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Metallization of oxide-ore-containing wastes with the use of brown coal semicoke from Berezovsky deposit of the Kansk-Achinsk Basin

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Abstract. The research of the metallization process of the roll scale and sludge after gas treatment in the BOF production with the use of brown coal semicoke mined in Berezovsky field of the Kansk-Achinsk Basin was carried out. A flow diagram of "cold" briquetting using a water-soluble binder was offered. The reduction of iron from its oxide Fe2O3 with brown coal semicoke in the laboratory electric-tube furnace in the argon atmosphere was studied. The mathematical models of dependence of the metallization degree on variable factors were developed. The optimal values of technological factors and essential characteristics of the obtained metallized products were revealed.

1. Introduction

Currently, metallization of oxide-iron-containing wastes is an important trend in the industry. This is especially true for the mini-plants with the absence in their structure of sinter production allowing the full cycle metallurgical enterprises to process mill scale, sludges from the BF and steelmaking production. The urgency of the problem is due to a significant number of mini-plants in the world – approximately one thousand [1], and, accordingly, a significant amount of generation of oxide-iron-containing wastes. High dispersion of these wastes determines the need for their agglomeration before use. It conditions the technological feasibility of engaging into the processing highly dispersed carbonaceous materials of technogenic origin and specifically manufactured. Brown coal semicokes (BCSs), in particular BCSs of Berezovsky mine in the Kansk-Achinsk Basin (KAB), in the long run can be used as reducing agents [2-6].

The aim of this research is to develop the scientific and technological bases for the use of BCSs in the process of metallization of oxide-containing technigenic raw material.

2. Current state of technologies used for metallization of oxide-iron-containing raw materials

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All metallization processes (direct iron reduction) are based on the following principle [7]. The initial oxide-iron-containing raw material is reduced to the state of solid sponge iron, also known as iron of direct reduction (DRI – Direct Reduced Iron), or to hot briquetted iron (HBI – Hot Briquetted Iron) having a degree of metallization 85-95%. At a less degree of metallization the resulting product is called pre-reduced (partially metallized).

Reduction processes depending on the used type of reducing agent are classified into gas and solid phase reduction. At an industrial scale the gas phase processes are carried out in the shaft furnaces, retorts and fluidized (boiling) layer. Solid reduction occurs in rotary furnaces, furnaces with a rotary hearth or multi-hearth furnaces.

The metallized products need to meet the requirements in granulometric composition, degree of metallization, carbon content and the compressive strength [8]. Table 1 shows requirements for metallized products depending on their function.

Table 1. Requirements to metallized products depending on their use.

Properties of metalized products	Use of metallized products	
	Blast furnace	Arc steel furnace
Size of pellets and briquettes, mm	16-22	8-14
The degree of metallization, %	85-92	> 90
Carbon content, %	4-7	1.5-3.0
Compressive strength, H	> 250	> 200

According to the authors [9], the most important characteristics of metallized products include the following: the degree of metallization – 90-94%; content of rock refuse (SiO_2) – not more than 5%; sulfur content – not more than 0.010%; phosphorus – not more than 0.015%; carbon content – 1-2%; bulk weight – not less than 1.8 tonne/m3; nitrogen content – 0.02-0.14%; the resulting product must be passivated, i.e. the secondary oxidation should be suppressed.

3. Experimental research: methodology, results, discussion

While conducting the research the non-roasted briquetted compositions produced by "cold" briquetting (Figure 1) were tested, consisting of oxide-iron-containing component, carbonaceous reducing agent and a binder. The weight ratio between C and Fe_2O_3 briquettes was 4.44: 1.0 (i.e., 81.6% Fe_2O_3 and 18.4% C).

