PHYSICOCHEMICAL PARAMETERS OF CARBON REDUCERS FOR THE FERROSILICON SMELTING PROCESS.

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Abstract

The most important physicochemical parameters of several selected carbons from Polish coal beds in the context of using them as a material in ferrosilicon smelting process were analysed in this paper. Among coals presented in the paper, coal from Wujek Coal Mine has been used as a main reducer in the Polish ferroalloy industry until recently, but its resources have run out. Currently, coals from Staszic Coal Mine and Wieczorek Coal Mine are used as the main reducers for ferrosilicon smelting process. Coals from Bogdanka, Piast and Ziemowit Coal Mines are indicated to be potential substitutes of reducers for the ferrosilicon smelting process. Basic parameters of carbon, obtained using technical and elementary analysis, the chemical composition of ash as well as results of research on vitrinite reflectance and reactivity towards *SiO* and CO_2, have been compared in this paper.

Keywords: Reducer, ferrosilicon, coal, physicochemical parameters

1. INTRODUCTION

Appropriate quality of reducers is necessary in order to gain an alloy which fulfils specific qualitative requirements. Appropriate quality also influences the effectiveness of the electro thermal ferrosilicon smelting process which takes place in submerged arc furnaces [1-5]. Due to the exhaustion of coal resources from Wujek Coal Mine, the main supplier of this material for ferroalloy industry in Poland until recently, new resources are being searched for. In spite of large coal beds in Poland it is not easy to find new sources of this material [6, 7]. The carbon reducer for the ferrosilicon process should be characterised by appropriate granulometric composition, chemical composition and, in particular, low content of ash and undesirable pollutants such as *Al*, *Ti*, *P*, *S*. Reactivity towards *SiO* as well as invariability of parameters in time are also of great significance. Carbon reducers in the electro-thermal silica's reduction by coal process, have two main functions: they are a source of carbon C_{fix},, which is essential for silica's reduction and also act as a *SiO(g)* gaseous filter, which is one of the intermediate products in the reduction process and condenses in the upper zones of the resistance-arc furnace, as a result of reaction with coal [1 - 4]:

$$SiO(g) + 2C = SiC + CO(g) \qquad (1)$$

Reactivity of carbon reducers plays a significant role in the *SiO(g)* condensing process and influences the yield of the main element *Si* in the process of electro-thermal silica's reduction. Fundamental analysis describing the quality of carbon is technical analysis [7], which defines weight % in operating state: moisture content (W_t^r), ash content (A^r), and volatiles content (V^r). Carbon content C_{fix} in the reducer has essential meaning and is described on the basis of technical analysis in the following way:

$$C_{fix} = 100 - W_t^r - A^r - V^r \qquad (2)$$

2. REACTIVITY OF CARBON REDUCERS

Research on coal reactivity towards SiO are conducted under laboratory conditions using the SINTEF method [4], where equilibrium gas (13.5 % SiO, 4.5 % CO, Ar- rest) is generated isothermally at T = 1650 °C. Gas then reacts in the reaction chamber, passing through the tested reducer`s layer. The total volume of this oxide resulting from the reaction’s stoichiometry (1), recorded at a time when the decreasing share of CO in the gas leaving the condensing chamber is in the range of 10 - 18 % vol., is being used as a measure of the reactivity of the reducer towards SiO. Due to high temperature, studying reactivity using the SINTEF method is complex and costly. Therefore tests on the reactivity towards oxidizing gases (O_2, CO_2, H_2O) performed at a lower temperature of 800 - 900 °C, which to some extent coincide with the results of reactivity towards SiO tests [3, 4, 8, 9], are worth mentioning. Unlike the SINTEF method, the most commonly used reactivity measure is [6, 8, 9]:

- Value of reaction rate constant with oxidizing gas in the temperature range of 800 - 1000 °C,
- Time $\tau_{0,5}$ after which 50 % carbonate will gasify (coal after degassing of volatiles),
- Determination of the reactivity by comparing the course of the dependence curve of the degree of conversion on time.

