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Investigation of Chemical and Mineralogical Composition of Manganese Ores From Central Asia Deposits

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Chemical and mineralogical compositions of manganese ores from Central Asia deposits are investigated. The ores consist of the following minerals: pyrolusite, manganite, psilomelane, hausmannite, magnetite, hydrogoethite, calcite, quartz. Sample ore No.1 is regarded to be rich and quality ore since manganese content in it is approximately 54% and P/Mn ratio equals to 0.002. The given ore is the universal raw material for manganese ferroalloy production.

Keywords: MANGANESE ORE, PYROLUSITE, MANGANITE, MACROSCOPIC AND MICROSCOPIC DESCRIPTION, METALLOGRAPHIC SPECIMEN

Introduction

Despite the decline in steelmaking caused by the world economic crisis, the experts [1] forecast further stably high level of this branch of industry. This is related to the fact that steel was and remains the basic structural material. The steel ratio in total production of metals is very high due to lower material and power consumption of manufacture of unit mass of steelwork. And as any steel cannot be made with no manganese addition, manganese raw material reserves are a strategic base for development of metallurgical manufacture of any state.

The world reserves of industrial manganese ores are evaluated approximately in 17.8 billion tons, from which 12.6% are located in Ukraine [2]. The domestic manganese ore extracted in Nikopol and Bolshetokmakskiy deposits has low manganese concentration (22-24%), high phosphorus concentration (0.20-0.22%) and, hence, a lot of burden. Therefore, the application of domestic ore in direct smelting is impossible without preliminary dressing according to complicated technological schemes [3]. The natural chemical bond of phosphorus with manganese-ore minerals does not enable to remove it during ore-dressing treatment by conventional methods. As a consequence, the P/Mn ratio in obtained concentrates does not decrease and lies within the limits 0.004 - 0.006. As for the outside manufacturers, this ratio is 0.0007 - 0.002 (**Table 1**).

Therefore, imported manganese ores are used at domestic ferroalloy plants to obtain high-quality manganese ferroalloys with reduced content of phosphorus. The annual Ukrainian import of manganese ore is about 1.8 million tons. The largest exporters are: Ghana (39%), Gabon (26.5%), Australia (10.5%) and Republic of South Africa (10.45%) [4].

Industrial experience of manganese ferroalloy smelting with application of import ores indicates that manganese ore with high concentration of manganese and low concentration of phosphorus does not ensure the stable economic benefit through its application. Along with conventional foreign suppliers of manganese ores, there are new ones in the market. During past years, manganese ore reserves have been developed in Republic of Tadjikistan. Complex investigation of these ores was performed to estimate expediency of this deposit development.

Methodology

Investigation was performed according to the state and international standards with the use of equipment in National Metallurgical Academy of

Table 1. Character of manganese ores from domestic and foreign deposits

Exporting country	Weight percentage, %								P/Mn	Standard fraction, mm
	Mn	Fe	P	SiO_2	Al_2O_3	CaO	MgO	K_2O		
Ukraine	21-32	1.5-3.1	0.13-0.21	38.0-40.0	3.4-4.0	1.4-2.9	1.4-2.1	1.5-1.8	0.006	–
Ghana	30-40	1.2	0.06-0.1	10.7-18.7	2.4-2.6	4.1-4.5	3.0-3.2	0.7-1.2	0.002	6-80
Gabon	45-51	3.2-4.7	0.08-0.11	5.0-7.8	5.5-5.8	0.1-0.35	0.08-0.2	0.7-1.2	0.002	6-100
Australia	50-57	5-6	0.08-0.1	3.6-11.5	3.3-5.2	0.1-0.2	0.1-0.2	0.7-1.2	0.002	3-100
Republic of South Africa	38-51	5-16	0.02-0.04	3.0-6.5	0.3-0.9	4.0-11.0	0.3-0.6	0.02-0.1	0.0007	6-75
Brasilia	43-50	3.3-9.0	0.05-0.12	2.0-8.0	3.7-10.8	0.2-3.5	0.3-3.0	1.0-1.5	0.002	6-75
India	30-40	9.0-20	0.05-0.1	5.0-7.0	5.0-8.0	2.0-3.0	1.0-2.0	NA	0.002	6-100

Ukraine and Kryvyy Rih Technical University.

