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Experimental research on quality features of metallurgical coke

V Andrei[1] and N Constantin[1]

[1] University Politehnica of Bucharest, Materials Science and Engineering Faculty, 313 Splaiul Independentei, 060042 Bucharest, Romania

E-mail: victorandrei11@yahoo.com

Abstract. From all the solid fuels, the metallurgical coke is the most used in obtaining iron in the blast furnace. Together with the iron ore, manganese ore and fluxes, it constitutes the basis of raw materials and materials for elaborating pig iron. This paper presents the results of laboratory investigations by the authors to determine the most important quality characteristics of some types of coke used in the blast furnace charge.

1. Introduction

The metallurgical coke is a fuel obtained in the pyrogenic process (heating in the absence of air) at temperatures of 1000°-1100°C of agglutinated coal which are oily coals with 16-30% volatile (lately it's been used gas coals). At 950°C the volatiles are removed and dry residue is the only thing that remains (raw coke), in which is enclosed also the coal ashes. Out of 1 ton of coal, 0.6-0.8 tons of coke is obtained.

Metallurgical coke ensures the following functions in the blast furnace:

Fuel: its combustion has to provide the necessary heat for the processes in the blast furnace (ore reduction, carbonates decomposition, sulfides, water, forming of iron and slag, covering the heat losses etc.);

Reducing agent: takes part directly, through its Carbon content, but also indirectly through CO obtained from burned C in coke in the tuyeres, in reducing Fe, Mn, Si, P oxides in the ore;

Carburizing agent: in the crucible, gives away the C to the bain that is necessary to complete the irons composition (the carburizing of Fe begins in the tank at small temperatures of 1000°C to 1%C and continues at temperatures higher than 1100°C followed by the irons melting due to decreasing of t_{mel});

Refining agent: ensures the loads permeability with gas passing through (it occupies over 50% of the furnaces volume);

Sustaining the material column in the furnace, being the only one in a solid state near the tuyeres (coke does not melt, it burns and gasifies).

2. Coke properties

The most important properties of coke are porosity, electrical conductivity, grain size, mechanical resistance and reactivity.

Porosity is an important characteristic to determine the size of the active surfaces of coke, therefore the reaction power. It has values of 45-55% (total surface of 1 kg of coke = 40 m^2).

The apparent porosity (sum of open pores) is determined by introducing coke in water and vacuum degassing at a certain pressure.

The real porosity (sum of all pores) expresses the volume of goals in the coke piece and it is established using the formula:

$$P = \left(1 - \frac{\text{apparent specific weight}}{\text{real specific weight}}\right) \times 100, \% \qquad (1)$$

Electrical conductivity, this value indicates if the coking process went as it was supposed to (a good coking leads to values up to 30-40 times higher of the electrical resistance). This property is considered especially in electrical furnaces.

Grain size determines the permeability of materials column in the blast furnace and the gas flow through the load, the coke occupies 50-55% of the furnace volume [1]. Optimal grain size is controversial, medium size recommended is 45-60 mm (3 times larger than the medium size of the ores). The following indices have been established:

D_{50} – Medium dimension (dimension of grading screen meshes at 50% pass and 50% denial);

D_{75}, D_{25} – Quarters dimension (75% pass and 25% denial);

$\frac{D75}{D25}$ – Homogeneity indices;

$K = \frac{(40-80)mm}{(+80\ mm)+(25-40mm)}$, Uniformity coefficient. (2)

Nowadays, in most enterprises, before loading in the furnace the coke is passed through a grading screen in order to separate the small pieces. In furnaces up to 1000 m^3Vu the grading screen has holes of 25 mm wide and in larger furnaces of 30-40 mm wide.

In general, the maximum dimension of the pieces of coke is not limited [1].

Basically, in furnaces that operate with well classed ore, the coke must have a dimension between 25-74 mm. In the case of ore insufficiently classed, especially if it contains pieces under 8-10 mm and pieces over 60-70 mm, the dimension of coke must be larger than 40-120 mm.

The operating results of the furnaces which work with classed ore loading and which shred the coke grain size over 60-70 mm simultaneously with the removal of small pieces (below 25-30 mm) have proven some advantages.

The coke that is under moderate mechanical stress followed by classing, improves its mechanical resistance, as well as its homogeneity, but the medium dimension becomes smaller.

Standardized method for determining the granulometric composition consists in passing a determined quantity of coke through a grading screen, each time weighting the remaining material on the screens, as well as passing through the last screen.