It has been established [3, 4] that great reactivity towards SiO as well as towards gases (O_2, CO_2, H_2O) characterizes sorts of coal with high content of volatiles V^{daf} . This is due to the kinetic conditions of the reaction in solid-gas system. The high content of volatiles, which releases at elevated temperatures, affects the porosity of the coal and increases the surface of the reaction. This also applies to hygroscopic moisture. Unlike oxidizing gases, the conditions for gas transport of SiO oxide to the reaction zone are important only at the initial stage of the process. As the reaction progresses, the pores are sealed with SiC carbide, whereas in reactions with oxidizing gases they enlarge. However, in the initial stage of the reaction, the porosity of the carbon reducers has a decisive influence on the reactivity towards SiO and also on the reactivity towards the oxidizing gases. Reducers with highly developed surface, which are hardly graphitized have great ability of reaction.

The highest reactivity towards SiO is achieved by the reducers with highest content of volatile components such as lignite ($V^{daf} \approx 54$ %), and wood chips ($V^{daf} \approx 77 \div 80$ %). Wood chips are used by almost all ferrosilicon manufacturers [1, 2], although they only bring a small amount of carbon as a reducer in the silica reduction process. The addition of wood chips facilitates the discharge of gases from the reaction zones and reduces the formation of exhaust. Porosity of the charge in the entire volume of the furnace, even and slow gas flow across the whole surface of the furnace create better conditions for the condensation of the gaseous SiO oxide as an effect of reaction (1). Moreover, the addition of wood chips increases the electrical resistance of the furnace charge, and also has a positive impact on the temperature conditions of the process.

The experiments carried out by Raames and Gray [4] indicate that also the reflectivity index R_0, which is the basis for industrial and commercial classification of coals, may be useful in evaluating the reactivity of bituminous coal towards SiO [4, 7]. Index R_0 is, shown in percentage, ratio of intensity of light of a specified wavelength reflected from the polished surface of the section to the intensity of light falling perpendicularly on this surface. Results of laboratory research [4] show that coals with lower refractive index exhibit higher reactivity towards SiO. These are coals with lower carbonization and higher content of volatiles. Alike reactivity, the granulometric composition of carbon reducers has also a significant impact on the kinetics of chemical reactions in the solid-gas system. In the Polish ferroalloy industry, mainly pea coal (Gk) with a grain size of 8 - 31.5 mm is used as a reducer. It is required that the number of subgrain does not exceed 10 % and the number of supergrain (max. 35 mm) is less than 5 %. Subgrain (<5 mm) hinders the flow of gases from the reaction zones, and is the reason of strong gas emissions from the ferrosilicon furnace.

This has a negative effect on the *SiO* condensation process, and the raw material loss associated with blasting and entrainment by the furnace exhaust gases. Also supergrain has very disadvantageous influence on the technological process. This is due to the lower electrical resistance of the charge. This results in a shallower placement of the electrodes in the charge, and adversely affects the distribution of heat generated by the electricity flow in the furnace's working area. Some mines offer coal assortment with granulation of 6 - 25 mm (GkI - "Eco pea"), and granulation of 5 - 15 mm can be obtained by special order. A smaller particle size reducer affects positively the technological process. The problem is a small supply of coal with restricted granulometric composition, so these granulations have not been used as a raw material for the ferrosilicon smelting process in Poland until now. Simultaneous fulfillment of all quality requirements for the reducers for the ferrosilicon smelting process by one bituminous coal is difficult to achieve. Therefore, in industrial practice, a mixture of two carbon reducers of varying properties is most commonly used in the charge stage. This concerns the content of carbon C_{fix} and the reactivity towards *SiO* [2]. When choosing bituminous coal, the highest attention is paid to its basic technical parameters, in particular: content of ash A^r and its chemical composition. Until recently, the primary reducer was coal from the KWK "Wujek" mine, which had a low ash content ($A^r < 5$ %) and a high carbon content C_{fix} = 60 ÷ 62 %. In recent years, attention has been paid to the reactivity of reducers. For this reason, a mixture of two coals of varying characteristics is currently used the most often. Approximately 70 % of the carbon weight required for the silica reduction process is introduced in the form of highly carbonized coal (C_{fix} > 60 % weigh), with low ash content ($A^r < 5$ %). The remaining carbon weight required for the silica reduction process is provided in the form of high-reactivity coal ($V^{daf} \approx 38\%$, C_{fix} = 52 - 53 %).

