

Conference paper

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The physicochemical bases of the pyrometallurgical processing of the titanomagnetite ores

DOI 10.1515/pac-2016-1201

Abstract: The questions of an experimental study on the qualitative characteristics of iron ore raw materials (durability, reducibility, softening and melting temperatures) and their influence on indicators of blast furnace smelting (coke consumption and productivity) are considered.

Keywords: agglomeration; blast furnace smelting; Mendeleev XX; production indices; quality rating; titanomagnetite ores.

Introduction

The blast-furnace process is one of the basic stages of the metallurgical treatment of iron ores under the scheme “blast furnace – converter”. The efficiency of blast furnace smelting depends on the iron ore materials and the coke quality. Now the requirements for the raw materials have become harder.

The coke rate as energy carrier (heat and reducing agent source) can be decreased generally in two ways [1]. First, it can be decreased by using the extensive factors, such as increased iron content of burden; utilization of direct coke substitutes (natural gas, oil, pulverized coal, reducing gas, including top gas without carbon dioxide); increased blast temperature; utilization of high potential heat, etc.

Second, the coke consumption can be reduced by using the intensive factors, such as increasing of the utilization heat and reducing the potential of gas as a result of improvement of the iron ore raw materials and coke quality indicators, namely, reducibility, cold and hot strength, softening and melting temperatures of iron ore raw materials, and the coke reactivity index (CRI) and the coke strength after reaction (CSR) index.

The reserves necessary for the first technique have been exhausted. Thus, the main option for decreasing coke consumption and improving the technical and economic parameters of blast furnace smelting is to improve the quality of iron ore materials and coke [2, 3].

At the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, a technique for the analysis of the influence of the qualitative characteristics of iron ore raw materials and coke on the technical and economic indicators of blast furnace smelting, allowing for the definition of the metallurgical value of new types of mineral raw materials, is being developed [4].

The preliminary estimate of the technical and economic indicators of the pyrometallurgical processes of treatment of ores on the basis of trial test results, as it is accepted in practice now, is complicated for technical

Article note: A collection of invited papers based on presentations at the XX Mendeleev Congress on General and Applied Chemistry (Mendeleev XX), held in Ekaterinburg, Russia, September 25–30 2016.

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and economic reasons as negative results or even an emergency in a blast furnace is possible. The method consists of the following steps.

1. *In vitro* producing of sinter or pellets, definition of the metallurgical properties (strength, reducibility, softening and melting points). Reducibility of raw material is defined according to Russian state standard 17212-84, strength – 15137-84 (ISO 13930), temperatures of softening beginning and melting of iron ore material – 26517-85.
2. Calculated forecasting of coke properties (strength, CRI) based on properties of components of coal mix for coking. Coke reactivity index (CRI, %) and coke strength after reaction (CSR, %) are defined according to Russian state standard R 50921-2005.
3. Definition of technical and economic parameters of blast furnace smelting by means of mathematical models. Mathematical models of blast furnace smelting include the balance logical statistical model [5] and a complex of two-dimensional models (gas dynamics, heat change, reduction, cohesion zone [6]). The mathematical models allow the use of the metallurgical characteristics of iron ore raw materials and coke as the source data, including two-dimensional adaptation. The mathematical analysis allows for the estimation of the possibility of the use of iron ore raw materials and coke as charge in blast furnace smelting.
4. Trial testing with the guaranteed receipt of positive results.

Use of mathematical models allows the definition of the quantitative influence of the quality of iron ore raw materials, including new deposits, on the basic technical and economic parameters of blast furnace smelting.

Metallurgical characteristics of titanomagnetite sinter and pellets

Titanomagnetite sinter and pellets are investigated (iron ore concentrate the same). The chemical composition is shown in Table 1.

Micro X-ray diffraction also has been carried out to study the mineralogical composition of sinter and pellets. Studies of samples are conducted with the X-ray diffractometer XRD 7000 (SHIMADZU, Japan) with automatic program control, with the use of CuK_α -radiation (stress on tube 40 Kv, current on tube 30 mA) and a graphitic monochromator. Identification of formed phases in investigated samples is performed using a database of PDF2 (ICDD).