The results are expressed in mass percentage, in rest on the grading screen, as well as the passing through the last screen. The weight of the sample, depending on the cokes size, the correlation between them is shown in Table 1.

Table 1. The correlation between the weight of the sample and the cokes size:

	Coke with a large grain					Small coke	
Max dimension of coke pieces, (mm)	≥80	63	40	20	10	5-10	5
Min weight of the sample, (kg)	100	80	30	10	5	1.5	0.5

Mechanical resistance is the main characteristic on which the coke behaviour depend the most in the blast furnace where it undertakes falls and friction. These falls and frictions could lead to the shredding of the pieces, also leading to a worsening flow of gas through the load.

Coke shredding in the furnace leads to the worsening of the gas flow through the load and to accumulation of chopped coke, producing in some areas problems at the loads descent, tuyeres burning, increased specific coke consumption.

The cokes resistance represents the sum of the resistance at compression, shearing, friction, pressing, dynamic shock and it is determined using samples in which the coke is the subject of hitting and friction efforts through rolling in a tambour. The resistance is determined at the carbonization plant, as well as at the furnace (the resistance indices is greater, the coke being stabilized during transport and depositing). The resistance, in Micum drum, is an international standardized method, being the most used one, indices obtained in the test are:

M_{40}= mechanical resistance

M_{10} = abrasion

For a high quality coke these indices must have values between M_{40}= 80 ÷ 85% and M_{10} = 5 ÷ 7%.

In the recent years it has been used also a method of establishing the cokes mechanical resistance with chemical attack and heating. This way, the CSR (Coke Strength after Reaction) index is being determined. The CSR represents the resistance of coke after the reaction with CO_2. A high quality metallurgical coke must have a CSR of 55-60%.

The reactivity of coke is the ability to react with oxidizing gases in the furnace conditions, being of utmost importance the reaction of the coke with oxygen or injected air, the reaction of coke with CO_2, the coke reaction with H_2O. Reactions of carbon coke, before reaching the tuyeres, and O_2, CO_2, H_2O occur in the oxidizing area of the crucible.

Determination of reactivity is carried out when a stream of CO_2 passes through a granular mass of coke of 10 to 25 mm, at a temperature of approx. 900°C. The reactivity is expressed by the amount of CO_2 that had passed into CO after the reaction with carbon coke. The variation of cokes reactivity influences, in restricted ranges, the size of the combustion area from the crucible.

The reactivity of coke expresses, through a conventional index its affinity for oxygen, carbon dioxide and water vapour reactions [2].

Measurements are conventional, the results depending on porosity, grain size, the gas flow rate, the determination temperature and type of coal from which the coke was made.

Depending on the oxidizing agent the cokes property to react with CO_2 is determined ($C + CO_2 <,> 2CO$) and rarely the cokes property to react with H_2O ($C + H_2O <,> CO + H_2$) or the cokes property to react with O_2 ($C + O_2 >,< CO_2$). Coke reactivity determines in a more important manner the coke consumption in the furnace.

From the reactivity point of view, the cokes are classified as follows:

Cokes slightly reactive (R = 100-200%);

Cokes medium reactive (R = 50-100%);

Cokes heavily reactive (R < 50%).

Furnaces in Romania are currently working with several types of coke, cokes from their own coke plants in the case of Arcelor Mittal Galati, which represents approx. 50%, the rest consisting of various cokes import (China, Japan, Poland, Czech Republic and Russia) [3].

In general, the compositions of the coke used (technical analysis) are known, and followed systematically. Similarly is done also with the cokes grain, determinations are performed less frequently and with an informational purpose.

Taking into account the lack of data on the characteristics of reactivity of coke used and the structural characteristics that together determine their behavior at high temperatures in the furnace, it will be researched in the lab “Iron Metallurgy" in University Politehnica of Bucharest (UPB) selected representative samples from the coke used frequently in Arcelor Mittal Galati furnaces, in order to reach conclusions about how they might influence the reduction processes.

The best known method for determining the reactivity is the Koppers method. The determinations are done with equipment made of quartz tube with a diameter of 20 mm, electric furnace whose temperature can be adjusted and kept constant, CO_2 cylinder, pressure reducer and needle valve for fine tuning of the gas flow, tight valves binding the quartz tube to the gas line and gas analyzer.

Through the quartz tube filled with 34 cm^3 coke, grain size 0.5 - 1 mm, is passed for 15 minutes a stream of CO_2, which is introduced into the furnace.

