REACTIVITY OF COKE USED IN THE ELECTRIC FURNACE FOR FERROALLOYS PRODUCTION[1]

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Abstract

The properties of coke required for the different metallurgical processes vary significantly. Therefore, reductant selection has become an important step in process optimisation. Coke reactivity to CO_2 is the most important parameter used by ferroalloy producers to evaluate the reductant quality. Six different metallurgical cokes, supplied by Vale S.A., have been studied in this work. Coke sample characterisation has been carried out by proximate analysis, mercury porosimetry and micro-textural analysis. Coke reactivity has been measured by standard CRI/CSR test and by thermogravimetry using thin slabs. It has been found that some coke samples are, in fact, mixtures of metallurgical coke and char. The reactivity index (CRI) of the studied cokes varies from 20% to 40%, while for chars it ranges from 42% to 57%. Thermogravimetric experiments have also shown that chars are the highly reactive types of carbon studied. A good correlation has been found between the gasification rate measured by thermogravimetry at 1100°C and the CRI. The CRI/CSR test, using different coke size ranges, could be a better solution for measuring coke reactivity for ferroalloy production. A more specific test, associated with texture analysis and mathematical modelling of coke bed gasification, becomes a key tool for reductant selection.

Key words: Coke; Char; CO_2 reactivity.

REATIVIDADE DO COQUE USADO EM FORNOS ELÉTRICOS PARA A PRODUÇÃO DE FERROLIGAS

Resumo

As propriedades do coque necessárias aos diversos processos metalúrgicos variam significativamente e a escolha do redutor tornou-se importante para a optmização de processos. A reatividade do coque ao CO_2 é o parâmetro mais importante usado pelos produtores de ferroligas para avaliar a qualidade do redutor. Seis coques metalúrgicos, fornecidos pela Vale S.A., foram estudados no presente trabalho. A caracterização das amostras foi feita através da analise imédiata, porosimetria ao mercúrio e analise textural. A reatividade dos coques foi medida usando-se o teste CRI/CSR padrão e termogravimetria sobre finas plaquetas. Descobriu-se que algumas amostras são, na realidade, misturas de coque metalúrgico e char. O CRI variou entre 20% e 40% para os coques e entre 42% e 57% para os chars. Os ensaios termogravimétricos também mostraram que os chars são os materiais mais reativos estudados. Encontrou-se uma boa correlação entre a taxa de gazeificação medida por termogravimetria a 1100°C e o índice CRI. O teste CRI/CSR, usando diferentes faixas granulométricas, pode ser uma solução para medir a reatividade do coque usado na produção de ferroligas. Um teste mais especifico, aliado à analise textural e ao modelamento matemático da gazeificação do leito de coque, torna-se uma ferramenta fundamental na escolha de redutores.

Palavras-chave: Coque; Char; reatividade ao CO_2.

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1 INTRODUCTION

The properties of coke required for the different metallurgical processes vary significantly. Therefore, reductant selection has become an important step in process optimisation. The desirable coke properties for the production of ferromanganese in the submerged electrical arc furnace are not well established so far, but coke reactivity to CO_2 is the most important parameter used by ferroalloy producers to evaluate the reductant quality. However, researchers are not in agreement on whether coke should have high or low CO_2 reactivity.

According to Lindstad et al.,[1] it is very important to avoid the Boudouard reaction in the submerged electrical arc furnace as much as possible, in order to reduce coke and energy consumption caused by this very endothermic reaction. Their work was focused on the influence of potassium on coke gasification rate in manganese production.

In contrast, Kamalpour and Rankin,[2] in their study of the behaviour of coke in the electrical furnace for ferromanganese smelting, concluded that the reductant selected to be used in this reactor should be more reactive than those normally used in the iron blast furnace.

The Boudouard reaction has the stoichiometric equation:

$$C_{coke} + CO_{2(g)} = 2CO_{(g)} \qquad (1)$$

Regarding this chemical reaction, coke reactivity is defined as the “ability” of carbon present in coke to react with carbon dioxide under specified conditions. Experimental evidence indicates that the forward and reverse reactions of equation (1) are relatively fast.[3] Therefore, it may be assumed that the establishment of equilibrium between carbon present at the coke pore surface and the gas phase consisting of CO_2 and CO occurs.

Using the Langmuir-Hinshelwood rate theory, the rate at which CO_2 reacts with carbon present in coke, i.e. the intrinsic rate of the Boudouard reaction at the surface of coke pores can be expressed as:

$$r_g = \frac{k_1 p_{CO_2}}{1 + k_2 p_{CO} + k_3 p_{CO_2}} \qquad (2)$$

where r_g is the intrinsic coke gasification rate, k_1, k_2 and k_3 are rate constants and p_{co2} and p_{co} are the partial pressures of CO_2 and CO, respectively. According to Aderibigbe and Szekely,[4] these rate constants are specific to the particular coke sample under investigation.