The autoemission electronic microscope TESCAN MIRA 3 LMU (TESCAN, Czech Republic) allows to receive the image of a surface of studied object with high resolution: resolution (In-Beam SE) – 1 nm at 30 kV and 2 nm at 3 kV; resolution (ET type SE) – 1.2 nm at 30 kV and 2.5 nm at 3 kV. It is equipped with system of the X-ray power dispersive microanalysis of Oxford Instruments INCA Energy 350 X-max 80 with the nitrogen-free detector X-max 80 Standart (silicon-drift detecting element, the active area – 80 mm²; resolution on the Mn K α line – 127 eV).

Sinter

The basic phase in the sinter is Fe_3O_4 (magnetite). The diffraction pattern of the sinter is shown in Fig. 1. It comprises Fe_2O_3 (hematite) and a Ca-containing silicate of difficult composition; $\text{Ca}_{2,3}\text{Mg}_{0,8}\text{Al}_{1,5}\text{Fe}_{8,3}\text{Si}_{1,1}\text{O}_{20}$ is well represented in the sample.

Table 1: The chemical composition of investigated sinter and pellets, %.

Name	Fe _{total}	FeO	CaO	SiO ₂	V ₂ O ₅	TiO ₂	Mg
Sinter	54.1	9.5	10.3	4.74	0.54	2.59	2.63
Pellets	61.2	3.33	1.04	3.72	0.60	2.71	2.49

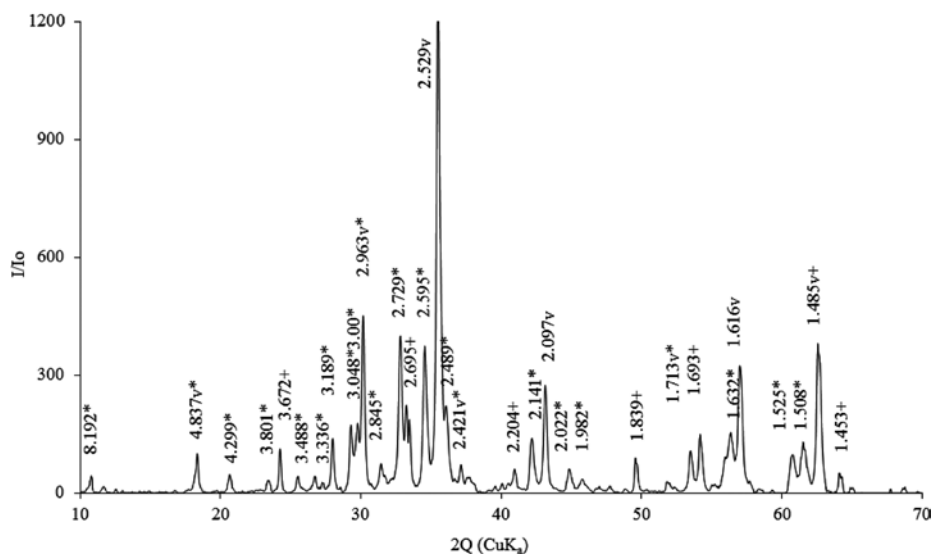


Fig. 1: Diffraction pattern of the initial sinter (Table 1), X-ray diffractometer XRD 7000, Symbols: v – Fe_3O_4 ; + – Fe_2O_3 .

* – $\text{Ca}_{2,3}\text{Mg}_{0,8}\text{Al}_{1,5}\text{Fe}_{8,3}\text{Si}_{1,1}\text{O}_{20}$.