3. SMELTIG BITUMINOUS COAL FOR THE FERROSILICON PROCESS

Despite the large beds of bituminous coal in Poland, it is not easy to find a carbon reducer that meets the requirements of electrothermal ferrosilicon smelting process. Apart from the chemical composition, local suppliers encounter difficulties to meet granulometric requirements and to ensure a stable supply of raw materials, taking quality and quantity requirements into consideration [10-13]. In the Polish ferroalloy industry pea coal with a grain size of 8 - 31.5 mm is the most widely used as a reducer. **Tables 1 and 2** show the basic properties of bituminous coals, that are currently available in the form of pea (Gk 8 - 31.5 mm, Gkl 6 - 25 mm).

The data shown in the **Tables 1, 2** contain coals, that are currently used as raw material in the ferrosilicon smelting process ("Staszic", "Wieczorek", "Chwalowice") and coal used in the past ("Wujek"). In addition, **Tables 1** and **2** indicate carbon parameters that have not previously been applied as reducers for ferrosilicon melting process ("Bogdanka", "Ziemowit") or have been used only to a limited extent ("Piast"). Data from **Tables 1, 2** show that the major cause of disqualification of these carbons as a raw material for the ferrosilicon smelting process is the increased content of harmful dopants (Al_2O_3, TiO_2, *S*).

The coals presented in **Tables 1, 2** are ranged according to the increasing reactivity towards *SiO*, basing on the results of laboratory tests [3, 4, 6, 8, 9]. It has been considered that the reactivity of the reducer is the higher, the greater the content of volatiles and also the reflexivity, while the content of C_{fix} decreases. The arrangement prepared according to this principle, is presented graphically in **Figure1**.

Currently, the basic mass of carbon in the bearing charge for ferrosilicon smelting process (~ 65 % weigh) is supplied by "Wieczorek" or "Staszic" coal which are substitutes of the relatively recently used (until 2015) "Wujek" coal. The remaining C_{fix} mass required in the electro-thermal silica reduction process is supplied in the form of "Chwalowice" pea coal, characterized by increased reactivity, and wood chips. The typical composition of the bearing charge for the FeSi75 ferrosilicon smelter is as follows: kg: quartzite 500, carbon ("Wieczorek") - 200 ÷ 220, coal ("Chwalowice") - 100, wood chips - 120, mill scale - 74. For such proportions of coals in the mixture of carbon reducers, the lower C_{fix} content in "Chwalowice" coal does not effect in increase of carbon consumption in the process of ferrosilicon smelting. Higher reactivity of "Chwalowice" coal has a positive impact on the effectivity of technological process, especially on the process of condensation of *SiO* oxide, and improvement of Si yield.

Data presented in **Figures 1 and 2** indicates that the carbon-reducing system current in the Polish industry is optimal. The dependency shown in **Figure 1** shows that the reactivity of coal from Bogdanka, Piast and Ziemowit mines is higher than "Chwalowice" coal. These coals may to a limited extent be substitutes for "Chwalowice" coal. To reduce the amount of harmful pollutants (Al_2O_3, TiO_2, *S*) entering the process, the fraction of this should not exceed 25% in the process of the silica reduction.