Turkdogan et al.[5,6] showed that the gasification rate depends on the size and type of carbon, pressure of CO_2 and temperature. The carbon gasification rate increases with increasing temperature and CO_2 partial pressure. For a given temperature and pressure of carbon dioxide, gasification rate increases with decreasing carbon particle size. In a subsequent publication, Turkdogan and Vinters[7] showed the poisoning effect of CO and the consequent retardation of the rate of gasification of charcoal, graphite and metallurgical coke in CO_2-CO mixtures over wide ranges of pressure and temperature.

Coke carbon forms (texture) and internal surface area influence coke reactivity as well. It is established that anisotropic carbon is less reactive to CO_2 than isotropic carbon.[8,9] This implies that an increase in isotropic carbon volume will increase coke reactivity. With increasing internal surface area, coke reactivity becomes greater too.[10-12] The catalytic effect of alkalis on the Boudouard reaction is well known, being potassium the strongest catalyst. Kaczorowski et al.[13] showed that the reactivity of coke samples impregnated with potassium was significantly higher than that for non-impregnated ones, being as much as 25 times higher.

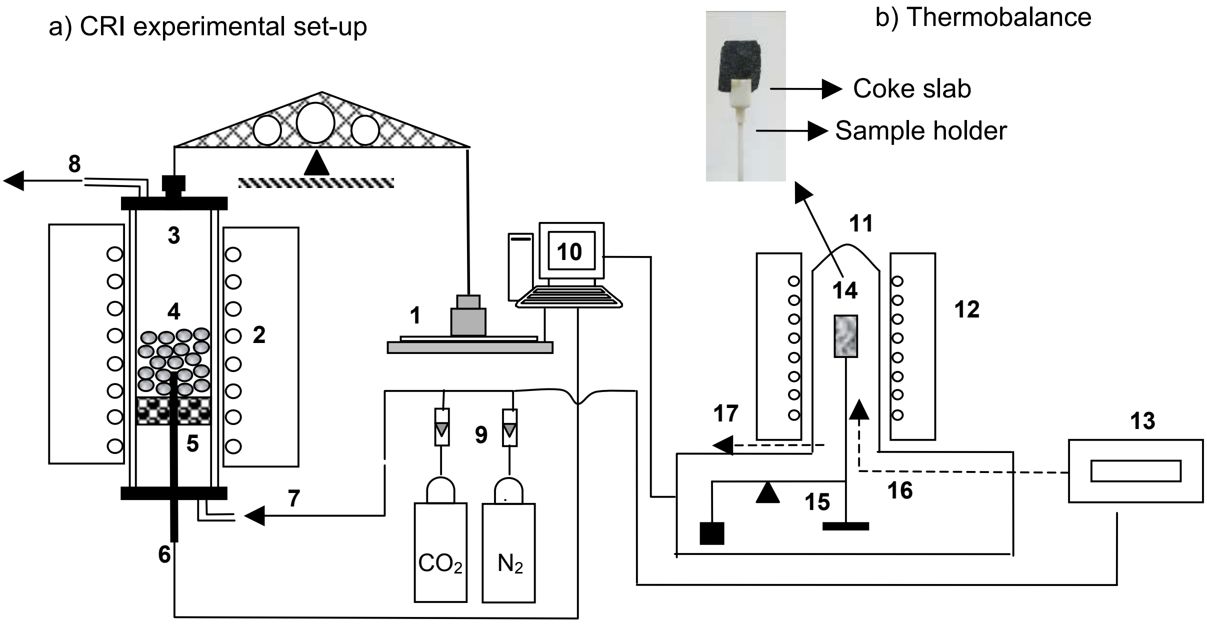
There are several methods to measure coke reactivity, but the result interpretation depends on the experimental parameters of the reaction system (temperature, gas flow rate, coke particle size and arrangement – single particle, fixed bed, moving bed, etc.). The test based on the NSC procedure (CRI/CSR) is the most usually employed. Nevertheless, there is a need for a specific test (or at least a procedure) enabling ferroalloy producers to assess the coke quality, and especially its reactivity. The aim of this work is to demonstrate such a necessity.

2 MATERIALS AND METHODS

Six different metallurgical cokes have been studied in this work. All coke samples have been supplied by Vale S. A. (Brazil). These cokes have been commonly used as raw materials in the production of manganese ferroalloys in the submerged electric arc furnace at different plants.