The tube is connected to the circuit through metal reinforcements to the gas agent network whose flow rate is maintained constant at 10.8 L / h for 60 minutes. After 10 minutes of placing the tube in the oven the first sample of resulting gas is collected from the reaction monitored and analysed with an Orsat apparatus. The operation is repeated 5 times under the same conditions, collecting and analyzing the resulting gas each time.

The reactivity calculus reaction is:

$$R = \frac{CO}{CO_2 + 1/2CO} \times 100, [\%] \quad (3)$$

The reactivity is defined through a coefficient of the reaction velocity between the CO_2 and coke:

$$K_m = \frac{V_0}{m} \times 2\ln\left(\frac{2\frac{C1}{C0}}{1+\frac{C1}{C0}} + \frac{1-\frac{C1}{C0}}{1+\frac{C1}{C0}}\right) \quad (4)$$

C_1 = CO_2 concentration in the reacting gas [%]
C_0 = CO_2 concentration in the initial gas (practically 100%)
Vo = CO flow (cm^3/s)
m = cokes mass [g]

A quality coke for the furnace must have a low reactivity (~50%). The reactivity of coke is influenced by the catalytic effect of ash contained therein.

The deficiency of this method is that the determination is made for the laboratory samples of crushed coke, with a 0.5 - 1 mm or 1 - 3 mm grain and the pieces are introduced into the furnace 40 - 60 mm.

Such differences in behavior arise due to the pores and specific surface pieces. Since coke reactivity is a feature of its surface, the reaction taking place between C and CO_2 on grain surface and in the open pores, it should be reported to the sample surface. In this case, results from laboratory to industrial conditions should be very close.

To overcome this obstacle, researchers from the University POLITEHNICA of Bucharest (UPB), in collaboration with the researchers at ICEM Bucharest have developed a method for determining the reactivity of coke “to pieces".

Measurements are carried out on pieces of coke size 25 - 30 mm, using the operating principle and of the Koppers plant.

The adaptation to the new conditions is achieved by using a reaction tube having a diameter of 40 mm and a flow rate of 67.5 L / h to ensure the same reaction velocity in the same contact time „gas - solid". In order to maintain the sample at the same temperature zone of the oven, we were working with 50 grams coke sample that is placed in a reaction tube corresponding to the height occupied by the 34 cm^3 Koppers sample.

Values of the determinations made using this method retains the same meaning for different coke samples with values obtained by conventional methods.

3. Experimental research for the determination of the cokes mechanical resistance

In the United Kingdom and the USA is used for resistance research a method that consists of performing 4 drops on an iron board from a height of 1.83 m of a coke sample weighting 23 kg in pieces larger than 51 mm. The resistance is expressed depending on the cokes granulation after shredding (% coke larger than 51 mm and % coke over 38 mm). In Western Europe, IRSID is used, in the USA and Japan the ASTM method. In Romania, Micum drum test is being used, more rarely Sundgreen drum test. In the laboratory, a smaller drum is used, Nedelmann drum [2].

Experiments are being conducted with coke samples used nowadays in the loading of blast furnaces in Romania. This paper will pursue in comparison the mechanical resistances of different types of coke, also the correlations between the cokes technical analysis especially the ash (A) content, the volatile (V) and the mechanical resistance.

Endpoints of the installations for determining the mechanical strength of coke and the conditions imposed on the samples to be tested are presented in Table 2.

Table 2. Features of laboratory drums used to determine the mechanical strength:

Drum	Diameter [mm]	Length [mm]	Coke grain [mm]	Revolutions [rev/min]	Sample weight [g]
Nedelmann	250	750	15-25	930/1	100
Sinuk	300	1000	40-50	40/50	1000
MICUM	500	2000	25-40	50/10	1000

3.1. Experimental laboratory installation

The experimental installation used is a Nedelmann drum, with a reel of 180 mm in diameter, 70 mm wide and 3 bits on the shaft. The reel is driven in rotation via a motor – reducer group. The shaft with bits has a rotating movement in reverse of that of the reel. The rotation speed is of 18 revolutions / minute. This is the same installation as used in determining the ore resistance.

3.2. Research methodology

The sample used for analysing with a weight of 100 g and the grain size of 10-25 mm is introduced in the reel which is rotated for 2 minutes (36 rotations). Next the coke is passed through 10 mm and 1 mm square screens, and then it is determined by weighting the denial at the screens of 10 mm and the passing at the screens of 1 mm.

For the experimental research, the coke sample is loaded in a drum with the inner diameter of 1000 mm and the length of 1000 mm with 4 angle sections (100×100×10), displayed at equal distances throughout the length of the drum. Using a fork with 50 mm distance between the horns is taken the pile of 160 kg (consisting of 24 incremental samples each of 7 kg), large grained coke, making up to 3 samples of 50 kg for two parallel determinations and a spare.

