Blast furnace and metallurgical coke's reactivity and its determination by thermal gravimetric analysis

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The aim of the present work is to adapt tests that are typically used for blast furnace cokes, such as coke reactivity index (CRI) and coke strength after reaction, to ferroalloy production in electric furnaces by developing easier equipment that meets with ISO 18894 standards. Moreover, a new technique has also been developed using thermal gravimetric analysis in order to quickly, inexpensively and reliably find the CRI parameter. As result of this work, a polynomial relationship between coke's reactivity and mass loss slopes of the record line obtained in the gravimetric thermal analysis tests was found.

Keywords: Coke reactivity index, Coke strength after reaction, Ferroalloys, Electric furnace, TGA test analysis, Manganese metallurgy

Introduction

The optimum coke quality required by electrical furnaces used in manganese industry is not the same as that required in blast furnaces used in siderurgy (related to mechanical degradability and chemical reactivity).[1] However, the manganese industry is, nowadays, working with a great variety of cokes, which have the same quality parameters [coke reactivity index (CRI) and coke strength after reaction (CSR)] that are used in siderurgy, though the quality parameters that should be used for manganese metallurgy should not be the same as that for siderurgy.

Ferroalloy industry (FeMn and SiMn) uses a large variety of cokes; so, following blast furnace practices, reactivity and degradability of these metallurgical cokes will be studied. By means of these studies, it will be known whether coke properties are suitable for achieving their function in electric furnaces. Some authors question the influence of low reactivity to CO_2, even coke degradability is downplayed,[2] as an important factor for coke savings and a correct reduction of minerals in the manufacture of ferroalloys, as postulated for the blast furnace[3] and for other furnaces. It must be accepted, therefore, that a poor quality coke, i.e. with high reactivity and degradability,[4,5] will not provide adequate coke consumption, elevating them and wasting the excess CO produced, since the electric furnace's shaft is too short, having low distance for its roles as low temperature reducing material. Gas flow is altered by coke's degradability, leading to operation and coke consumption problems that have been well established in blast furnace practice and that cannot be ignored in electric furnace practice.

Thus, the idea is to come to a simple criterion that will allow us to develop a quality control system for cokes and semicokes used in ferromanganese industry. This development is possible due to the fact that, nowadays, the quality control system used is the same as that used in siderurgy, CRI and CSR tests. It is our aim to relate the CRI with thermal gravimetric mass losses (from the graphic slope parameter obtained by means of thermal gravimetric analysis), in order to get a system that will allow a quality control of cokes fed to manganese industry electric furnaces.

Six standard cokes [provided by the Spanish Coal Institute (INCAR-CSIC)] with known reactivity have been taken. With these cokes, it has been proved that the procedure and equipment developed (taking into account ISO 18894 standard) work properly. Once the furnace was standardised, properties (CRI and CSR) for some cokes used in Spanish ferroalloy industry were calculated.

A simple and complete method has also been developed to calculate the CRI by thermal gravimetric analysis using a 1500°C thermal balance. The aim was to find a parameter provided by thermal gravimetric analysis, which might be related to each coke's reactivity. The slope in the thermal weight loss line record is this parameter.

Coke reactivity

High temperature coke reactivity can be defined as the mass loss produced when it reacts with oxidising agents, such as CO_2, water vapour, O_2, etc., under certain conditions.

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When talking about coke's reaction with CO_2 in blast furnace, reactivity (called carboxyreactivity) process is regulated by the Boudouard equilibrium

$$C(s) + CO^2(g) \rightarrow 2CO(g) \quad + \Delta H^\circ = 163\,kJ \qquad (1)$$

The functions that relate temperature with ΔG° (kJ) and ΔH° (kJ) are obtained by means of HSC data software[6]

$$\Delta H^\circ = 0.177 - 0.0074T(K) \qquad (2)$$

$$\Delta G^\circ = 171.13 - 0.175T(K) \qquad (3)$$

Using equation (1), it is possible to know when Boudouard's reaction becomes favourable. Boudouard's reaction becomes favourable from 977.9 K.

Coke temperature increases progressively from its entry into the furnace while in contact with a gas stream containing CO_2, which makes the balance of the equation (1) move to the right, increasing coke consumption. The high reactivity of coke, i.e. the greater reaction speed with CO_2 under certain furnace (pressure and temperature conditions), increases its specific consumption; therefore, the coke used in a metallurgical process must have low carboxyreactivity. Saving the differences, something similar happens in the electric furnace.

