ECONOMICAL EVALUATION OF REDUCIBILITY OF COMPACTED METALLURGICAL WASTE WITH HIGH RATIO OF Fe

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Abstract

Reducibility of raw materials such as iron ore and sinter is a significant parameter characterizing the quality of input materials of blast furnace feedstock. It is considered to be a tool for optimizing of production process in shaft aggregates referring to economical production of pig iron. The paper deals with evaluation of reducibility of metallurgical waste. It aims at study of reduction process of fine waste from metallurgical production typical with high ratio of Fe and compacted into cylindrical briquettes. In the introduction, the paper sumps up the economic indicators important for waste management in metallurgical industry and presents worldwide experience with techniques for fine waste materials compacting, as same as recycling of the materials originated from production process in the same company. It presents methodology for testing of reducibility of non-traditional metal materials such as iron-bearing waste compacted into briquettes. It describes the experimental procedures for results acquiring. The results of testing are discussed in relation to production parameters such as reduction kinetics of the waste, reduction of iron oxides and reduction gas consumption and they are interpreted in economical point of view.

Keywords: Metallurgical waste, blast furnace, reducibility, economical evaluation

1. INTRODUCTION

Production of iron and steel is accompanied by generation of a great amount of wastes. It is important the waste would become secondary raw material. From the total amount of waste originating during production of one ton of steel 15 - 20 kg is on direct landfilling of dangerous waste. [1] The basic component of the charge payable for risk waste storage has reached to 1700 CZK kg/t, the risk fee is nowadays 4500 CZK kg/t. [2] Regarding the proposal of the Ministry in 2014 the fee is supposed to raise. The waste management in metallurgical companies presents significant cost [3] therefore it is necessary to find possibilities for metallurgical waste exploitation in the production and define attitudes for optimization of the whole production cycle. The aim of the paper is study of fine-grained waste recycling possibilities and identification of its effects on production parameters of blast furnace aggregate with economical interpretation. A wide range of industrial waste such as blast furnace slag and steel furnace slag is used in the construction industry. [4] The usage of some metallurgical waste with high content Fe is limited by its fine, powder granulation. For technological reasons, feedstock for blast furnace aggregates mustn't be in fine powdered state. Fine grained materials are compacted by several technologies such as sintering, pelletizing and briquetting. [5] Briquetting is used in many industrial fields such as chemical, pharmaceutical industry. Very often it is used for compacting of biomass and coal. In Japan was developed a process of bio-briquetting of coal reducing emission SO_2 in habited areas. [6, 7] For metallurgical industry thanks to insufficient production capacity, briquetting means just an alternative for fine grained materials compacting in limited scale. It is used for briquetting of fine grained metallurgical waste with high Fe content. It presents an ecological technological for these materials preparation for their recycling in shaft aggregates such as blast furnaces. During briquetting at high temperature and pressure there are not emitted emissions like at sintering of these materials in sinter plants. Possibilities of briquetted metallurgical waste recycling are verified in many metallurgical companies. There has been known Austrian technology of steel dust briquetting since 1989 [8] Voest Alpine Industrieanlagenbau developed a methodology for briquetting of scale in mixture with fine grained hematite and binder on base of calcium hydrate or molasses. [9] In ironworks of Neue Max Hütte are successfully recycled waste compacted to briquettes Mölle. The briquettes are made with usage of special binder called ceramic gluten. These briquettes are suitable for recycling in electric furnace, inductive furnace and also blast furnace. [10]

2. MATERIAL AND EXPERIMENTAL METHOD

There were tested reducibility properties of fine-grained metallurgical waste compacted into cylindrical briquettes (**Figure 1**). It was made from mixture of metal waste such as steel dust and sludge. **Figure 2** and **Figure 3** present its heterogeneous microstructure. In **Table 1** is analysis of the sample.