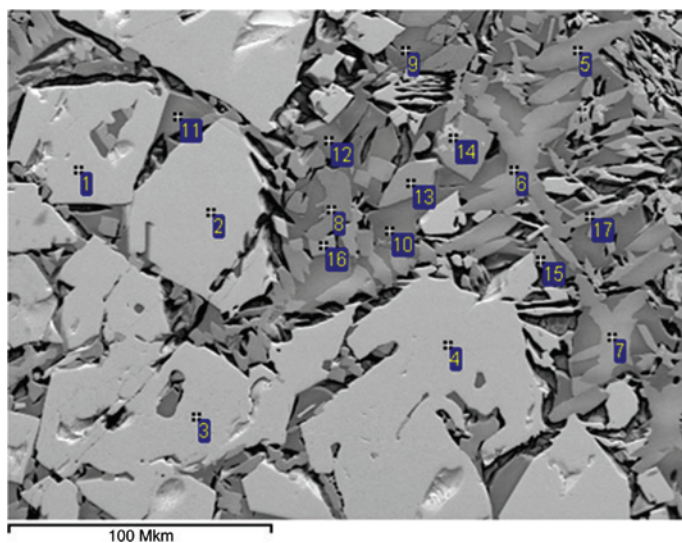


Fig. 2: Phase composition of sinter (Table 1) in BES mode ($\times 500$), electronic microscope TESCAN MIRA 3 LMU.

The most typical field of sinter microstructure has been chosen. The chemical composition of the basic mineral phases is defined (Fig. 2, Table 2; results are shown in atomic %).

In the initial sinter, one can isolate phases of magnetite Fe_3O_4 , calcium titanate (perovskite) $\text{CaO} \cdot \text{TiO}_2$, lime CaO and dicalcium silicate, one of which is stabilized by aluminum $\text{Ca}_{2,3}\text{Mg}_{0,8}\text{Al}_{1,5}\text{Fe}_{8,3}\text{Si}_{1,1}\text{O}_{20}$. Dicalcium silicate $\text{CaO} \cdot \text{SiO}_2$ (phase 4, 5 in Table 3) is not stabilized and as a result will form sinter fines.

According to [7, 8] phase, SFCA has a considerable influence on sinter strength.

Pellets

To study pellet mineral composition, micro X-ray structure phase analysis was also performed. In the pellet sample, the most specific part of the micro structure was selected and the chemical composition of the main mineral phases was determined (Fig. 4, Table 4; the results are shown in atomic %).

Table 2: Results of quantitative analysis in points 1–17 (Fig. 2) with locality 1–2 microns and averaged result (total spectrum), atomic %.

Spectrum	O	Na	Mg	Al	Si	Ca	Ti	V	Fe
Total spectrum	57.88		0.92	1.78	5.58	9.36	1.50	0.29	22.69
Phase	Magnetite Fe_3O_4								
1	53.50		2.17	1.48		1.06	0.26		41.52
2	53.75		2.28	1.48		1.03	0.32		41.15
3	53.53		2.68	1.74		0.75	0.33		40.97
4	53.79		2.14	1.39		1.10	0.32		41.26
Phase	Calcium titanate (perovskite) $\text{CaO} \cdot \text{TiO}_2$								
5	60.09			0.50	3.66	20.18	8.18		7.39
6	61.91			0.57	4.35	19.22	6.21		7.73
7	63.05			0.53	4.58	18.82	5.35		7.67
8	56.23			0.60	4.40	21.92	7.43		9.42
Phase	Dicalcium silicate (SFCA) $\text{Ca}(\text{Mg, Fe, Mn})\text{O} \cdot \text{SiO}_2$								
9	57.13			3.07	14.12	18.26	0.95	1.09	5.38
10	62.00			3.31	13.06	15.68	0.77	0.88	4.29
11	58.05			3.72	13.44	17.36	0.81	0.86	5.76
12	59.90	0.39		3.26	13.64	16.59	0.84	1.00	4.38
Phase	$\text{Ca}_{2.3}\text{Mg}_{0.8}\text{Al}_{1.5}\text{Fe}_{8.3}\text{Si}_{1.1}\text{O}_{20}$								
13	55.99		0.40	5.03	4.63	9.17	0.78		24.01
14	55.00		0.33	4.42	3.94	9.07	0.70		26.53
15	55.96		0.46	5.54	4.67	9.25	0.79		23.33
16	56.16		0.37	5.29	4.63	9.04	0.77		23.74
17	55.62			4.59	4.49	9.18	0.83		25.28

The most typical field of sinter microstructure has been chosen. The chemical composition of the basic mineral phases is defined (Fig. 2, Table 2; results are shown in atomic %).