Spectrograph ISP-28 was applied for semiquantitative spectrographic analysis (SQSA). Active alternating-current arc from oscillator IVS-28 was as excitation source. Spectra were filmed on spectral plates with sensitivity 9 units. The working range of spectrum was 2300−3600 A. The majority of analytical spectral lines of chemical elements are in this part of spectrum.

Mineral composition of initial ore was determined on transparent and polished sections. Quantity of minerals was counted with the use of integration table ISA-3. Simultaneously, granulometry of basic minerals of ore was preestimated with the use of micrometer eyepiece.

The mineral analysis was carried out for classified mineral breakage of initial samples. Secondary test charges were taken from each fraction by quartering method. This material was divided into two classes: pure fragments and aggregations. The content of minerals in each fraction was calculated.

Results and Discussion

The samples of rich manganese ore (1 and 2) from Obikhingouskiy and Khaburabadskiy deposits were investigated. Chemical and mineral compositions are given in **Tables 2** and **3**.

Sample 1 of rich manganese ore, which is of the greatest interest, was subjected to more detailed mineralogical analysis in view of metallurgical value. Three run-of-mine samples (1.1, 1.2 and 1.3) with different color and texture-structural characteristics were selected from this sample. The polished and transparent metallographic specimens were made from them. The microscopic results are presented in **Table 4**.

Sample 1.1. Black color solid with colloform laminated structure consists of pyrolusite, manganite and hydrogoethite that in the form of earthy aggregates fills the cavities. Sample does not respond to declination needle action.

Sample 1.2. Dark grey color solid with a subtle brown shading, structure is fine-grained, cryptocrystalline, texture is laminated, sometimes spotty. It consists of pyrolusite, manganite, hydrogoethite, calcite and magnetite as well.

Sample 1.3. Brown-black color solid with white strings. Structure is fine-grained, texture is spotty, vein. Sample consists of pyrolusite, manganite, hydrogoethite and calcite, weakly responds to declination needle action - there is small amount of magnetite.

Manganite ($MnO{\cdot}Mn(OH)_2$) and hausmannite (Mn_3O_4), that compose the ground mass, are identified by distinct brown internal patterns and low reflective power (**Figure 1**). The minerals are very close to each other by physical properties; therefore precise diagnostics is processed with account of chemical and mineral compositions (**Tables 2, 3**).

Hypidiomorphic grains of hausmannite of tetradypyramidical habitus with characteristic shears in the polished plane (**Figure 1c**) and contortion areas (**Figure 3a, b**) are observed. Sometimes, there are noncontinuous interlayers of thin inclusions in calcite mass (**Figure 3d**).

Pyrolusite (MnO_2) is found in hausmannite – manganite mass in the form of separate inclusions which interlay with manganite and hausmannite and form a complex sinter aggregate (**Figure 1b, e**).

Table 2. Full chemical composition of manganese ores from deposits in the Republic of Tajikistan

Sample No.	Weight percentage of components, %							
	Mn	MnO_2	MnO	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3
1	54.00	40.60	36.60	6.76	1.20	1.50	0.37	3.50
2	49.80	35.80	35.10	7.52	0.97	2.36	0.71	2.06

Sample No.	Weight percentage of components, %						Impurities	P/Mn
	BaO	TiO_2	K_2O	Na_2O	P_2O_5	S		
1	0.08	0.06	0.02	0.056	0.279	0.124	9.20	0.002
2	0.10	0.05	0.16	0.38	0.833	0.110	13.51	0.007

Table 3. Mineral composition of manganese ores from deposits in the Republic of Tajikistan

Sample No.	Weight percentage of minerals (M) and manganese bounded to them (Mn), %									
	Pyrolusite		Psilomelane, vernadite		Hausmannite, manganite, braunite		Manganous carbonates		Calcium phosphate	
	M	Mn	M	Mn	M	Mn	M	Mn	M	Mn
1	5.1	3.2	0.6	0.4	70.2	47.2	8.3	3.2	0.8	–
2	4.0	2.5	36.9	23.0	24.9	17.2	15.5	7.1	2.2	–