Figure 1 Tested briquettes

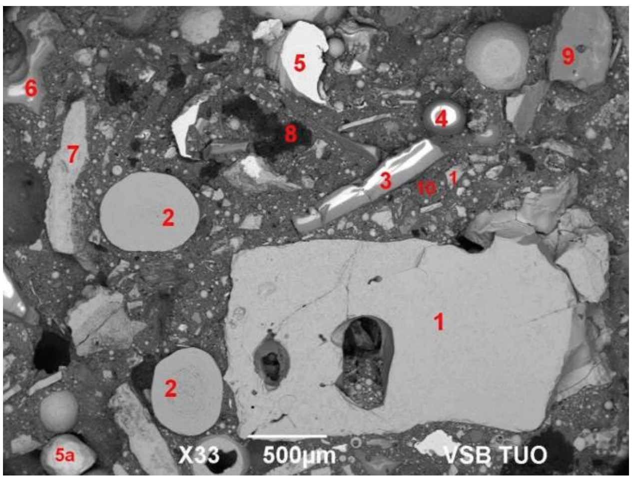

Figure 2 Microstructure analysis of tested briquette

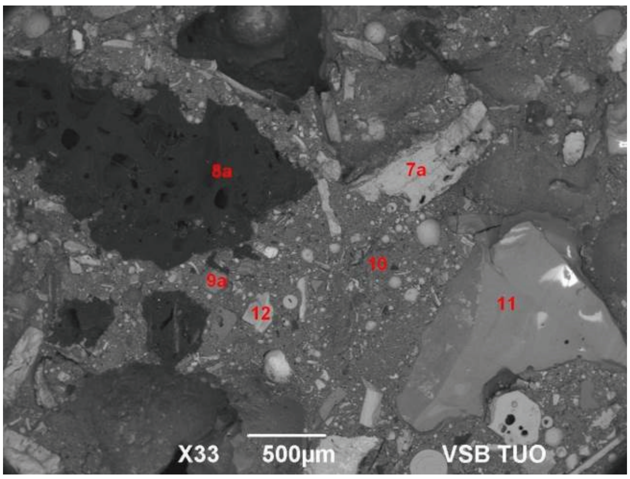

Figure 3 Mictrostructure analysis of tested briquette

Test of briquette reducibility dR/dt [%/min] was conducted according to ISO 4695: 2007. The sample was oven-dried to constant mass at 105 °C $\pm$ 5 °C and before preparation of the test portions it was cooled to room temperature. The test portion of 500 g was isothermally reduced at 950 °C in a fixed bed of reduction tube (**Figure 4**) with a removable perforated plate inside ensuring uniform gas flow using reducing gas consisting 40.0 % of CO and 60.0 % of N_2.

Table 1 EDX analysis of tested briquette

Point	C	O	F	Na	Mg	Al	Si	P	S	K	Ca	Ti	Cr	Mn	Fe
1		31.4												0.83	67.78
2		37.2				0.48									62.28
3		46.5	8.37	4.4	1.2	6.91	16.3				14.8	0.11		1.39	
4		74.4		2	4.08	5.42	9.51				3.13				1.45
5							1.06						1.09	0.87	96.97
6		70.4			4.73	1.48	12.2	0.5			7.62			1.04	2.02
7		30.5				0.28								1.03	68.16
8	90.6	7.7				0.34	0.13		0.41		0.4				0.46
9		48.3			5.92	1.42	14.6	0.71			17.9	0.18		6.23	4.72
10	21.3	47.1		0.82	0.39	1.42	3.84		0.55	0.73	18.7				5.17
11		51.2	28.3	9.83	0.99	2.82	6.41				0.51				
12		33.2					2.68				0.33			0.78	62.99

Figure 4 Reduction tube for sample testing

The portion was weighed at specified time intervals until its degree of reduction reaches 65 %. The degree of reduction Rt, relative to the iron (III) state after t [min] is calculated, as follows (1). [11] The content of metal iron in the sample was not included into calculations because it does not take part in the reduction process and does not affect the oxygen loss in the sample during reduction. The reduction degree Rt was calculated from evaluation of mass loss in the time of reduction during reduction gas activity. The initiation of reduction process was presented by zero mass loss. The mass loss during sample heating was not for calculation Rt considered. Its calculation is summarized in **Table 2**.

$$R_t = \left(\frac{0.111w_1}{0.430w_2} + \frac{m_1 - m_t}{m_0 \cdot 0.430w_2} \cdot 100\right) \cdot 100 \qquad (1)$$

where: m_0 is the mass of the test portion [g]
m_1 is the mass of the test portion immediately before starting the reduction [g]
m_t is the mass of the test portion after reduction time t [g]
w_1 is the iron (II) oxide content [%]
w_2 is the total iron content [%]

The reducibility index (dR/dt), expressed as the rate of reduction at the atomic ration of O/Fe of 0.9 [%/min] is calculated from equation (2) and presented in **Table 2**.

$$\frac{dR}{dt}\left(\frac{O}{Fe}=0.9\right)=\frac{33.6}{t_{60}-t_{30}} \quad (2)$$

where: t_{30} is the time to attain a degree of reduction of 30% [min]
t_{60} is the time to attain a degree of reduction of 60 % [min]

3. RESULTS AND DISCUSSION

The reducibility index dR/dt of tested briquettes was higher than typical sinter of Czech metallurgical plants. The acquired data were used by mathematical model to simulate reduction process of tested briquette.

Table 2 Calculated reduction degree and reducibility index of tested material

time [min]	testing measurement		verification measurement	
	mass loss [g]	reduction degree [%]	mass loss [g]	reduction degree [%]
0	0	9.7	0.0	9.4
10	5.7	19.8	5.4	19.5
20	10.5	32.5	10.2	32
30	16	46	15.7	45.3
40	19.5	57	19.3	57.1
50	22	62	22.2	62
60	23	64	23.0	64.6
70	24	65	24.4	65.3
dR/dt	1.2		1.14	

The reduction process in the briquettes started with reduction of hematite and carried on with reduction of magnetite to FeO and partially Fe. The reduction process of iron oxides was described by kinetic constants calculated by mathematical model summed up in **Table 3**. The reduction from hematite to magnetite as $k_1 = 0.00289$, reduction from magnetite to FeO as $k_2 = 0.0005$ and from FeO to Fe as $k_3 = 0.000012$. The kinetic constants are determined by concentration of oxygen in material. K_3 is the most important constants determining the rate of direct reduction which increases metallurgical coke consumption. In the case of reduction briquette is the constant lower and shows slow reduction of FeO to Fe. While the oxygen is reduced in the feedstock, the oxygenation of blast furnace gas increases. The **Figure 5** graphically presents the reduction process. There is depicted mass loss (presenting oxygen reduction in feedstock) in time of the test.