Table 3: Results of quantitative analysis in points 1–7 (Fig. 3), atomic %.

Spectrum	O	Na	Mg	Al	Si	Ca	Ti	V	Fe
Phase	Magnetite Fe_3O_4								
1	53.64		2.11	1.25		1.21			41.78
Phase	Calcium titanate (perovskite) $\text{CaO} \cdot \text{TiO}_2$								
2	64.12			0.56	4.20	18.29	6.05		6.77
Phase	Dicalcium silicate (SFCA) $\text{Ca}(\text{Mg, Fe, Mn})\text{O} \cdot \text{SiO}_2$ (stabilized Al)								
3	61.35			3.45	13.66	15.98	0.71	0.83	4.01
Phase	$\text{CaO} \cdot \text{SiO}_2$ (not stabilized)								
4	59.68	0.27			13.92	24.83		0.43	0.87
5	56.10				13.05	29.62		0.48	0.75
Phase	Lime CaO								
6	57.69			0.64	4.28	21.11	7.28		9.00
7	56.98			1.31	4.11	19.54	7.52		10.53

In pellets, the main phase is hematite. There is also magnesioferrite, helenite and anorthite. An X-ray diffractogram of pellets (Fig. 5) shows the presence of mainly Fe_2O_3 (hematite). Fe_3O_4 (magnetite) is detected very poorly. On the level of instrument threshold, SiO_2 (quartz) and TiO_2 и MgSiO_3 phases are determined.

Mathematical modelling

As an example, the study results of three different pellet laboratory samples received from iron ore concentrate of one deposit with different titanium dioxide content are shown below. Their chemical compositions are shown in Table 5.

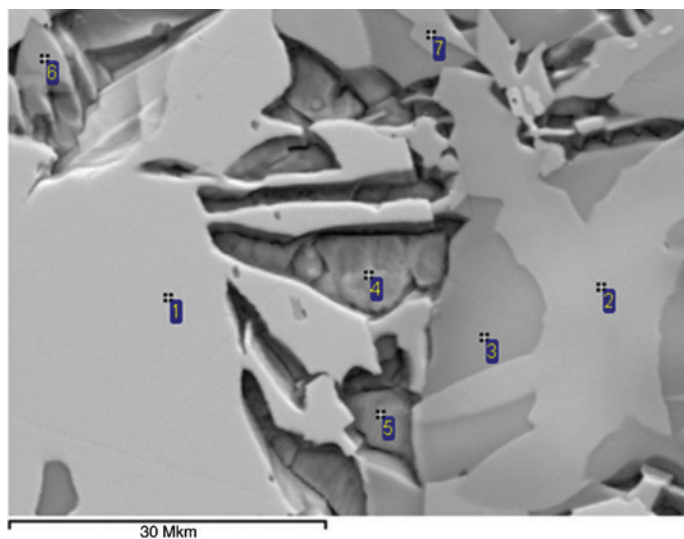


Fig. 3: Phase composition of sinter (Table 1) in BES mode ($\times 2000$), electronic microscope TESCAN MIRA 3 LMU.

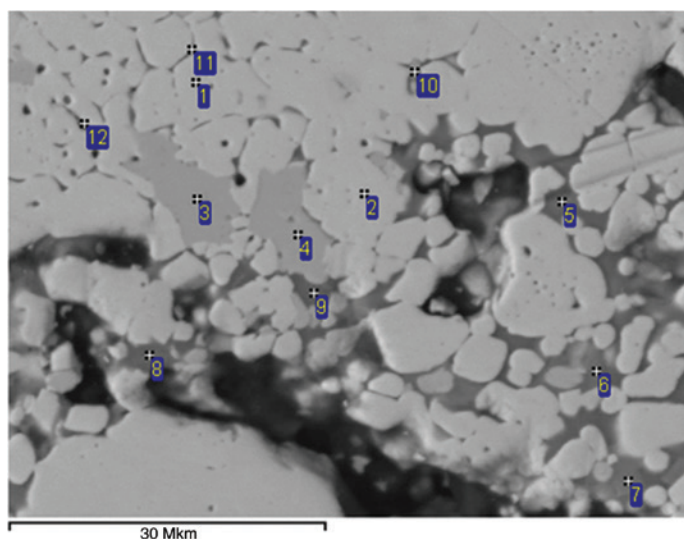


Fig. 4: Phase composition of pellets (Table 1) in BES mode ($\times 2000$), electronic microscope TESCAN MIRA 3 LMU.

