64	11,35
C	1,56	7,35	6,27
CaO	0,87	9,61	7,99
Mn	0,16	23,99	2,98
Extraction ratio / %			
Mn	4,73	95,3	100
Fe	88,2	11,8	100
SiO ₂	16,5	83,5	100
C	4,62	95,4	100
CaO	2,02	97,9	100

and of the nature of chemical bond (isomeric shear denoted as δ), of the space symmetry of electronic wave fractions (quadrupole splitting ΔEQ) and of the magnetic nature of the matter studied (effective magnetic field).

In the presented work there were studied the following samples by the method of Mossbauer spectroscopy:

Sample 1: magnetic fraction at 0,4-1,2kE from the burned ferrous manganese ore of Zapadny Kamys deposit (Table 1);

Sample 2: non-magnetic fraction at 1,2kE from the burned ferrous manganese ore of Zapadny Kamys deposit (Table 1);

Sample 3: magnetic fraction at 1,2kE from the burned ferrous manganese concentrate of Zhomart deposit (Table 2);

Sample 4: non-magnetic fraction at 1,2 kE from the burned ferrous manganese concentrate Zhomart (Table 2).

EXPERIMENTAL WORK

The source was cobalt 57 in the chrome matrix of activity 100 mCi. The spectra were processed on PC by the

method of "the least squares". Isomeric shear values (δ) are presented relative to α -Fe. The temperature of taking spectra was 293 K. A spectrometer type was SM 2201.

$\Delta IS = \pm 0,03$ mm/s; $\Delta QS = \pm 0,03$ mm/s; $\Delta H_{\text{eff}} = \pm 5$ kE; $\Delta S = \pm 3 - 5$ %.

All the samples present a multi-phase mixture including both magnetic-ordering and paramagnetic state of iron. Due to a small iron content samples 2 and 4 showed a very small effect (ϵ), which made it difficult to obtain quality spectra (see Figure 1).

Sample 1 contains replaced magnetite with strongly perturbed stoichiometry ($Fe_{1-x}M_x)_3O_4$. The Mossbauer spectrum in Figure 1 shows the presence of three magnetic sublattices (at "correct" magnetite at the room temperature there is observed only two) which is obviously connected with the differences in the nearest iron surroundings. As the value of the observed magnetic field in the third sublattice is lower than for the "correct" magnetite, we can suppose that metals (M), replacing iron are located to the left of it in the periodic table [4]. Besides, this sample contains paramagnetic phases which are presented and described in Table 3.

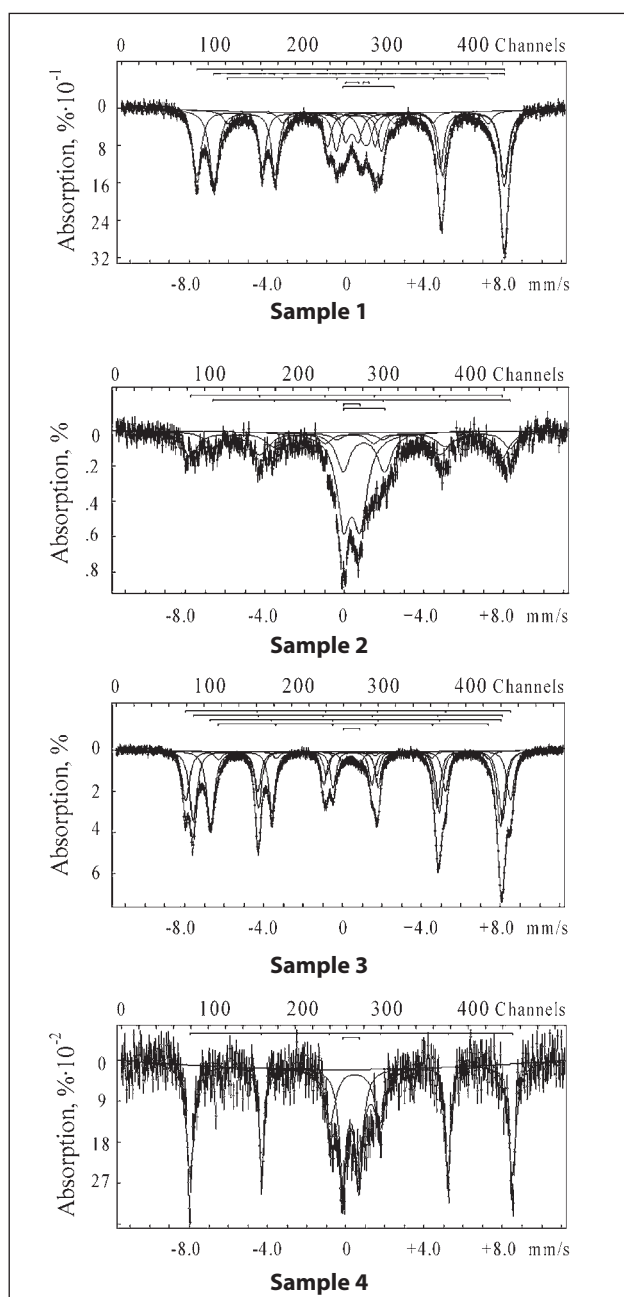
Sample 2 also contains magnetite with strongly perturbed stoichiometry which is indicated by the ratio of the iron relative content in magnetic sublattices. In stoichiometric magnetite the ratio of iron relative content in the sublattice with a larger H_{eff} to the iron content to the sublattice with a smaller H_{eff} is to be $\sim 1/2$. Stoichiometry perturbation is indicated by the presence of a significant quadrupole splitting QS (stoichiometric magnetite is practically free from it). Besides, the sample contains paramagnetic phases which are presented and described in Table 3.