The proximate analysis, namely ash and volatile matter content in the coke samples, has been carried out according to the ISO standards. The open porosity, the pore-size distribution, the bulk and skeletal (true) densities of the coke samples have been measured using the mercury intrusion technique (Micromeritics PoreSizer 9320). The micro-textural analysis has been performed on a metallographic optical microscope on polished coke particles mounted on epoxy resin. The reactivity of cokes to CO_2 has been measured by two distinct methods:

- standard CRI/CSR test,
- thermogravimetric analysis (TG) of a single small coke particle.


a) CRI experimental set-up

b) Thermobalance

Figure 1. a) Experimental set-up for CRI/CSR measurement: (1) balance, (2) furnace heating element, (3) reactor tube, (4) CRI coke sample, (5) Al_2O_3 balls for gas preheating, (6) thermocouple, (7) gas inlet, (8) gas outlet, (9) mass flowmeters and (10) personal computer. b) Experimental set-up for TG analysis: (11) silica tube reactor, (12) furnace, (13) mass flowmeter, (14) coke sample, (15) microbalance, (16) gas inlet, (17) gas outlet.

The determination of Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) has been performed according to ISO standard using a DASFOS system. A schema illustrating the CRI experimental set-up is shown in Figure 1(a). Such a system enables to record the change in weight of the sample with time automatically.

The Thermogravimetric analysis (TG) has been performed using a Linseis L81 thermobalance (Figure 1(b)), in order to assess the intrinsic reactivity of coke samples to CO_2. The samples have been cut from massive coke lumps using a diamond saw to make thin slabs measuring 15 x 10 x 2.5 mm. In the TG experiments, a sample is heated up to 1000°C in a N_2 stream at 30 K/min and is kept at this temperature for 10 min, in order to release its residual volatile matters. Then, the gas flow is changed to CO_2 and the sample is cooled at 30 K/min up to 800°C, temperature at which a set of rate measurements under isothermal conditions begins. The sample is kept at 800, 850, 900, 950, 1000, 1050 and 1100°C for 10 min at each temperature in the same run, being heated at 30 K/min between two dwell temperatures. A fixed CO_2 flow rate of 0.7 l/min is used during the experiment.

3 RESULTS

The measured characteristics of the six coke samples studied in this work are listed in Table 1.

Table 1. Characteristics of the coke samples studied.

		Cokes						Chars		
		A	B	C	D	E	F	B1	B2	E1
Char fraction	wt.%	0	40	0	0	55	0.			
Ash (d.b.)	wt.%	11.5	11.2	11.2	8.4	11.1	9.2	6.5	20.1	8.8
VM (d.b.)	wt.%	1.5	2.0	0.3	0.5	2.0	1.0	7.0	15.0	4.5
Bulk density	g/cm^3	1.08	1.16	1.18	1.25	1.20	1.01	0.67	1.36	1.28
Skeletal density	g/cm^3	1.78	1.83	1.86	1.90	1.81	1.83	1.62	1.63	1.43
Porosity	Vol.%	39	37	37	34	33	44	59	17	11

First, it should be pointed out that cokes B and E are, in fact, mixtures of metallurgical coke and char. The char particles have been identified by naked eye, according to their external surface features and have been separated from the ("true") metallurgical coke ones by hand. In addition, it has been found that the char present in coke sample B is composed of a swollen char (B1), with high porosity and low residual volatile matter content and of a dense char (B2), with low porosity and high volatile matter content. Their differences in microstructure and texture have been assessed by cross-sections examination (Figure 2). The "true coke" is uniformly porous. The swollen char B1 exhibits alternated layers of porous and dense carbonaceous matter. The char B2 is uniformly dense (still as a coal lump) but irregularly cracked.

The results of CRI/CSR tests as well as the gasification rate measured by thermobalance at 1100°C are presented in the Table 2.

“True” coke B		Char B1 (swollen)		Char B2 (dense)

Figure 2. Cross-sections of coke B and the char lumps B1 and B2.

Table 2. Characteristics of the metallurgical coke samples studied.

		Coke						Char		
		A	B	C	D	E	F	B1	B2	E1
r_g x 10^4 at 1100°C	s^{-1}	0.47	0.47	1.20	1.55	2.00	1.59	4.22	3.22	3.50
CRI	%	20	24	26	29	30	40	57	42	49
CSR	%	68	57	60	47	65	55	37	34	45

4 DISCUSSION

4.1 CRI/CSR

Coke sample characterisation results, summarized in Table 1 and 2, show a great variability of coke qualities used by Vale S.A. Their reactivity index (CRI) varies from 20% to 40%. Chars found in the “mixtures” are even more reactive. Their CRI changes from 42 to 57%. It is interesting to note that, despite almost the same CRI value, cokes D and E have quite different CSR values. It should be also highlighted that the obtained results are in good agreement with the correlation between CRI and CSR (Figure 3) established by Menéndez et al.[14] for more than 60 cokes with a wide range of reactivities.