Determination of reactivity and degradability of coke (CRI and CSR indices)

The most common tests used in the iron blast furnace industry, and specifically in Spanish mills, are the Nippon Steel Corporation ones, the CRI and the CSR tests.[7]

Coke reactivity index is expressed as per cent weight loss in the coke sample due to the reaction with CO_2, under determined conditions according to ISO 18894 standards. Calculations are made as follows

$$CRI = \frac{A - B}{A} \times 100$$

where A is the original test sample weight before reaction, and B is the sample weight after reaction in CO_2.

Temperature is 1100°C, CO_2 flow is 5 L min^{-1} and time is 2 h, as in ISO 18894 standard.

A good quality coke has CRI values equal or lower than 20–30%.[8]

Coke strength after reaction index shows coke's degradability in furnace operation and gives a parameter related to gas permeability in the blast furnace, as it depends on the fines produced. This index is similar to the low temperature degradation index used in iron ore degradability studies.[9] It is obtained as follows

$$CSR = \frac{C}{B} \times 100$$

where B is the sample weight after reaction in CO_2, and C is the sample weight of 10 mm material under tumbling.

The index is defined by the weight percentage of the fraction larger than 10 mm, in accordance with ISO 18894. A good quality coke has CSR values larger than 60%.[8]

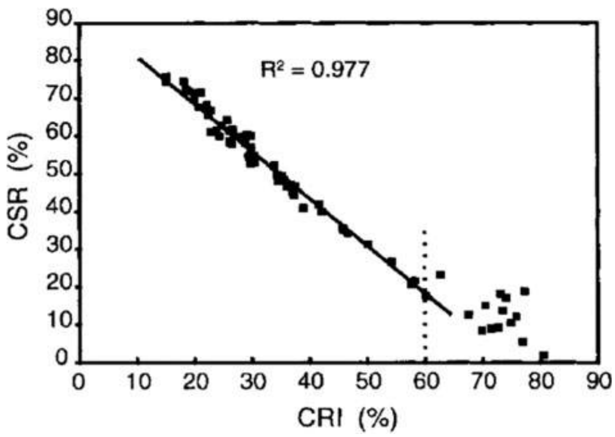
Some researchers have found a relationship between reactivity (CRI) and degradability (CSR).[8,10–12] Menéndez *et al.*[10] proposed a linear equation (Fig. 1) obtained from significant number of cokes, where they observed that when coke's reactivity was great, then coke's resistance was less in degradability test, and vice versa.

Experimental work CSR/CRI by means of ISO 18894 standard

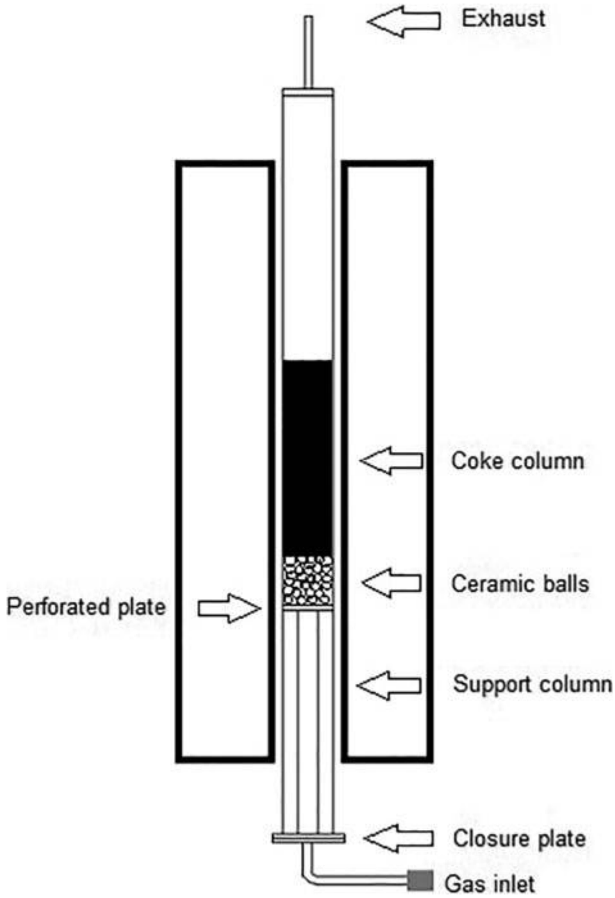
Equipment used to determine CRI

A furnace was built for the purpose of determining coke's reactivity, based on the Nippon Steel Corporation method and ISO 18894 standard (Fig. 2).

The furnace that has been designed for this work is a resistance furnace, with a vertical tube of 80 cm height. It consists of a ceramic cylinder into which a 60 mm



1 Relationships of %CSR to %CRI for various cokes[10]



2 Constructed furnace section for reactivity determination

diameter refractory steel tube is inserted, within which the coke sample is located. Coke charge lies on a base of ceramic balls,[13] 6 mm in diameter, which serve as diffuser, on a perforated refractory steel plate located on an alumina tube, supported by the bottom closure cap, which has the gas supply pipe.