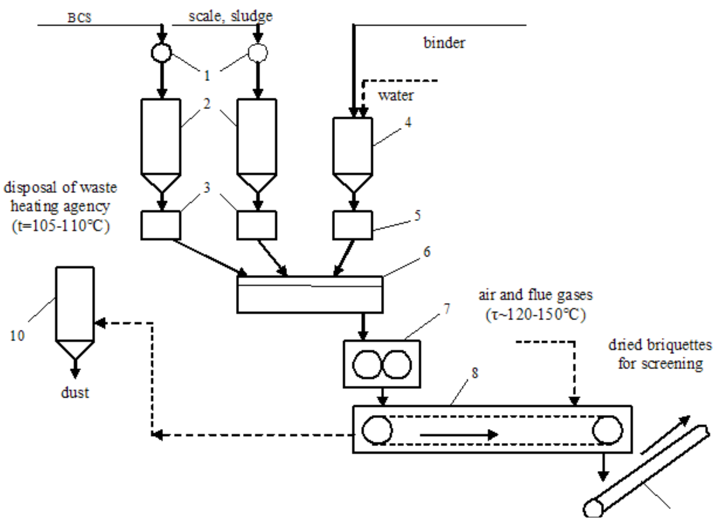

Figure 1. Technological scheme for production of non-roasted briquettes (1 – milling unit; 2 – proportioning bunker; 3 – dispensers; 4 – storage container for aqueous binder solution; 5 – binder dispenser; 6 – double spiral mixer; 7 – roll press; 8 – belt drier; 9 – conveyor belt; 10 – cyclone).

Consumption of binder (molasses) in all cases was 10% by weight of the mixture of oxide-iron-containing. As oxide-iron-containing components in experiments we used iron oxide (III) (chemically pure), as well as mill scale and sludge from gas treatment of BOF production at JSC "EVRAZ ZSMK". As carbonaceous reducing agents we used BCSs from Berezovsky field of KAB, small coke of JSC "Koks" (SC) and the dust of dry coke quenching from JSC "EVRAZ ZSMK" (CD).

The investigation of the metallization process was carried out in two stages. At the first stage in the laboratory electric-tube furnace in the protective argon atmosphere (Figure 2) we studied the reduction of iron from its oxide Fe_2O_3 with BCS. The study was conducted using the method of the planned experiment [10]. The optimization parameters, factors, influence of which was taken into account, and the range of their variation are given in Table 2.

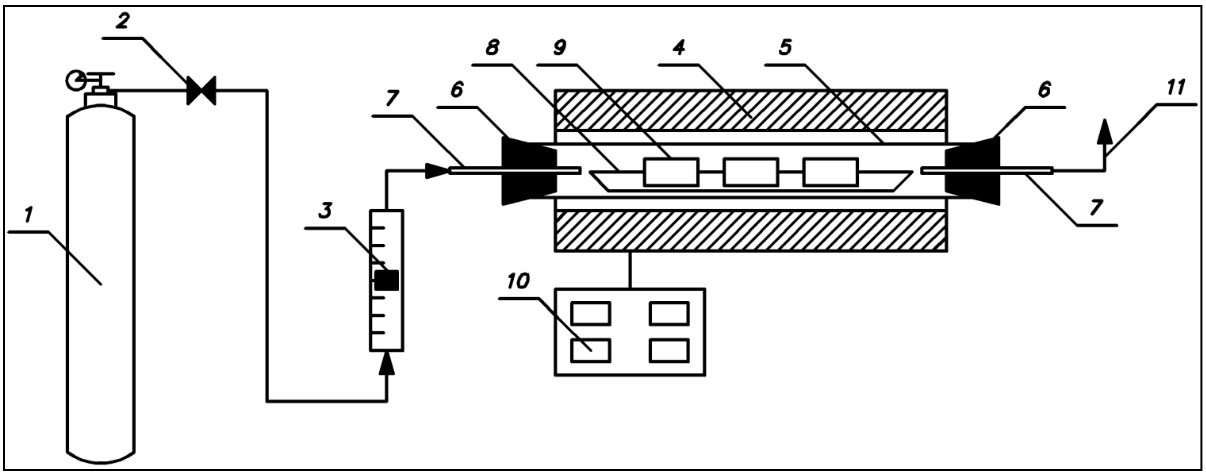

Figure 2. Installation for the study of metallization of oxide-iron-containing technogenic raw material (1 – tank with; 2 –valve for fine regulation of argon flow; 3 – rotameter RS-3A; 4 – electric-tube furnace SUON 0.3.2 / 12.5-I1; 5 – corund tube with diameter 0.032 m, 0.36 m long; 6 – rubber stopper; 7 – metal tubes for argon supply (left) and for argon, gaseous products of metallization outflow (right); 8 – metal boat; 9 – briquettes; 10 – furnace control panel; 11 – release of argon and gaseous products of metallization into the atmosphere).