The sample is then loaded in the drum by hand. After loading, the drum is closed and rotated at 25 revolutions / minute for 4 minutes.

Following cokes mechanical screening, the round mesh screens 40, 20 and 10 mm, arranged in cascade. The coke is characterized in terms of quality indices M_{40} and M_{10}.

Index M_{40} is the expression as a percentage of the fraction greater than 40 mm that is left in the drum.

M_{10} index is the percentage fraction less than 10 mm from the test resulting.

Research has shown the importance that the heat resistance to characterize the quality of coke in the blast furnace operating conditions [3].

For this determination different methods were developed, based on:

-Heating the coke drum where the determination is to be made;

-Heating the coke in a nearby furnace and moving it to a testing drum.

The researchers of UPB, IMOMM Department, have developed an installation consisting of an electric furnace with a tight cylindrical muffle, of which the lower flap can be opened from distance, together with a laboratory MICUM drum with 500 mm diameter, 2000 mm length with 3 angles on each generator of 35×35×4 mm, rotating at 50 revolutions / min.

For setting a resistance value closer to normal to the industrial MICUM drum, experiments have indicated the best results at 500 rpm. [4]

The coke sample used in the experiment is obtained from crushing and screening through a 40 mm and a 25 mm round mesh of the sample of air-dried industrial coke. An amount of 1 kg of the industrial coke sample is introduced into the drum and is subject to 500 rotations, for determining the resistance to cold.

1 kg sample used for determining the high temperature resistance is charged into the oven and heated for 3 to 4 hours by means of electrical resistances, up to the temperature of 1000°C, which is maintained for 1 hour. Proof seal of the sample in the retort prevents loss through combustion or partial gasification.

The hot sample is passed through the drum, the duration of the operation being 2 minutes, and the loss of temperature of 50-60°C. Once the lid is closed the drum starts rotating at 50 revolutions / minute for 10 minutes. The resistance is expressed as a percentage, after screening the sample through the mesh of 25 and 10 mm, the results obtained are presented in Table 3.

Table 3. The resistances of coke, at high and low temperatures for the MICUM laboratory sample:

Details		Coke Romania	Coke Russia	Coke Czech Republic	Coke briquettes ICEM
Resistance at low temperatures, %	> 25 mm	87,32	89,06	87,04	76,88
	10-25 mm	6,42	4,01	4,99	12,87
	< 10 mm	6,26	6,93	7,97	10,30
Resistance at high temperatures, %	> 25 mm	80,10	89,78	86,15	81,15
	10-25 mm	13,11	2,59	8,24	8,50
	<10 mm	6,79	7,63	5,61	10,35
Change, %	> 25 mm	- 8,28	0,83	- 1,02	5,63
	<10 mm	8,5	10,1	29,20	0,48
Loss	Weight, %	4,35	4,67	4,57	6,75

4. Experimental research for the determination of the cokes reactivity

4.1. Experimental laboratory installation

The Iron Metallurgy laboratory from UPB, allows the testing of samples of coke having the dimensions which they are normally in a furnace.

The experimental laboratory installation for the determination of the cokes reactivity is shown in Figure 1.

It should be noted that this method is used with good results in recent years in Italy at Italsider and in France by Chercer Morieau [3].