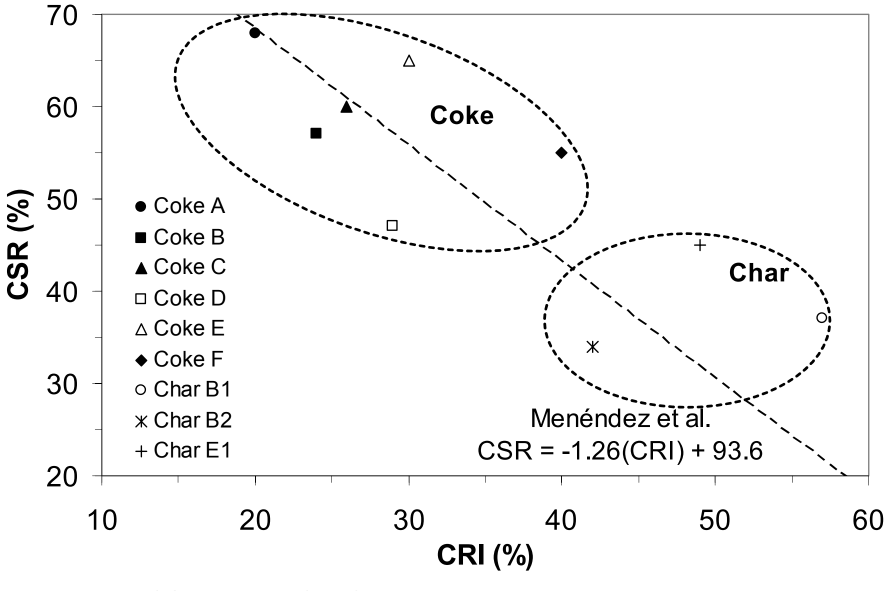


Figure 3. CSR versus CRI for the metallurgical coke samples studied.

4.2 Gasification Rate

Thermogravimetrical measures of the gasification rate are easier to carry out than CRI/CSR test. A typical TG curve, for the gasification of a thin slab (15 x 10 x 2.5 mm) of coke D under pure CO_2 atmosphere, is shown in Figure 4. The weight of the sample decreased slightly during heating under N_2 atmosphere, due the release of residual volatile matters and became constant after a few minutes at 1000°C. During the sample gasification under CO_2, the slope of the mass loss curve increases with temperature but it remains constant at a given dwelling temperature. From this slope, it is possible to calculate the coke gasification rate at different temperatures by the following equation:

$$r_g = -\frac{100}{\left(m_i \cdot C_f\right)}\frac{dm}{dt} \quad (s^{-1}) \qquad (3)$$

where r_g is the coke carbon gasification rate, m_i is the initial sample mass in grams and C_f is the fixed carbon in the coke sample in wt.%.

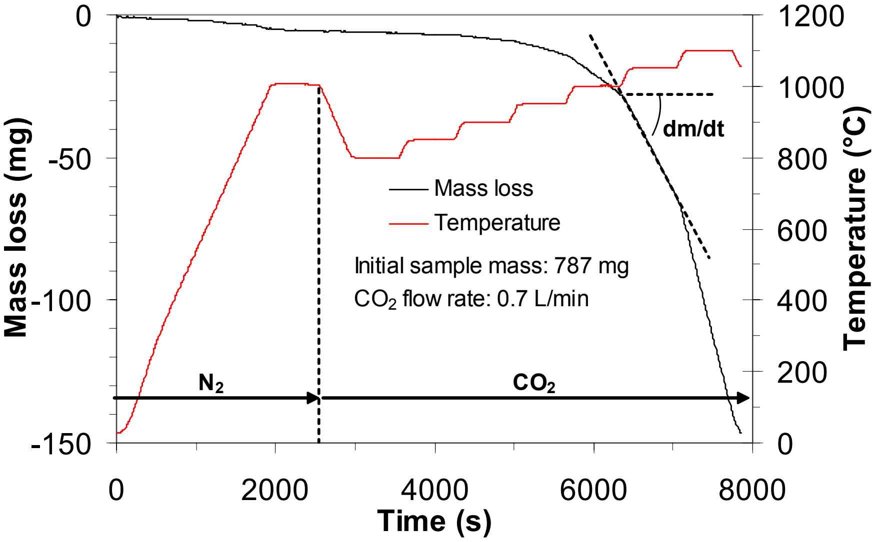


Figure 4. Typical TG analysis result, for the gasification of a thin slab of coke D.