Sample No.	Weight percentage of minerals (M) and manganese bounded to them (Mn), %									
	Iron hydroxides		Iron sulphides		Quartz		Silicates, argillaceous materials, etc.		Total	
	M	Mn	M	Mn	M	Mn	M	Mn	M	Mn
1	3.1	–	0.2	–	5.7	–	6.0	–	100	54.0
2	4.2	–	0.1	–	5.1	–	7.1	–	100	49.8

Table 4. Mineral compounds of rich manganese ore (sample 1)

Mineral	Sample 1.1	Sample 1.2	Sample 1.3		Average
	polished section	polished section	specimen	polished section	
pyrolusite	6.3	4.7		4.4	5.1
manganite	61.2	44.8		24.4	43.7
psilomelane	1.1	0.2		0.4	0.6
hausmannite	26.9	24.1		28.1	26.4
manganite	–	5.3		3.9	3.1
hydrogoethite	2.2	4.9		8.7	5.3
calcite	1.3	13.1	15.9		10.1
quartz	1.0	2.9	14.2		5.7
TOTAL	100	100	100		100

Psilomelane ($mMnO \cdot MnO_2 \cdot nH_2O$) is not revealed macroscopically and microscopically. Precise diagnostics of mineral is carried out only by means of chemical analysis. The results are given in **Table 2**. Barium oxide is a reference mineral-forming component. It is contained only in psilomelane in amount of 12-17 wt. %. Small content of BaO (0.08 wt. %) indicates the presence of mineral in small amount (up to 1%).

Hydrogoethite (FeOOH) is contained in small amount, fills the cavities in manganite mass, composes the independent interlayers and forms small folds (**Figure 2a, 3a**). It is sometimes observed in the form of non-continuous strings which intersect the general interbedding (**Figure 2b**).

Quartz (SiO_2) is in the form of veins which cut the sinter aggregate of pyrolusite-hausmannite-mangenite composition (**Figure 1e**). It is found in the form of individual grains, also fills the slots which are often intersected by calcite strings (**Figures 3, 4**).

Magnetite (Fe_3O_4) is observed in the form of thin shots in manganese minerals and calcite interlayers (**Figure 2c**).

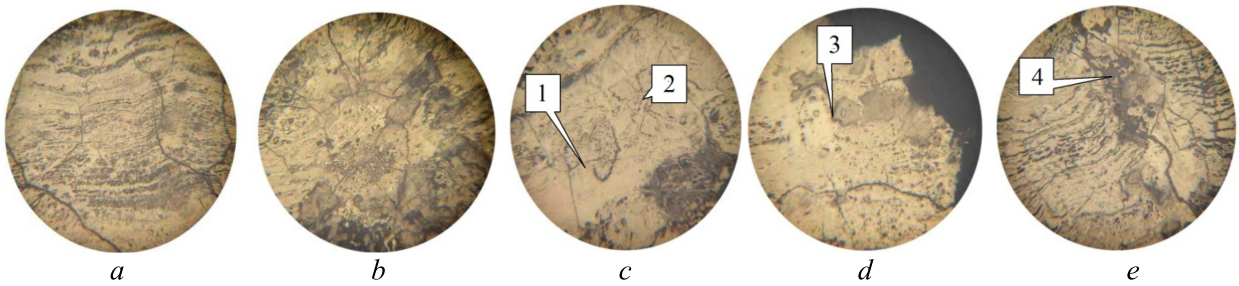

Figure 1. Observation of run-of-mine sample 1.1 in reflected light ($30^{\times}$): *a* – manganite mass with features of colloform structure; *b* – separate shapeless inclusions of pyrolusite (the lightest) in manganite mass; *c* – hypidiomorphic grains of hausmannite: cross-section along symmetry axis of the fourth order (1) and shear of subparallel horizontal plane of symmetry (2); *d* – concentration of several grains of calcite (3) in manganite; *e* – quartz string (4) which intersects the pyrolusite-manganite aggregate