Table 1 Comparison of the basic properties of several selected coals

Parameter			Mine						
Name	Symbol	Unit	Wujek [12]	Wieczorek [13]	Staszic [2]	Chwalowice [3]	Bogdanka [6]	Piast [6]	Ziemowit [6]
Humidity	W_t^r	% wt.	3.92	7.50	4.50	7.09	7.80	10.30	11.40
Ash	A^r	% wt.	3.36	2.73	3.89	5.94	5.30	5.60	7.00
Volatiles	V^r	% wt.	30.78	30.00	30.65	33.48	33.44	33.55	32.64
Volatiles	V^{daf}	% wt.	33.20	33.42	33.46	38.49	38.48	39.89	40.00
Fixed carbon	C_{fix}	% wt.	61.94	59.77	60.96	53.49	53.46	50.55	48.96
Coal	C^a	% wt.	79.03	78.13	78.33	78.90	75.1	73.10	68.60
Hydrogen	H^a	% wt.	4.07	4.36	4.45	-	4.79	4.67	4.30
Oxygen	O^a	% wt.	9.90	10.40	8.75	-	7.24	11.38	11.51
Nitrogen	N^a	% wt.	1.18	1.21	1.14	-	1.44	1.12	1.05
Sulphur	S_t^r	% wt.	0.47	0.40	0.42	0.64	1.10	0.81	0.88
Heating val.	Q_i^r	MJ/kg	30.959	29.434	30.062	27.790	28.208	26.436	25.167
Reflexivity	R_0	%	0.83	0.74	0.72	0.66	0.65	0.61	0.52