Determination of pellet reducibility was made at the unit which corresponds to requirements of State Standard 17212–84. The calculated rate of reducibility for samples 1, 2 and 3 are equal, correspondingly 0.75, 0.98 and 0.70 %.

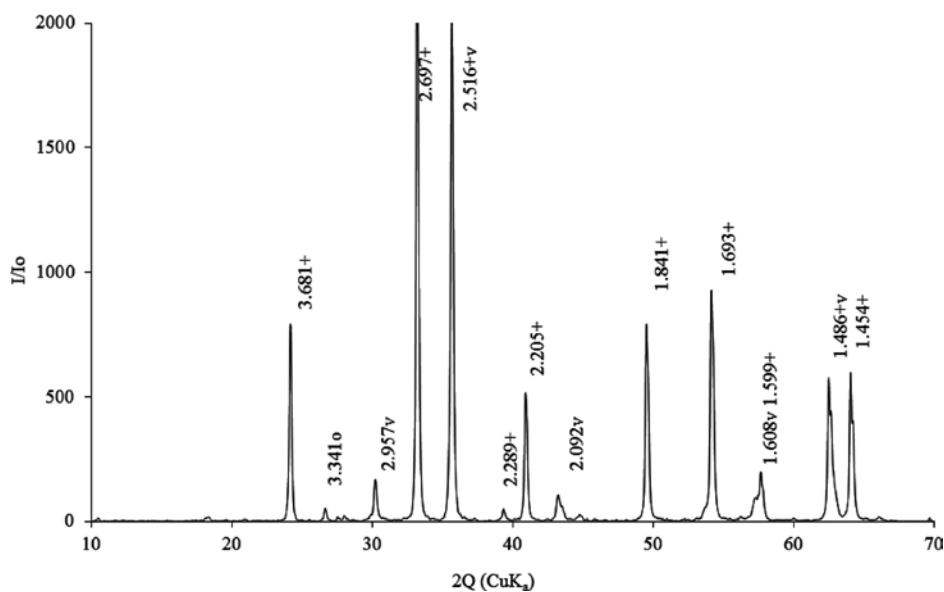
Calculated degrees of reducibility are provided in Table 6. Results of research of pellets durability at low-temperature reduction on ISO 13930 are given in Table 7, and a temperature interval of a softening in Table 8.

Pellet strength results at low temperature reducibility ($LTD_{+6,3}$) as per ISO 13930 for samples 1, 2 and 3 were correspondingly 65.71, 69.92 and 78.58 %; softening temperature ranges were correspondingly 1210–1300, 1180–1310 and 1130–1340 °C.

Thus, the study of three samples of laboratory iron ore pellets with different content of titanium dioxide showed that pellets (sample 2) with less content of TiO_2 have the best reducibility. Pellets (sample 3, variant

Table 4: Results of quantitative analysis in points 1–12 (Fig. 4), atomic %.

Spectrum	O	Na	Mg	Al	Si	Ca	Ti	V	Mn	Fe
Phase	Hematite Fe_2O_3									
1	57.59		0.65	0.88			0.98	0.38		39.52
2	58.40		0.44	0.86			0.51	0.30		39.49
Phase	Magnesioferrite $\text{MgO} \cdot \text{Fe}_2\text{O}_3$									
3	56.20		11.75	5.47					0.42	26.17
4	56.95		11.28	4.74					0.56	26.47
Phase	SiO_2 + helenite $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$									
5	63.69	0.45	3.20	5.58	18.19	5.83	0.11	0.76		2.19
6	58.53		5.86	4.44	17.31	7.45	0.19	0.31	0.17	5.73
7	58.03	0.31	7.32	3.81	18.72	8.18		0.57		3.06
Phase	Anorthite $(\text{Ca}, \text{Na})(\text{SiAl})_4\text{O}_8$									
8	61.90	0.87	0.66	10.81	17.26	6.52				1.98
9	61.18	1.02	0.49	11.54	17.05	6.25				2.48
Phase	Hematite Fe_2O_3 + MgO + Al_2O_3 + SiO_2									
10	56.07		9.06	4.60	2.79	0.74	0.35		0.51	25.89
11	57.47	0.36	0.94	3.36	5.07	1.64	0.70	0.49		29.96
12	49.82		0.97	2.33	0.75	0.31	1.57			44.26