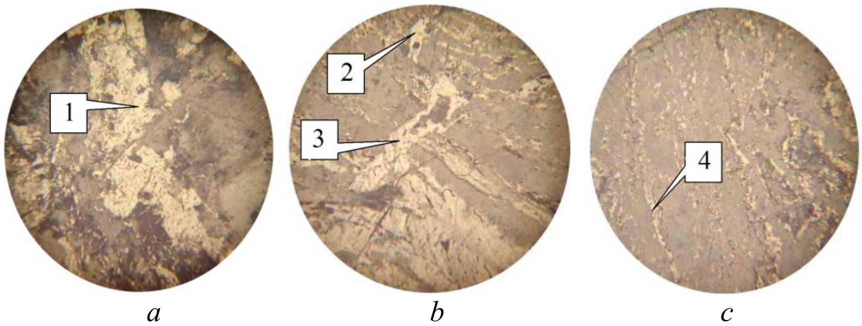

Figure 2. Observation of run-of-mine sample 1.2 in reflected light ($50^{\times}$): *a* – hydrogoethite interlayer (1); *b* – two fragments of hydrogoethite string (2, 3) which intersect the general interbedding; *c* – fine inclusions of magnetite (4) in thin interlayers which are between calcite interlayers

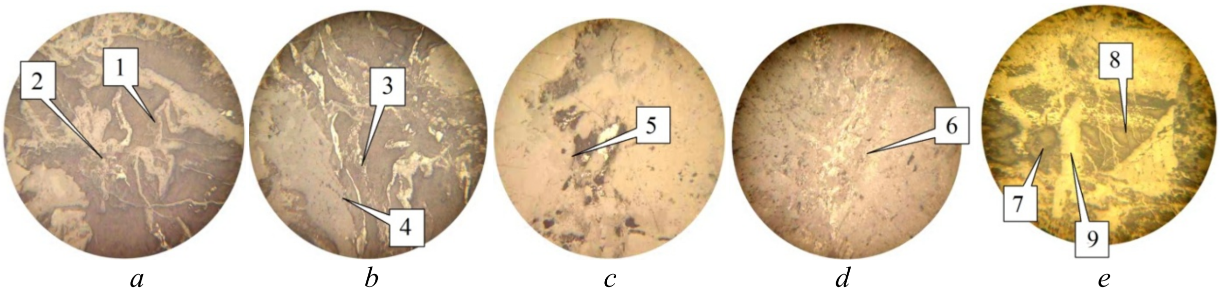

Figure 3. Observation of run-of-mine sample 1.3 in reflected light ($50^{\times}$): *a* – hydrogoethite (1) and pyrolusite-manganite (2) interlayers with traces of contortion; *b* – pyrolusite-manganite (3) and calcite (4) interlayers; *c* – pyrolusite inclusion in calcite mass (5); *d* – a tail of thin inclusions of manganite and pyrolusite (6); *e* – quartz slot (7) with pyrolusite interlayers (8) intersected by calcite strings of different power (9)