On the base of calculation, the model graphically interprets the course of reduction process in 3D diagram presenting direct reduction degree (rd) depended on gas consumption (U) and time of blast furnace feedstock in the zone of non-direct reduction (CS). The point of intersection of rd and U parameters areas defines the necessary time for feedstock in the zone of non-direct direction. The diagram is possible used as a tool for the optimizing of production process as same as in by other models [12].

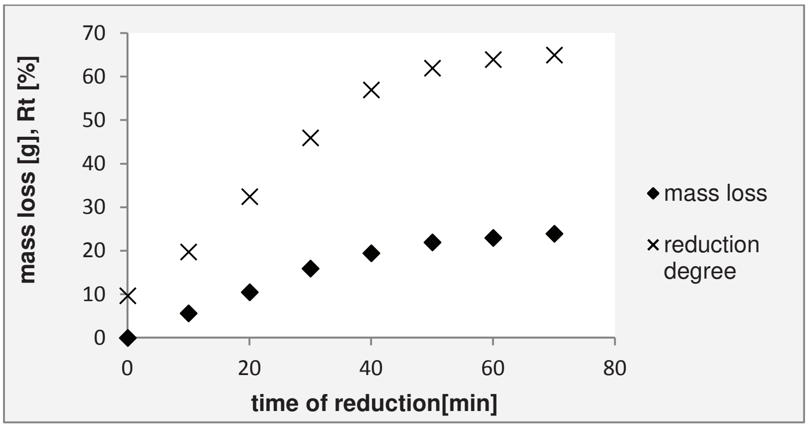

Figure 5 Process of reduction of average sample

The model also determined approximation equation (3) for calculation of parameter ω. This parameter originated from Rist's diagram describes disposition for approximation to point W defining a thermodynamical limit of the process.

$$\omega = a_0 + a_1 CS + a_2 CS^2 \tag{3}$$

where: a_0. a_1, a_2 variables calculated by the model

CS time of feedstock in the zone of non-direct reduction

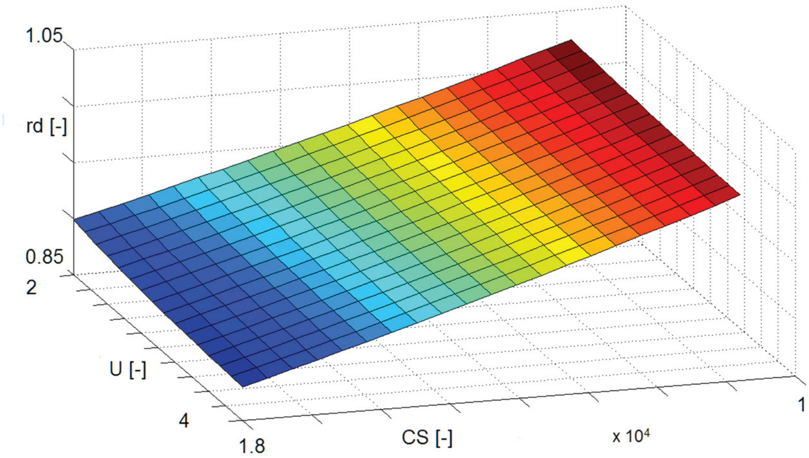

Figure 6 Area for optimizing of some process parameters

The lower parameter ω, the better reducibility is supposed. The model calculated variables a_0. a_1, a_2 using input data of reducibility tests. It is possible to evaluate it for various parameter CS and compare ω calculated from ISO 4695 with parameter ω calculated from operative system of blast furnace in industrial operation and refers to possible coke reserve [13]. The parameter ω for various time of feedstock in zone of non-direct reduction is presented in **Table 3**.

Table 3 Outputs of mathematical model calculation

Kinetic constants $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe_{1.5}$			**ω calculated from ISO 4695**		
k_1	k_2	k_3	ω_{3h}	$\omega_{3.5h}$	ω_{4h}
0.00289	0.0005	0.00012	0.9727	1.1616	1.4865856

4. CONCLUSION

Reducibility is one of the basic quality properties of blast feedstock material. It is a possible tool for optimizing of ironmaking process. Reducibility of briquette studied in the paper reaches a good value 1.17 meaning its very well suitability for recycling in blast furnaces. The model calculated possible effects of its recycling on operation parameters. Its processing contributes to saving costs for waste management and blast furnace operation. There were calculated a possible coke reserve presented in Rist's diagram as parameter ω. Three hours' stay of the feedstock in the zone of non-direct reduction results in the most convenient operation with ω = 0.9727.

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