**Fig. 5:** Diffraction pattern of initial pellets (Table 1), X-ray diffractometer XRD 7000. Symbols: v – Fe_3O_4 ; + – Fe_2O_3 , o – SiO_2 ; x – MgSiO_3 .**Table 5:** The chemical composition of investigated pellets, %.

Sample	TiO_2	V_2O_5	CaO	SiO_2	Fe	MnO	MgO	Al_2O_3
1	3.25	0.75	1.21	3.72	62.0	0.21	2.51	2.83
2	2.13	0.76	0.83	2.63	65.0	0.159	1.35	2.58
3	2.56	0.55	1.23	4.12	61.1	0.24	2.48	2.50

1) with medium content of titanium dioxide have the best strength during reducibility. Pellets (sample 1, variant 2) with high TiO_2 content have the highest onset temperature of softening and lowest softening temperature range.

Table 6: Calculated degrees of pellets reducibility, %.

Sample	Degrees of reducibility			
	Absolute degree of oxidation, %	Absolute loss of weight, %	Actual loss of weight, %	Absolute extent of reduction of initial probe
1	79.86	55.46	79.70	0.75
2	67.64	47.67	67.32	0.98
3	82.78	56.37	82.66	0.70

Table 7: Results of research of pellets durability at low-temperature reduction, %.

Indicator\Sample	1	2	3
LTD _{+6,3}	65.71	69.92	78.58
LTD _{-3,15}	12.87	11.39	9.19
LTD _{-0,5}	2.17	1.67	6.43

Table 8: Results of research of temperature interval of pellets softening.

Indicator/Sample	1	2	3
Temperature of softening beginning, °C	1210	1180	1130
Temperature of softening end, °C	1300	1310	1340
Temperature interval of pellets softening, °C	90	130	210

Table 9: Calculated technical and economical parameters of blast furnace smelting.

Parameters	Unit	Variant 1	Variant 2
Coke rate	kg/tons of pig iron	321	323
Natural gas rate	m ³ /tons of pig iron	75	75
Blast			
temperature	°C	1145	1145
humidity	g/m ³	26	26
oxygen	%	31.5	31.5
Iron composition			
Si	%	0.07	0.07
Ti	%	0.14	0.15
Mn	%	0.29	0.128
V	%	0.454	0.541
Slag quantity	kg/tons of pig iron	358.0	315.0
Slag composition			
CaO	%	32.55	28.91
MgO	%	12.97	13.49
SiO ₂	%	26.68	23.69
Al ₂ O ₃	%	15.15	17.05
TiO ₂	%	10.53	14.82
MnO	%	0.36	0.16
V ₂ O ₅	%	0.28	0.33

Based on the chemical composition of iron ore pellets, their reducibility and strength characteristics, the main parameters of blast furnace smelting were calculated (Table 9) by means of a balance logical statistical model [5]. Calculation results of blast-furnace indices for laboratory pellet samples no. 2 and 3 are similar, so

Table 10: Change of agglomerate durability on stages.

Stage	Stage 1	Stage 2	Stage 3 (300 g/t)	Stage 3 (500 g/t)
Durability LTD _{+6,3} , %	11.01	13.68	12.57	39.9

Table 11: Change of agglomerate reducibility on stages.

Stage	Stage 1	Stage 2	Stage 3 (300 g/t)	Stage 3 (500 g/t)
Reducibility, %	74.75	64.74	64.9	69.61

Table 12: Change of agglomerate temperature interval softening on stages.

Stage	Stage 1	Stage 2	Stage 3 (300 g/t)	Stage 3 (500 g/t)
Temperature of softening beginning, °C	1060	1140	1140	1150
Temperature of softening end, °C	1200	1280	1190	1220
Temperature interval of pellets softening, °C	140	140	50	70

Table 13: Change of blast furnace indices.