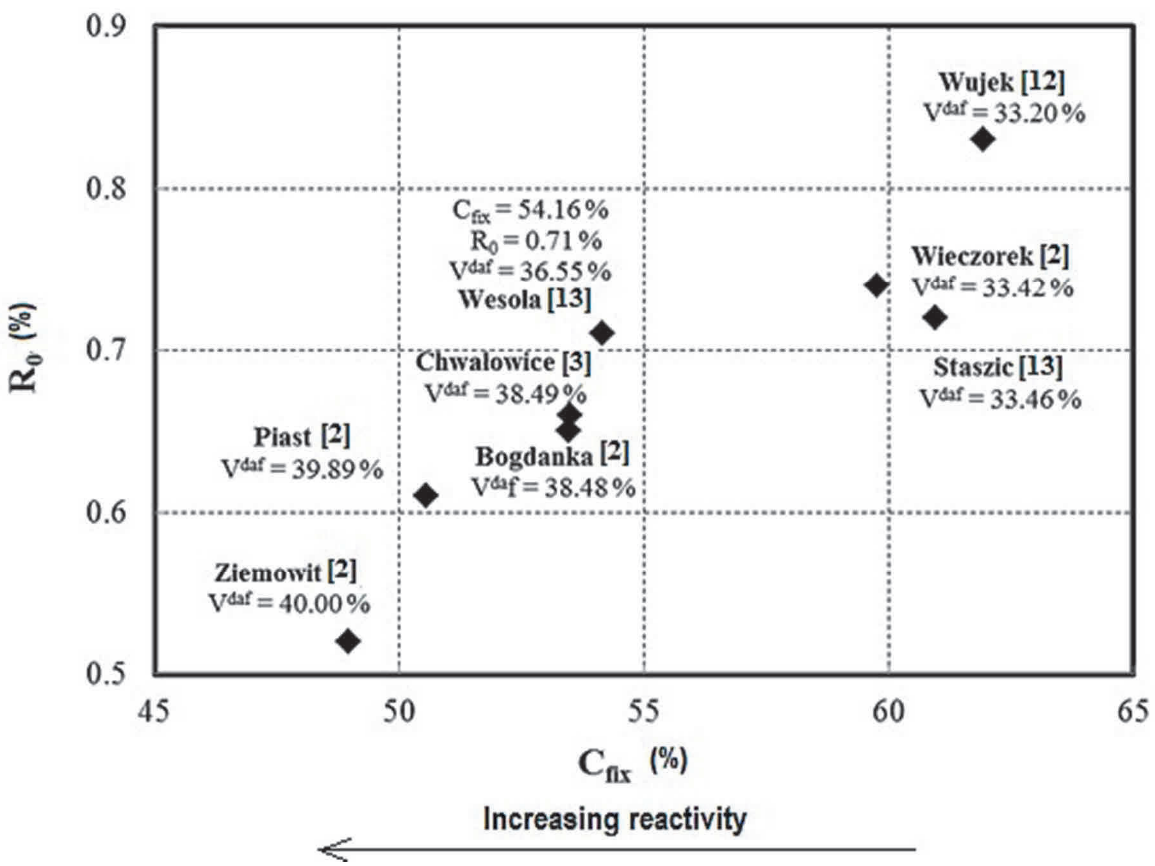

Figure 1 The dependence of reflectivity as a function of C_{fix} in hard coal

Table 2 Ash chemical composition of the selected coals

Chemical composition		Mine						
Symbol	**Unit**	**Wujek [13]**	**Wieczorek [13]**	**Staszic [2]**	**Chwalowice [3]**	**Bogdanka [2]**	**Piast [2]**	**Ziemowit [2]**
SiO2	% wt.	34.59	15.46	23.07	26.70	49.58	33.46	37.87
Al2O3	% wt.	24.37	11.95	18.07	18.60	37.48	23.02	27.56
Fe2O3	% wt.	15.24	17.09	13.11	16.40	4.69	10.07	8.25
CaO	% wt.	7.12	17.25	15.56	8.83	1.27	9.07	7.07
MgO	% wt.	4.77	9.55	8.97	4.25	0.39	3.87	3.56
Na2O	% wt.	1.97	2.93	2.39	1.95	0.64	5.62	5.88
K2O	% wt.	1.41	0.77	1.00	1.45	1.63	2.25	0.81
SO3	% wt.	7.22	22.84	14.59	-	0.45	10.19	6.38
TiO2	% wt.	1.26	0.42	0.67	0.80	1.32	1.25	1.41
P2O5	% wt.	0.75	0.48	1.06	1.10	1.50	0.65	0.17
BaO	% wt.	0.38	0.31	0.37	-	-	-	-
Mn3O4	% wt.	-	0.20	0.18	-	0.01	0.38	0.26
SrO	% wt.	0.24	0.19	0.24	-	0.18	0.10	0.06
ZnO	% wt.	0.14	0.23	0.23	-	-	-	-

4. GRANULOMETRIC COMPOSITION

As already mentioned, the granulometric composition and reaction surface have a significant impact on the kinetics of chemical reactions in the solid-gas system. The surface of the reaction increases as the granulation of the reactants decreases. The reduction effect of the reducer's granulation is similar to the use of a reducer with higher reactivity. Apart from that, the granulometric composition of the carbon reducers affects the electrical characteristics of the charge. The resistivity of the bulk carbon reducers is a resultant of two magnitudes: the actual resistivity of the carbon reducer (ρ_s) and the contact resistance between its grains [10]. With the increase in the diameter of the pieces and pressure the contact surface also increases. As a result, the contact resistance between the pieces decreases and therefore the resistivity of the layer in the bulk state decreases. Using the layer model as a system of parallel chains formed from contiguous pieces and partially adhering one to another, the publication [10] presents an empirical relationship to the resistivity of carbon reducers layer in the dry state in dependence with the diameter of the pieces d

$$\frac{\rho'_s}{\rho_s} = M + \left(X + \frac{d}{Y + Z \cdot d^2}\right) \cdot \frac{1}{\sqrt{P}} \tag{3}$$