Table 2. Variable factors selected for the study of metallization process.

Factors	Levels of factors			Variation interval
	–1 (low)	0	+1 (upper)	
First series				
x_1 – violates yield from BCS, V^{daf}, %	0.6	5.05	9.5	4.45
x_2 – temperature, t, °C	600	750	900	150
x_3 – duration of metallization, τ, min	25	37.5	50	12.5
x_4 – pressing pressure during briquetting, P, MPa	10	25	40	15
Second series				
x_1 – reactivity of the reducing agent with CO_2, K, $cm^3/(g \cdot s)$	0.33	2.025	3.72	1.695
x_2 – temperature, t, °C	700	800	900	100
x_3 – duration of metallization, τ, min	15	27.5	40	12.5
x_4 – pressing pressure during briquetting, P, MPa	10	25	40	15

The mathematical models in the form of the following equations are obtained:

$$\eta_1 = -183.40 + 0.62\,V^{daf} + 0.37\,T + 1.86\,\tau - 0.008\,V^{daf}\cdot\tau - 0.002\,T\cdot\tau; \quad (1)$$

$$\eta_2 = -430.28 + 10.52\,K + 0.55\,T + 8.80\,\tau - 0.08\,K\cdot\tau - 0.01\,T\cdot\tau, \quad (2)$$

whereV^{daf}– violates yield from BCS (0.6 – 9.5 %);
T – temperature (600 – 900 °C);
τ – duration of metallization (15 – 50 min);
K – reactivity of the reducing agent with CO_2 (0.33–3.72 $cm^3/(g\cdot s)$).

Figures 3-6 shows graphical dependences of the degree of metallization on volatiles yield from the reducer and the temperature at metallization duration 40 minutes (Figure 3), on the reducer reactivity and temperature at metallization duration 50 minutes (Figure 4), on the violates yield from reducer and duration of metallization at 900 °C (Figure 5), as well as on the reducer reactivity and the duration of the metallization at a temperature 900 °C (Figure 6).

The first most important factor is a temperature. Thus, for the same duration of metallization if the temperature is increased from 700 to 900 °C, then η increases from 1.1 to 96.7%. The second most important factor is the reactivity of the reducing agent. For example, during the reduction of iron oxide (III) (ch. p.) using a carbonaceous reducing agent with reactivity 3.72 $cm^3/(g\cdot sec)$ at a temperature 900 °C and duration of the metallization 40 minutes η = 96.9%, whereas the use of a carbonaceous reductant with the reactivity 0.33 cm3/(g·s) under the same conditions – 47.8%. The third factor is the value of the metallization duration (when it is changed from 15 to 40 min).

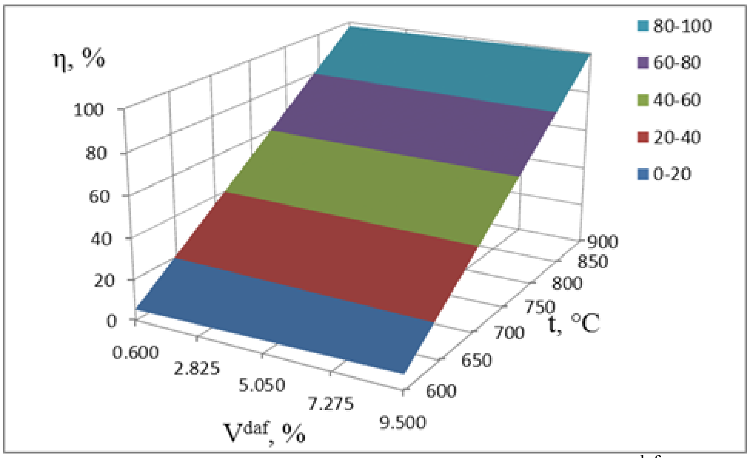

Figure 3. Graphical representation of the dependence [η] = f (V^{daf}, t) at τ = 40 min.