Sample 3 contains a phase close by its parameters to γ - Fe_2O_3 . However, a somewhat smaller magnetic field H_{eff} (for γ - Fe_2O_3 $H_{\text{eff}} \sim 517$ kE) can indicate a small replacing of iron in γ - Fe_2O_3 lattice by the metal atoms which are located to the left of it in the periodic table.

Besides, this sample contains replaced magnetite with perturbed stoichiometry ($Fe_{1-x}M_x)_3O_4$, as the Mossbauer spectrum shows the presence in it of three magnetic sublattices. As to this spectrum component, there is true everything which is described relating to magnetite with perturbed stoichiometry for sample 1. In the sample there is present a paramagnetic phase described in Table 3.

Sample 4 contains a phase close in parameters to γ - Fe_2O_3 , similar to the phase found in sample 3. A paramagnetic phase present in the sample is described in Table 3.

Parameters of the replaced magnetic in samples 1 and 3 are mostly similar to the natural Vredenburgite and Jacobsite mineral, which have the same formula $(Mn, Fe)_3O_4$. However, in the latter lattice there can be present a certain content of magnesium (Mn, Mg, Fe_3O_4). Most likely, in the samples there is present a mixture of these two minerals, then in the Table there will be M – Mn or Mg.


Figure 1 Mossbauer spectra

CONCLUSION

Thus, the studies carried out permitted to establish a diversity of forms of iron presence in the materials studied: $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4$; (FeOOH) ; $\gamma\text{-Fe}_2\text{O}_3$; Fe_{1-x}O and Fe_3O_4 and their different content. These data can serve a base for evaluating the degree of completing the reducing processes in magnetizing burning, as well as going on the processes of forming solid solutions $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4$ and stabilizing Fe_{1-x}O from the eutectoid decay at cooling.

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Table 3 Results of processing Mossbauer spectra

Sample No	H_{eff} kE	IS, mm/s	QS, mm/s	S, %	Form*	
1	487	0,26	-0,03	37	$(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4$	
	460	0,67	0,01	42		
	413	0,61	0,00	7		
	Paramagnetic state					Phase close in parameters to Fe_{1-x}O ($x = 0,06-0,09$)
	-	1,05	0,30	5	Phase close in parameters to pyrite (FeS_2)	
		0,33	0,65	6	Phase close in parameters to Szomolnokite ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$), (Phengit $\text{KMg,Fe}_{0,5}\text{Al}_{1,5}[(\text{OH})_2/\text{Al}_{0,5}\text{Si}_{3,5}\text{O}_{10}]$ and Talc ($\text{Mg}_3[(\text{OH})_2/\text{Si}_4\text{O}_{10}]$)	
2	487	0,18	-0,16	27	Phase close in parameters to Fe_3O_4	
	463	0,69	0,14	19		
	Paramagnetic state					Phase close in parameters to Akaganeit (FeOOH)
		-	0,39	0,85	37	Phase close in parameters to Melilite ($\text{Ba}_2\text{FeSiO}_7$; SrFeSiO_7)
3		0,99	2,11	17	Phase close in parameters to $\gamma\text{-Fe}_2\text{O}_3$	
	511	0,37	-0,18	24	Phase close in parameters to $\kappa\gamma\text{-Fe}_2\text{O}_3$	
	487	0,27	-0,00	33	Phase close in parameters to $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4$	
	456	0,66	-0,00	36		
	425	0,58	-0,03	4		
Paramagnetic state					Phase close in parameters to Akaganeit (FeOOH)	
	-	0,46	0,86	3	Phase close in parameters to $\gamma\text{-Fe}_2\text{O}_3$	
4	510	0,37	-0,19	70	Phase close in parameters to $\gamma\text{-Fe}_2\text{O}_3$	
	Paramagnetic state					Phase close in parameters to Akaganeit (FeOOH),
Denotations:						
IS, (mm/s) – isomeric shear;						
QS, (mm/s) – quadrupole splitting;						
H_{eff} (kE) – Zeeman superAne magnetic splitting (effective magnetic Aeld);						
S / % – relative content;						
*M – metal						

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REFERENCES

- [1] M. Zh. Tolymbekov, Development of thermal dynamic and kinetic models of phase transformations in Mn-Fe-C-O system for the conditions of complex processing of Kazakhstan ferrous manganese ores, Report, Chemical-Metallurgical Institute n.a. Zh. Abishev, Karaganda, 2008, 146 p.
- [2] A.S. Baisanov, Phase equilibriums and kinetics of pyrometallurgical processing of ferrous manganese ores, Author's abstract to dissertation of candidate of technical science, candidate of technical science, Karaganda, 2007, 22 p.
- [3] D.S. Rodionov, Mossbauer spectrometer for analyzing iron mineralogy on Mars surface. Author's abstract to disserta-

tion of candidate of physical mathematical sciences, Moscow, 2006, 14 p.

- [4] V. V. Chekin, Mossbauer spectroscopy of iron, gold and tin alloys, Energoizdat, Moscow, 1981, 108 p.

Note: Translator - N. Drak, Karaganda, Republic of Kazakhstan

List of units of system of SI

mCi, curie - a unit of radioactivity equal to the amount of a radioactive isotope that decays at the rate of 37,000,000,000 disintegrations per second.

1 mCi = $3,7 \times 10^4$ Bq = $2,22 \cdot 10^9$ disintegrations per minute

T / K - Kelvin is a unit of measurement for thermodynamic temperature in the International System of Units (SI).

IS / mm/s - isomer shift;

QS / mm/s - quadrupole splitting.

H_{eff} / kE – Zeeman magnetic hyperfine splitting (the effective magnetic field);

S / % – proportion