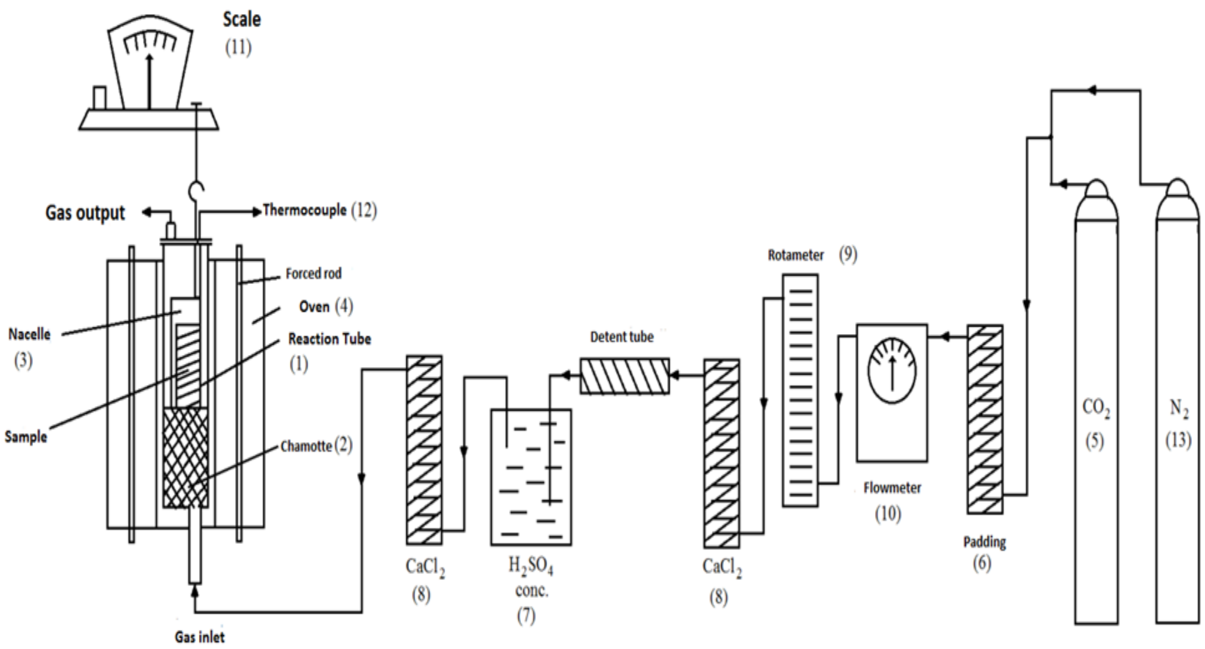

Figure 1. Schematic diagram of the experimental laboratory installation

4.2. Research methodology

It is used for coke samples weighing 400 grams and a grain size of 10 to 25 mm. The sample is loaded on the nacelle (3) of the stainless steel mesh with an inner diameter of 120 mm and a height of 300 mm. Platform coke sample is inserted into the stainless steel tube (reaction tube) (1) with a diameter of 140 mm, length 1000 mm, placed vertically inside the oven (4) heated with forced rod.

The determination is performed at a constant temperature of 900°C measured using thermocouple (12), Pt-Pt-Rh type introduced into the sample.

After ~ 5 minutes of nitrogen purging from the canister, CO_2 is blown from the bottle at a flow rate of 12 L / min for 30 minutes. Before reaching the incandescent coke sample, the gas passes through the flowmeter (9), the gas meter (10) and the cleaning vessel filled with cotton wool (6), sulphuric acid (7) and calcium chloride (8).

Sample weight variation during the blast of CO_2 balance is shown (11). After 30 minutes, the sample was again purged with nitrogen and then allowed to cool slowly to approx. 24 hours with a neutral atmosphere of nitrogen oven.

Next operation is extracting the sample, weighing it and screening it for determining the denial at 10 mm sieve.

Results for the cokes reactivity:

The results are determined by weighing the amount of C in coke which reacts with CO_2 as the difference between (M1) initial mass of the sample and (M2) final mass after reaction with CO_2. With laboratory work presented reactivity is determined by the relationship:

$$R = \frac{M1 - M2}{M2} \times 100, \% \tag{5}$$

Hereby established after weighing the denial at meshes of 10 mm, the amount of coke (q2) retains the original dimensions. This percentage relates to the initial mass (q1).

The results of laboratory measurements are presented in Table 4.

Table 4. The results of laboratory measurements for cokes reactivity

Details	Coke Romania	Coke Russia	Coke Czech Republic	Coke briquettes ICEM
Reactivity	64	76	82	103

It is noted that all coke types, irrespective of their origin have low reactivity with respect to CO_2, (with the exception of coke briquettes), which means that it will retain the same structural strength to the complete combustion. A low reactivity of the combustion zone size increases, with effect on lowering the load.

5. Conclusions

Currently, the trend worldwide is to practice heating methods for determining the mechanical strength and coke reactivity.

Introduction in the industrial practice of these methods, has led to the use in blast furnace of coke with superior quality indices, thus achieving optimum operating indicators of the blast furnace.

The results of experimental research for the determination of the cokes mechanical resistance show that all types of coke tested can be used in blast furnaces, with the difference that the coke obtained in Romania has a lower resistance, a high temperature than the coke of the Czech Republic or Russia provenance.

The results of experimental research for the determination of the coke mechanical resistance show very large differences between types of coke analysed.

The best value for the coke reactivity index was from the coke with Czech Republic provenance, followed by coke from Russia and Romania.

Coke briquettes tested has a very high reactivity index, which causes a negative influence through the burning zone of the crucible, decreasing at the same time the rate of descent of the load in a blast furnace.

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