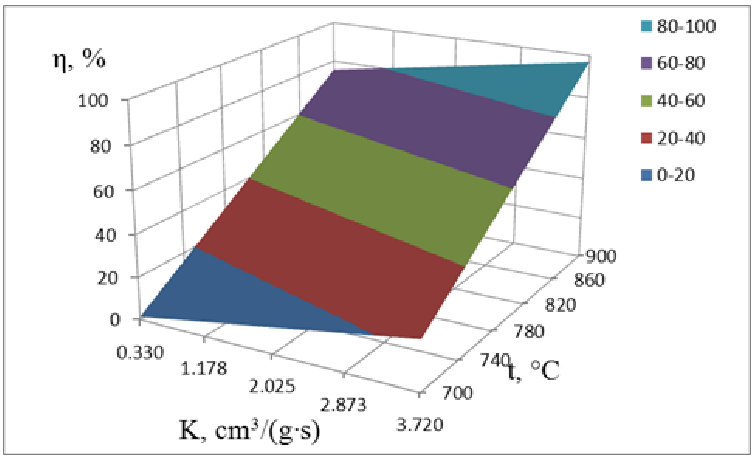

Figure 4. Graphical representation of the dependence [η] = f (K, t) at τ = 5 min.

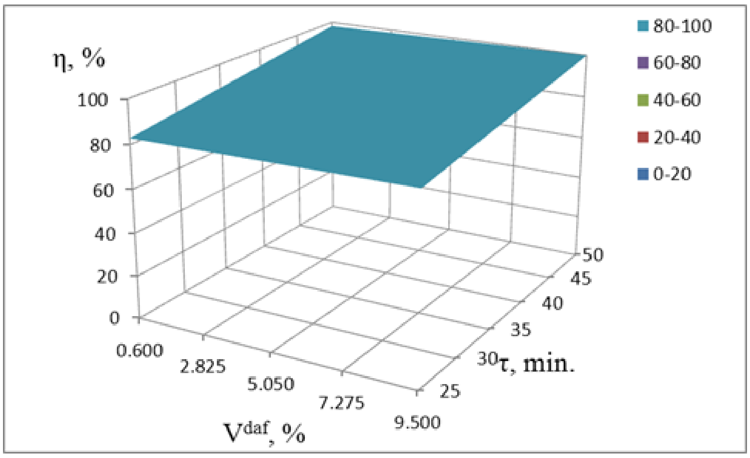

Figure 5. Graphical representation of the dependence [η] = f (V^{daf}, τ) at t = 900 °C.

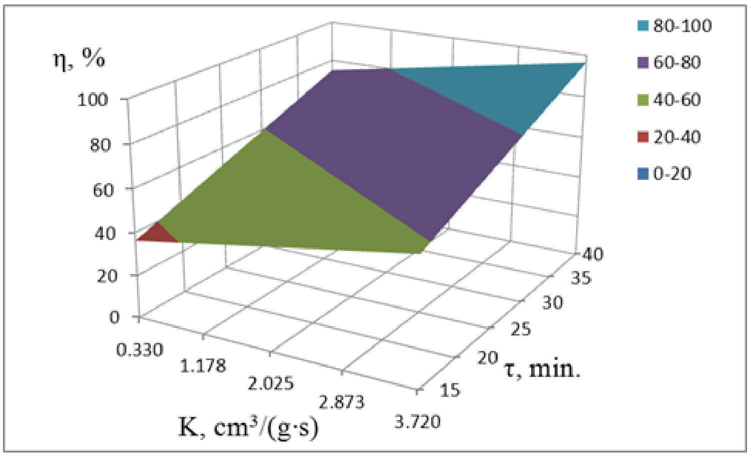

Figure 6. Graphical representation of the dependence [η] = f (K, τ) at t = 900 °C.