The obtained data for the gasification rates (r_g) at different temperatures, for all metallurgical coke and char samples, are shown in Figure 5 in the Arrhenius type plot. The gasification rates of cokes A and B are almost the same and the lowest among the studied samples. The gasification rates of chars are also nearly the same and the highest among the assessed samples. The apparent activation energies have been calculated from the slope of the lines. Their values, which vary from 176 kJ/mol to 261 kJ/mol, are in the range reported by Kawakami et al.,[12] Turkdogan and Vinters,[7] Aderibigbe and Szekely[4] and Kaczorowski et al [13]

The relatively great differences between intrinsic reactivity of the studied cokes could be, at least, partially explained by the differences in their textural composition. In Figure 6 are shown the micrographs of coke B, coke F and char B1. Low reactive coke B exhibits very anisotropic, mosaic texture that is considered as less reactive. More reactive coke F contains more isotropic textures and post-inertinite reactive fragments. The very heterogeneous microstructure of char B1 is rich in isotropic texture that is considered as the more reactive coke texture.

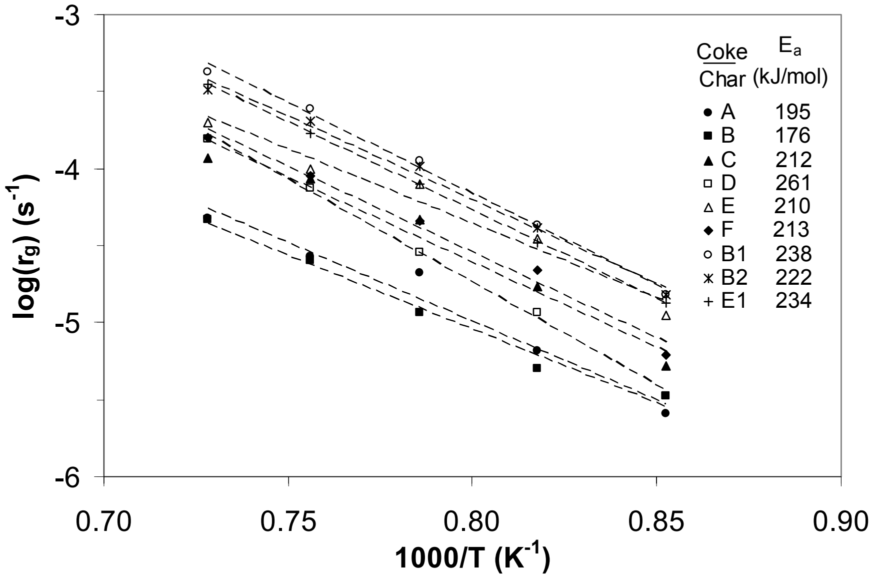
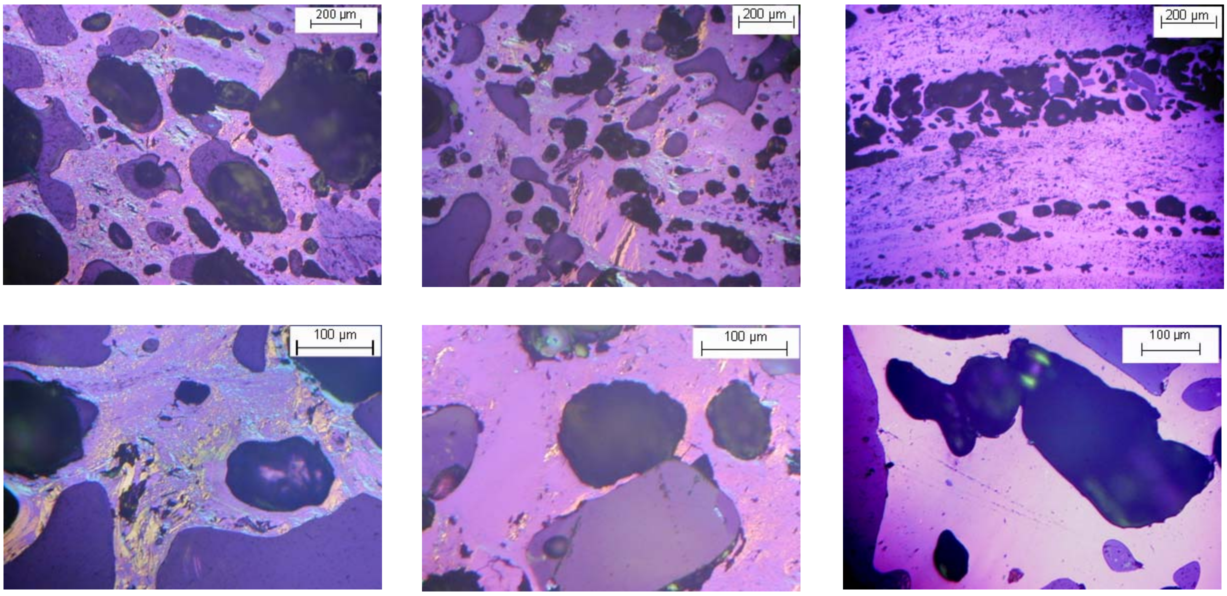


Figure 5. Arrhenius plot for the gasification rates (r_g) of metallurgical cokes and chars.