Different coke patterns [provided by the Spanish Coal Institute (INCAR-CSIC)] were tested to verify that reactivity results obtained with this furnace were correct. Coke generally has a particle size between 20 and 25 mm.

Equipment used to determine CSR

The tumble tube used for determining degradability of coke was constructed exactly as it is described in ISO 18894 standard.

Determination of reactivity and degradability of standard samples

Reactivity tests were carried out in the furnace described in the section on 'Equipment used to determine CRI'. Operation conditions were as follows: mass, gas flow (N_2 when heating and CO_2 for testing), exposure time, temperature and other factors as expressed in ISO 18894 standard.

Degradability tests were carried out as in ISO 18894 standard (time and tumbling speed defined in ISO 18894 standard).

Six coke INCAR patterns were tested in order to prove the correct operation of the equipment designed. As the same results were obtained (Table 1), taking into account tests tolerance (two units for both CRI and CSR), it is possible to say that the equipment has a correct design.

Determination of reactivity and degradability of various cokes

Reactivity

Once the CRI coke furnace was standardised, seven cokes were tested: blast furnace coke 1, blast furnace coke 2, metallurgical coke 1, metallurgical coke 2, metallurgical coke 3, petroleum coke 1 and petroleum coke 2. Petroleum cokes are typically used in electric furnaces for ferroalloys production, due to their low price. Nevertheless, this sort of coke has low quality and small grain size; this is why we need the criterion that we have proposed in this paper. Blast furnace cokes have high quality and are used in the iron and steel industries. Metallurgical cokes are used in casting.

A study was conducted previously in a thermal balance, which showed that some cokes had mass losses due to subcoking. Because of this, tested cokes and patterns underwent prior pyrolysis at 1000°C for a period of 1 h to determine mass loss. Those that were badly coked, 'semicokes' as they are called by Oliveira,[2] showed losses reaching 10% (see Table 2).

Table 1 Features of coke patterns [patterns provided by Spanish Coal Institute (INCAR-CSIC)]

Reference	Coke pattern A/%	Coke pattern B/%	Coke pattern C/%	Coke pattern D/%	Coke pattern E/%	Coke pattern F/%
CRI (±2)	20	40	55	27	30	35
CSR (±2)	68	45	20	63	58	54

Table 2 Coke mass loss by pyrolysis at 1000°C for 1 h

Coke	Mass loss/%
Coke pattern A	0
Coke pattern B	0
Coke pattern C	0
Coke pattern D	0.5
Coke pattern E	0.2
Coke pattern F	0
Blast furnace coke 1	0
Blast furnace coke 2	0
Metallurgical coke 1	0
Metallurgical coke 2	1.4
Metallurgical coke 3	8.7
Petroleum coke 1	7
Petroleum coke 2	9.1

Tests were carried out twice. In the case of cokes that had showed losses due to pyrolysis, these losses should be subtracted from the total loss, for calculating the reactivity after the ISO 18894 standard furnace test. Results for reactivity are presented in Table 3.

Coke grain size influence on reactivity

Owing to the fact that some of the industrially tested cokes had grain size lower than that specified in the ISO 18894 standard, the effects of particle size on reactivity have been studied. For this purpose, blast furnace cokes already characterised, blast furnace coke 1 and blast furnace coke 2 have been used for CRI determination. The grain size ranges from >25 mm down to 10–16 mm fraction (see Table 4).

As we can see in Table 4, as the grain size decreases, the reactivity increases. These results are in agreement with those published by Oliveira.[2]

A relationship between CRI (%) and coke grain aize (GS) (mm) can be established.

Table 3 CRI index for cokes tested

Coke	CRI/%
Coke pattern A	20
Coke pattern B	40
Coke pattern C	55
Coke pattern D	27
Coke pattern E	30
Coke pattern F	35
Blast furnace coke 1	30
Blast furnace coke 2	31
Metallurgical coke 1	37
Metallurgical coke 2	32
Metallurgical coke 3	50
Petroleum coke 1	20
Petroleum coke 2	19

Table 4 Blast furnace cokes 1 and 2 reactivities for varying grain sizes

	CRI/%	
Size/mm	Blast furnace coke 1	Blast furnace coke 2
>25	22.1	23.3
20–25	30.4	31.1
16–20	34.1	33.0
10–16	37.3	38.0

Blast furnace coke 1

$$CRI = -1.0284GS + 51.8; R^2 = 0.9459; \quad (4)$$

Blast furnace coke 2

$$CRI = -0.9618GS + 50.8; R^2 = 0.9536 \quad (5)$$

From these equations, it is possible to obtain the following approximate expression, CRI + GS = 50. There will also be a relationship between sizes and the CSR, as CRI and CSR are related as discussed above.