where: d - diameter of pieces, m; ρ_s - the actual resistivity of the reducer, mΩm; ρ'_s - resistivity of the reducer layer in the bulk state, mΩm; P - external pressure operating on the surface of the layer, kPa, M, X, Y, Z - empirical constants. For pea coke the dependence (3) is presented graphically in **Figure 2**. With less granulation, the electrical conductivity of the charge decreases. This results in deeper electrode placement, and improves the thermal and temperature conditions of the process. The dependence (3) indicates that the charge resistance depends not only on the granulometric composition of the reducers, but also mainly on the depth of the bed (P pressure). The heights of the bed and the greater pressure on the lower layers have a significant effect on the lower resistivity of the charge. So far in the Polish ferroalloy industry, mainly pea coal (Gk) with granulation of 8 - 31.5 mm is used. Few attempts to use reducers with lower granulation of 6 - 25 mm (GkI - "ECO Peas") have not brought expected effects. The reason for the failures was the too short duration of the trials conducted in industrial conditions. In addition to the GkI granulation, some manufacturers may provide coal granulation of 5 - 15 mm by special order. However, these are insufficient quantities to make reducers with such granulation possible to be used on a wider scale in the ferroalloy industry. This applies in particular to pea coal of GkI granulation ("Eco peas"), which is consumed in increasing quantities by individual recipients for heating purposes. This requires investments and organizational changes in the Polish coal industry so that high quality and quantity requirements can be met for coals with granulation of 6 - 25 mm, and 5 - 15 mm for the ferroalloy industry in Poland.

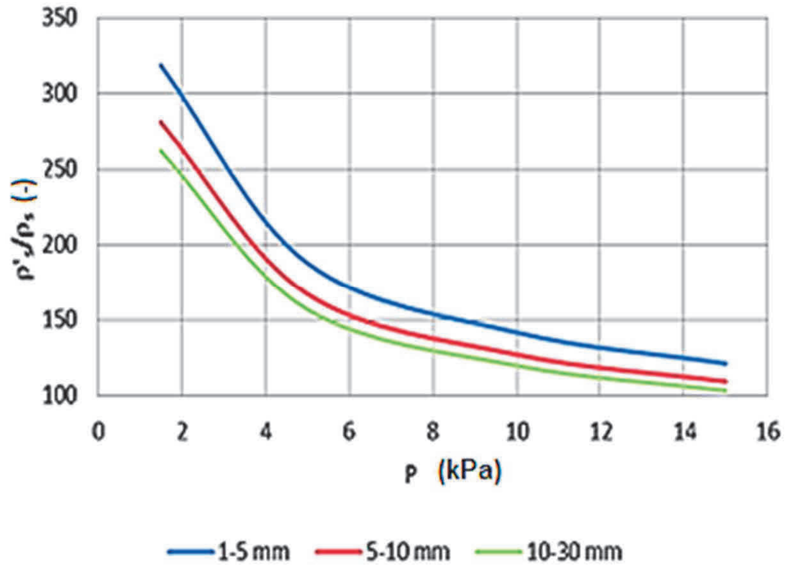

Figure 2 Impact of pressure on the resistivity of the coke layer for three different grain fractions, calculated on the basis of dependence (3), M = 33 ± 8, X = 530 ± 130, $Y \cdot 10^7$ = 1 ± 0.3, Z = 1.2 ± 0.4 [10]

5. SUMMARY

The depletion of coal beds used until recently as a primary reducer in the Polish ferroalloy industry has resulted in urgent need to find new sources of this raw material. The quality of carbon reducers has a significant influence on the efficiency of the electrothermal reduction of silica in resistive-arc furnaces and the content of impurities (Al, Ti) in the produced alloy. The choice of bituminous coals for the reducer for the ferrosilicon smelting process must be preceded by multiple studies of its properties. Apart from traditional technical analysis and studies on the chemical composition of ash, the reactivity towards SiO is of significant relevance. SINTEF reactivity tests are cumbersome and require sophisticated equipment. Given the kinetic conditions of the chemical reactions in the solid-gas system, the SiO reactivity tests to some extent coincide with the results of the reactivity tests towards oxidizing gases (CO_2, H_2O). These tests compared to the SINTEF method are simpler and conducted at lower temperatures. Also, the relationships between the carbon reactivity, the content of V^{daf} volatiles and the reflectance R_0 (**Figure 1**), are applicative. Considering the needs of the ferroalloy industry, it is advisable to expand the infrastructure in the Polish coal industry in order to meet the demand for pea coal. Aside from the granulation of 8 - 30.5 mm, usage of fine-grained pea coal fractures with granulation of 6 - 25 mm and 5 - 15 mm is recommended.

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