Anisotropic texture
Low reactive coke B
CRI = 24% r_g = 0.47x10^{-4} s^{-1}

Mixture of different textures
High reactive Coke F
CRI = 40% r_g = 1.59 x10^{-4} s^{-1}

Isotropic texture
Very high reactive Char B1
CRI = 57% r_g = 4.22x10^{-4} s^{-1}

Figure 6. The textures of the cokes B and D and swollen char B1.

4.3 Comparison Between Coke Reactivity Index (CRI) and Gasification Rate (r_g).

In the Figure 7 a relatively good correlation appears between the gasification rate at 1100°C (r_g), measured by thermogravimetry, and CRI Index. It can be expressed by the following linear regression equation (curve 4):

$$r_g^{1100°C}(s^{-1}) = 10^{-5} \cdot CRI(\%) - 0.0002 \qquad (4)$$

Considering that the rate of mass loss is constant during the CRI test (which is demonstrated in the Figure 8), it is possible to calculate the mean coke gasification rate in the bed ($r_{g\text{-}bed}$) and express it as a function of CRI:

$$r_{g-bed} = \frac{1}{m_i} \cdot \frac{dm}{dt} = \frac{1}{m_i} \cdot \frac{\Delta m}{\Delta t} = \frac{CRI}{120\,\text{min} \cdot 60 \frac{s}{\text{min}} \cdot 100} = 10^{-5} \cdot \frac{CRI}{7.2} \quad (s^{-1}) \qquad (5)$$

This relationship is also plotted in Figure 7 as the curve 5 and when compared with the curve 4 it shows that the gasification rate of coke in the bed is much slower than that measured at the thermobalance. Furthermore, this difference rises when the coke reactivity increases.

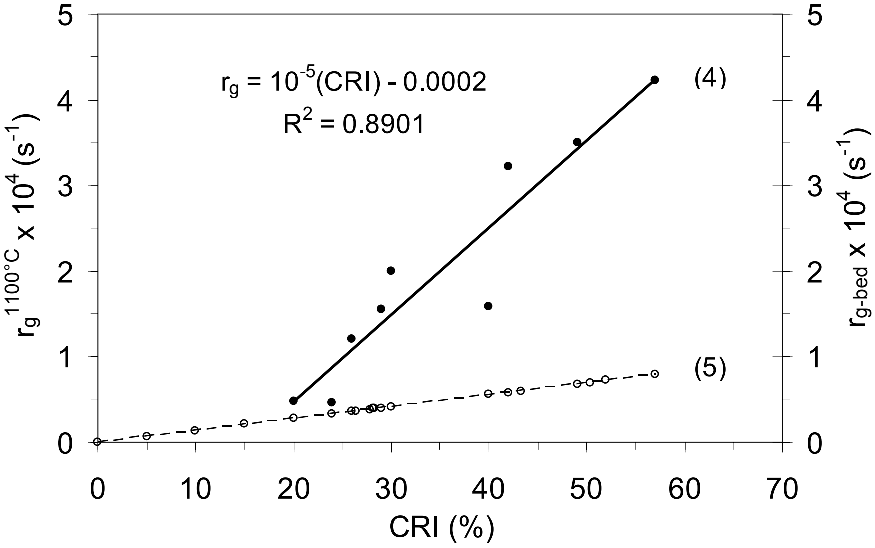


Figure 7. Relationship between CRI (%) and the gasification rate of a thin coke slab, r_g (s^{-1}).

To understand this difference, one should have in mind that the gasification rate depends on the experimental parameters that characterise the reaction system (temperature, gas flow rate, coke particle size and arrangement – single particle, fixed bed, moving bed etc.). The most important differences between the two methods which we use are the coke particle size and arrangement:

- $r_{g\text{-}bed}$ expresses the gasification degree of a fixed coke bed (200 g of 20 mm sized coke) during 120min;
- r_g expresses the gasification rate of a small single coke particle (thin slab with about 2 mm of thickness and 500 mg of mass).

There are, at least, two reasons for this difference in gasification rate: the gas concentration and the coke particle size. In the thermobalance experiments, even in the case of the gasification of the most reactive type of carbon studied in this work (char B1), the outlet gas does still contain more than 95% of CO_2, which leads us to consider that the reaction occurs under pure CO_2 atmosphere. During the standard CRI test, especially for highly reactive cokes, the outlet gas contains more than 30% of CO, which could be easily calculated from the gasification test mass balance. Such an enrichment of reacting gas (CO_2) by the product gas (CO) slows down the gasification rate.