Indices/Month	1	2	3	4	5	6	7
Coke consumption, kg/t pig iron	335.3	335.7	331.3	332.9	343.8	331.3	345.7
Natural gas consumption, m ³ /t pig iron	106	105.8	104	104.5	107.2	104.9	114.6
Pulverized coal consumption, kg/t pig iron	73.6	69.4	77.8	78.9	68.4	76.5	56.5
General fuel consumption, kg/t pig iron	483.2	479.2	480.5	483.6	486.0	478.5	482.9
Degree of use CO, %	51.8	51.4	51.9	51	50.3	50.3	50.2
Charge, %							
agglomerate	38.5	38.7	35.6	39.7	39.4	38.3	39.4
pellets	53.4	51.2	51.4	52.6	54.1	54.7	55.8
staflux	8.1	10	12.9	7.7	6.5	7.1	4.8
Agglomerate, kg/t							
consumption	624.84	634.51	582.02	644.85	644.04	615.2	635.58
siftings	101.35	103.55	89.612	100.91	82.5	82.66	88.4
Sowing (–5 mm), %	16.22	16.32	15.40	15.65	12.81	13.44	13.91
Durability (+5 mm), %	74.64	73.80	74.36	74.95	75.78	75.91	76.04

that the table shows only results for sample 3. The high content of titanium dioxide in blast furnace slag and the slag low ratio attract attention.

Industrial application

Improvement of processing of titan magnetite ores of the Gusevogorsky field of the Kachkanarsky fields group is made. Stages of 2015 in Tables 10–12: 1 – April-May, base (agglomerate basicity 2.1); 2 – June-July, agglomerate basicity 2,4; 3 – August-September, agglomerate basicity 2,4 with polymeric additive (300 g/t и 500 g/t). According to [9], increase of agglomerate basicity has a considerable influence on forming the phase SFCA and sinter strength.

In Table 13, the change of blast furnace indices is shown.

Conclusion

The method of the influence estimation of the iron ore raw material characteristics on the technical and economic parameters of the blast furnace smelting was reviewed. The examples of assessment of sinter and pellet metallurgical properties of titanium magnetite concentrate were made. The results of blast furnace smelting parameters were calculated. The influence of the phase composition of an agglomerate on its quality is shown. The results of industrial tests on the change of quality of the agglomerate (durability, reducibility, softening and melting temperatures) and its influence on blast furnace indices are given.

Acknowledgement: Work was executed with the financial support of Project No 0396-2015-0081 and the Russian Foundation for Basic Research, Project № 16-08-00062.

References

- [1] A. N. Dmitriev. *En. Anal. Eff.* **4–5**, 41 (2004).
- [2] A. N. Dmitriev. *Def. Diff. Forum* **258–260**, 91 (2006).
- [3] A. N. Dmitriev, Yu. A. Chesnokov, G. Yu. Vitkina. *Def. Diff. Forum* **334–335**, 375 (2013).
- [4] A. N. Dmitriev, G. Yu. Vitkina, Yu. A. Chesnokov. *Adv. Mat. Res.* **602–604**, 365 (2013).
- [5] A. V. Chentsov, Yu. A. Chesnokov, S. V. Shavrin. *Ekaterinburg: Ural Branch of Russian Academy of Sciences*, 164 (2003).
- [6] A. N. Dmitriev. *Ekaterinburg, the Ural Branch of the Russian Academy of Sciences* 163 (2011).
- [7] J. D. G. Hamilton, B. F. Hoskins, W. G. Mumme, W. E. Borbidge, M. A. Montague. *Neues Jahrb. Miner. Abh.* **161**, 1 (1989).
- [8] N. A. S. Webster, M. I. Pownceby, I. C. Madsen, J. A. Kimpton. *Metall Mater. Trans B* **43B**, 1344 (2012).
- [9] Z. Yu, G. Lu, T. Jiang, Y. Zhang, F. Zhou, Z. Peng. *ISIJ Int.* **55**, 907 (2015).