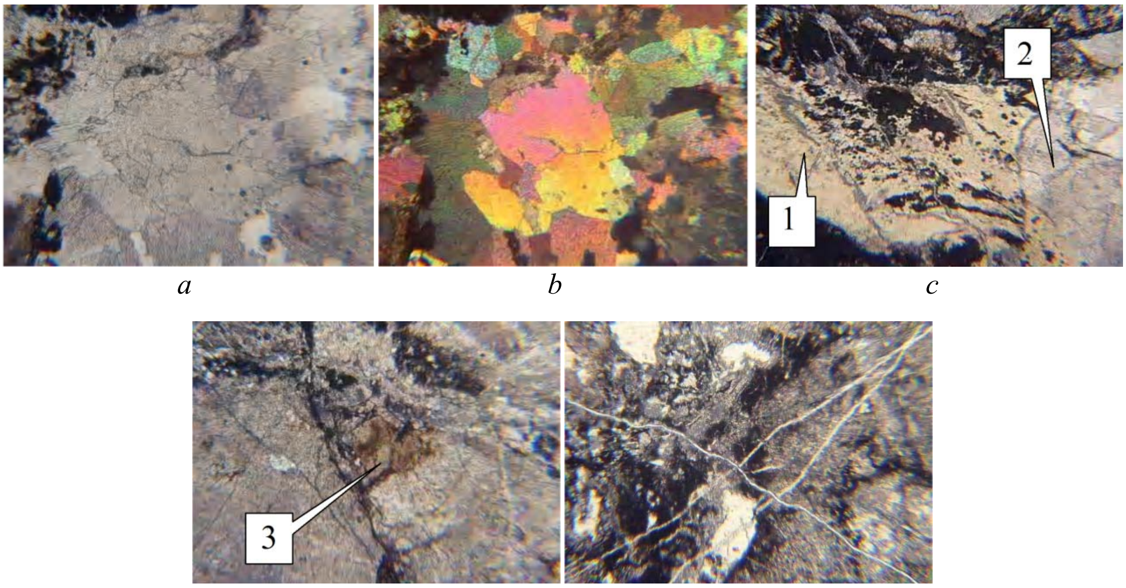

Figure 4. Observation of run-of-mine sample 1.3 in transmitted light ($50^{\times}$): *a* – fragment of calcite interlayer; *b* – the same; *c* – quartz slot (1) with ore interlayers (black) intersected by calcite strings (2); *d* – inclusion of earthy aggregate of hydrogoethite (3); *e* – thin strings of calcite (white)

Calcite ($CaCO_3$) forms the independent interlayers, in some places it is the total massive material (**Figure 3b, c, d**), besides it is found in the form of strings (**Figures 3e, 4**).

Conclusions

1. Investigated sample 1 is a rich manganese ore presented mainly by (vol. %) manganite 43.9 and hausmannite 26.4; also pyrolusite 5.1; psilomelane 0.6; calcite 10.1; hydrogoethite 5.3; quartz 5.7 and magnetite 3.1. Sample 1 is a high-quality raw material for manganese ferroalloy production. Ore structure is fine-grained by absolute grain size, cryptocrystalline in some places (grain size from 2 mm to unobservable size with the naked eye), colloform by morphology of grains. The texture is laminated, streaky, spotty and vein.
2. The size of ore mineral grains is up to tens of micrometers. Release of barren minerals (calcite and quartz) from manganese minerals is complicated due to ore complex texture that has the contortion pattern.
3. Manganese ore (sample 1) being high-grade raw material does not need to be dressed. It is necessary to crush the manganese ore to fractions of 10-100 mm, further this ore can be used for ferroalloy smelting.
4. When producing manganese ferroalloys, manganese ore (sample 2) with 49.8% of manganese can be partially charge-adjusted in amounts providing the target mass fraction of phosphorus in alloys.

References

1. V. I. Bolshakov, L. G. Tuboltsev. *Fundamental and Applied Problems of Ferrous Metallurgy. Collection of scientific papers*, Dnepropetrovsk, 2009, No. 19, pp. 3-12.*
2. M. I. Gasik, O. G. Gantserovskiy, A. N. Ovcharuk, I. P. Rogatchyov. *Ferroalloys of Ukraine-2000,* Systemnye technologii, Dnepropetrovsk, 2001, 143 p.*
3. M. I. Gasik, N. P. Lyakishev. *Physical Chemistry and Technology of Electroferroalloys,* Textbook for high schools, Systemnye technologii, Dnepropetrovsk, 2005, 448 p.*
4. Yu. I. Tretyakov, V. I. Martynyuk, A. G. Subottin et al. *Mineral Resources of Ukraine and World,* State Research and Production Enterprise "Geoinform Ukrainy", Kyiv, 2007, 560 p.*

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Исследование химического и минералогического составов марганцевых руд месторождений Средней Азии

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Исследованы химический и минералогический составы марганцевых руд месторождений Средней Азии. Руды представлены следующими минералами:

пиролюзит, манганит, псиломелан, гаусманит, магнетит, гидрогетит, кальцит, кварц. Руда пробы № 1 относится к богатым и качественным рудам, так как содержание марганца в ней порядка 54 %, а P/Mn = 0,002. Данная руда является универсальным сырьем для производства марганцевых ферросплавов, объемы которой уточняются.