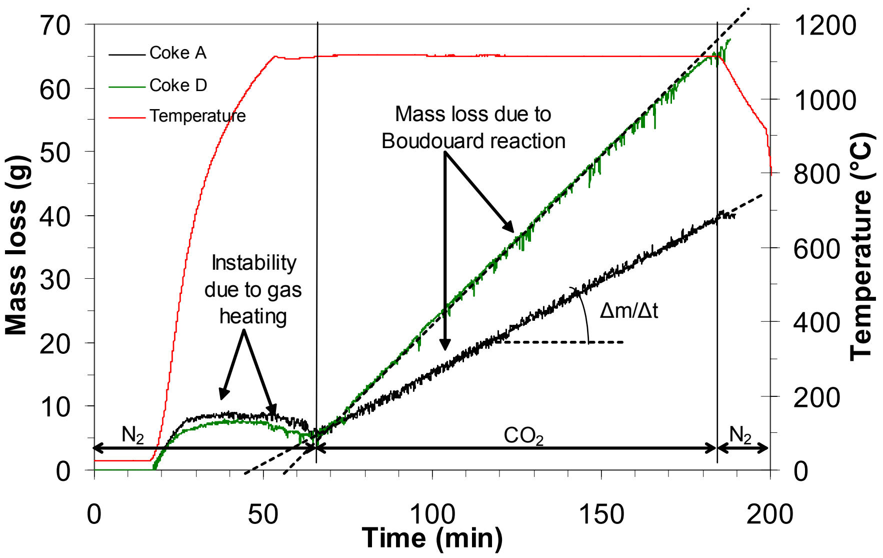


Figure 8. Mass loss curve obtained during the standard CRI test.

Thus, it could be postulated that the reaction rate is greater at the bottom of the bed, where pure CO_2 is blown, than at the top of the bed where gas is more or less enriched in CO. To show the differences in the reaction rate through the coke bed during the CRI test, tracer coke lumps, i.e. well-identified coke lumps, have been placed at three different levels - at the bottom, middle and top of the coke bed – and their gasification degree has been measured by weighting them before and after the test. The highly reactive coke has been chosen for that (coke F), in order to enhance the CO production in the reactor. The results are shown in Figure 9.

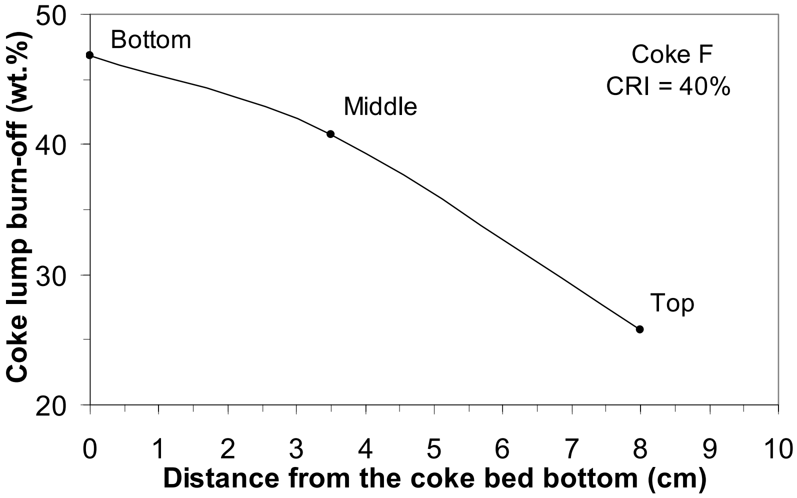


Figure 9. Coke lump burn-off as a function of the distance from coke bed bottom.

It shows that, in fact, the gasification degree (coke burn-off) of coke particle from the bottom is sensibly higher (47%) than those from the top (25%).

The second reason is surely the coke particle size. In the thermobalance experiments, thin slabs of about 2 mm in thickness and 500 mg are used, while in the CRI/CSR test coke lumps of about 20 mm in size and 4 - 5 g form a fixed coke bed. For the thermobalance experiences, the size and shape of the coke sample are chosen in order to limit as much as possible the lack of gas pore diffusion. In this situation, it is reasonable to assume that the reaction between CO_2 and carbon occurs at “the whole surface” of the sample (outer and inner). Consequently, it is also possible to say that the reaction rate is controlled by pure chemical reaction and is not influenced by mass transfer effects.

In contrast, in the CRI/CSR test, where the bigger coke particles are used, only a part of their volume (and inner surface) reacts with CO_2. Obviously, carbon from the outer shell of lumps is better exposed to CO_2 and gasifies more than that in the particle core. The gradient of CO_2 takes place inside the lumps, resulting in retardation of the gasification rate. This effect is greater for bigger coke particle sizes, higher reaction temperatures, as well as for higher intrinsic coke carbon reactivity. To prove that this occurs in CRI/CSR test, we measured the porosity of external shell and core of a gasified to 39 % coke lump (Figure 10).