Thus, to obtain the metallized product with the desired quality the metallization process should be performed at a temperature 900 °C (x2 factor), the duration of the metallization 40 min (x3 factor) and the reactivity of the carbonaceous reductant CO_2 3.72 cm3/(g·s) (x1 factor).

The optimum values of technological factors and essential characteristics of the obtained metallized products are given in Table 3.

At the second stage of the research under these conditions in the laboratory electric furnace the metallization of briquetted batches of 6 compositions was done: from scale and BCS, small coke (SC) and dust (CD), and from slurries with these carbonaceous reductants. To approximate conditions of metallization to industrial ones argon was not fed into the reaction area in the furnace. A comparative analysis of its indicators was performed and the physical and chemical certification of products was carried out (Table 4).

Table 3. The optimum values of technological factors of metallization process and the main characteristics of the obtained metallized products.

Process parameters of metallization and metallized product characteristics	Value
Metallization temperature, t, °C	900
Duration of metallization, τ, min	40
Reactivity of the reducing agent CO_2, K, $cm^3/(g \cdot s)$	3.72
Pressure pressing during briquetting, P, MPa	40
Degree of product metallization, η, %	96.7
Size of metallized briquettes, mm	20
Content in the metallized product, %:	
$Fe_{tot.}$; $Fe_{met.}$; FeO	86.1; 83.4; 3.5
S, P, C	0.04; 0.001; 3.0
CaO, MgO	0.9; 0.1

Table 4. Quality of metallized products.

Content of briquetted compositions	η, %	Content in metallized products, %							
		Fe_{tot}	Fe_{met}	FeO	S	P	C	CaO	MgO
Scale + BCS	97.5	92.5	90.2	3.0	0.07	0.017	1.8	1.1	0.3
Scale + SC	70.7	87.5	61.9	33.0	0.14	0.025	3.8	0.3	0.3
Scale + DC	71.1	88.0	62.6	32.8	0.11	0.026	3.6	0.4	0.3
Slurry + BCS	97.5	73.1	71.3	2.3	0.21	0.121	1.8	17.4	0.4
Slurry + SC	68.9	70.2	48.4	28.1	0.28	0.130	3.8	16.6	0.3
Slurry + DC	69.2	69.7	48.2	27.7	0.25	0.131	3.6	16.7	0.3

The metallization degree was from 69 to 97.5% with the best results achieved by using BCS as a reductant. Metallization products from the scale burden and BCS in their degree of metallization, content of sulfur, phosphorus, carbon and waste rock meet the requirements concerning metallized products for the production of electric steel.

4. Conclusions

The technological scheme for obtaining non-roasted strong briquettes from charges with the compositions mill scale – semicoke, slurry – semicoke with 10% of water-soluble binder – molasses was developed and implemented. Drop strength of oxide-iron-containing briquettes is 98-99% and conserved during exposure in sand at 900 °C for 30 min. We experimentally studied the metallization processes of batches with compositions oxide-containing components (scale, sludge) – (BCS, SC, DC). Carried out metallization at a temperature of 1173 K and a duration of 40 min and made a comparative analysis of its indicators for briquetted batches of six types: scale – BCS, SC and DC, sludge – BCS, SC and DC. Determined the degree of metallization and the content of metallic iron, which with the use of BCS are 97.5 and 90.2% for scale, 97.5 and 71.3% for sludge, DC 70.7 and 61.9% for the scale 68, 9 and 48.4% for sludge, DC 72.1 and 62.6% for scale, 69.2 and 48.2% for sludge. Developed mathematical models describing the dependence of the degree of metallization on temperature, its duration, reducer reactivity and content of volatiles in it.

Found the optimum temperature and time conditions for metallization of briquetted batch scale – brown coal semicoke with reactivity 3.72 cm3/(g·s): temperature 1173 K with the duration of 40 minutes. Performed physical and chemical attestation of metallization products, which includes the study of phase, chemical, particle size distribution and morphology. Metallization products of briquetted batch scale – BCS on the degree of metallization, content of sulfur, phosphorus, carbon, waste rock meet all necessary requirements.

5. References

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