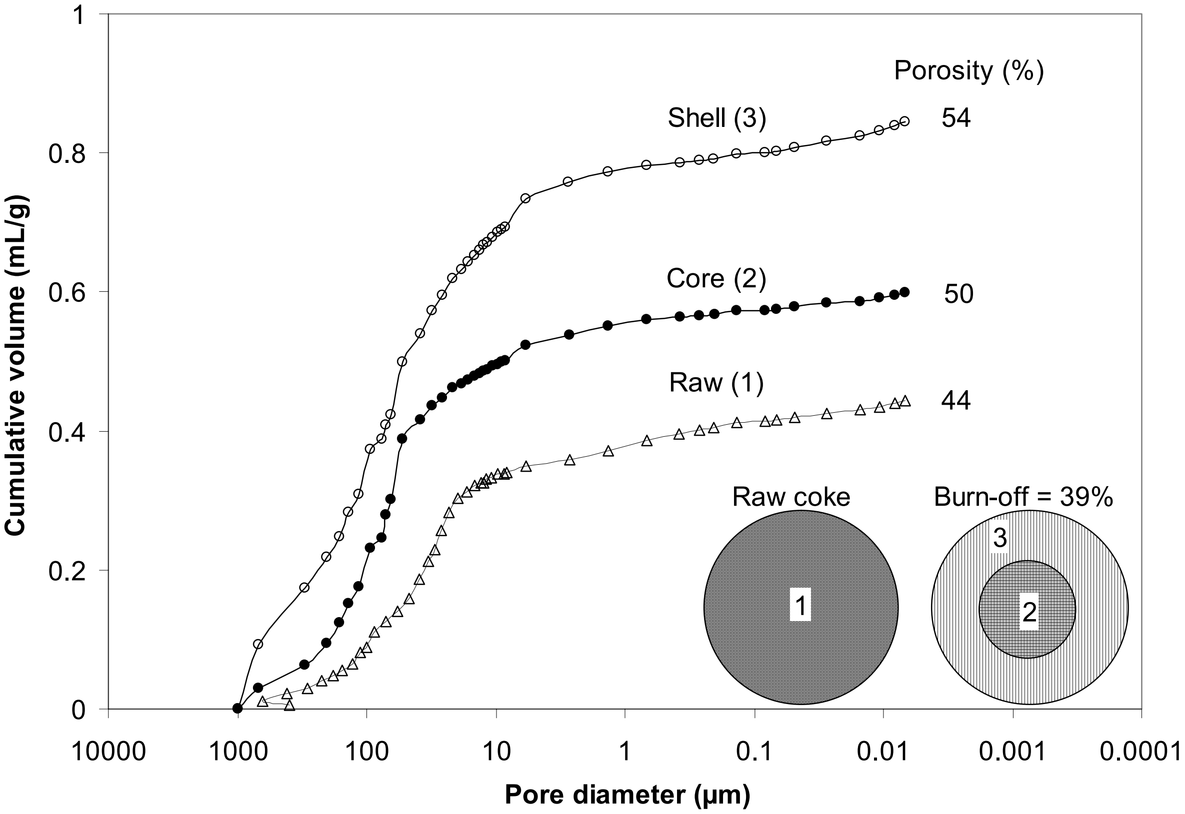


Figure 10. Pore size distribution in the raw and gasified to 39% coke lumps. For the gasified coke lump two parts were analysed separately: external shell and core.

It is seen from Figure 10 that indeed the pore volume and their size increased much more in the shell than in the core of the gasified lump. This obviously means that the reaction proceeds preferentially near particle surface. Being controlled by the gas diffusion in the coke pore the gasification rate depends on the particle size as well.

5 CONCLUSIONS

Coke selection for ferroalloy production is especially difficult because the production of other cokes than blast furnace coke became very limited. Thus, there is a temptation for sellers to compose a needed “reactive coke” by mixing the small undersized metallurgical cokes having low reactivity with the high reactive chars. The mean characteristics of such a coke fit the user specification but such a mixture seems to be a bad solution for the submerged electrical arc furnace due to the high residual volatile matters, low fixed carbon and particle size differences which could result in a harmful segregation inside the furnace.

A better solution to increase coke reactivity is to use a smaller and uniformly sized coke but, in this case, reactivity as the criterion of coke selection should be replaced by the gasification rate of a coke bed measured by a specific test. The CRI/CSR test, using different coke size ranges, could be a good solution. But to better assess the differences between the commercial cokes from different sources, the additional measures of intrinsic reactivity (by thermobalance) as well as finer characterisation of coke (texture, porosity) appears to be very useful. These measures, when combined with mathematical modelling of coke bed gasification will be the best tools for coke selection and optimisation of the ferroalloys production process.

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