Degradability

Once coke reactivity testing has been carried out, tested coke is placed into the tumble tube for calculating its degradability (CSR) (see results in Table 5).

Relationship between tested CRI and CSR

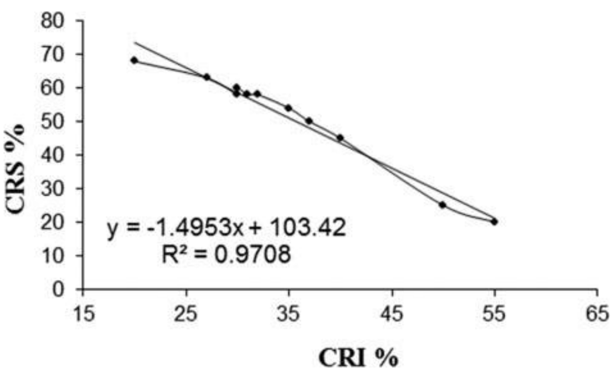
At the beginning of this work, it has been seen that a relationship between these two parameters exists, as it is described in the literature.[10] Therefore, this relationship should be fulfilled for the cokes tested. Only INCAR coke patterns and carbon cokes should be used because the two petroleum cokes have different behaviours. In Fig. 3, the relations between the obtained data are represented.

In this study, using the furnace designed (taking into account ISO 18894 standard descriptions), a very similar formula to that of the other authors was found.[10,11] Small differences may be due to the number of tested cokes.

$$CRS(\%) = -1.4953CRI + 103.42; R^2 = 0.9708 \quad (6)$$

Table 5 Coke strength after reaction index obtained in trommel for cokes tested

Coke	CSR/%
Coke pattern A	68
Coke pattern B	45
Coke pattern C	20
Coke pattern D	63
Coke pattern E	58
Coke pattern F	54
Blast furnace coke 1	60
Blast furnace coke 2	58
Metallurgical coke 1	50
Metallurgical coke 2	58
Metallurgical coke 3	25
Petroleum coke 1	40
Petroleum coke 2	63



3 Coke reactivity index and CSR index correlation

This relationship is not applicable to petroleum cokes. This has been concluded after testing petroleum cokes: petroleum coke 1 and petroleum coke 2, with pyrolysis losses at 1000°C of 7.0 and 9.1 respectively.

In any case, they show low reactivity values on the order of 20%, due to the relation between physical and mineralogical properties and reactivity.[14,15]

The extrapolation of the CRI/CSR relationship from carbon cokes to petroleum ones is not valid. In fact, in testing the two petroleum cokes, there are great differences: 40% for petroleum coke 1 and 63% for petroleum coke 2, not expected for similar reactivity value (20). This confirms the prior point. Petroleum cokes are presented in this paper as they are used in ferroalloy manufacturing because of their low price.

Experimental work: thermal balance study of blast furnace and metallurgical coke's reactivity

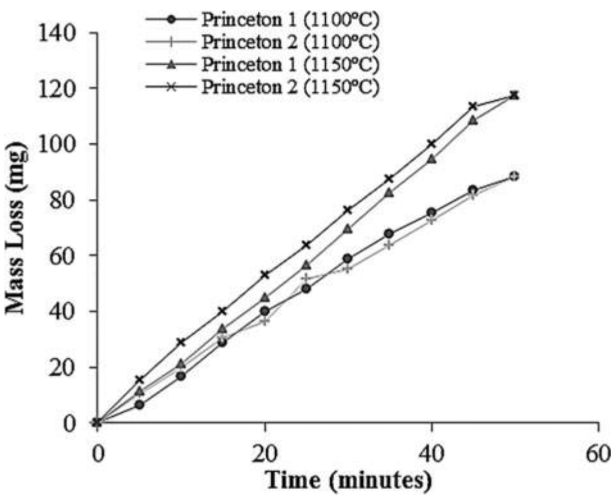
In 2010, Oliveira showed the relationship between the slopes of the electric furnace mass loss line for the Boudouard reaction, under certain test conditions, testing different cokes, using a common thermal balance and a designed macrobalance.[2]

Oliviera studied the possibility of obtaining the carboxyreactivities for the cokes using thermal gravimetric analysis by determining the slope of the gravimetric loss in the graph line record obtained at the beginning of the test, where the slope is constant.

Effect of temperature and CO_2 flow on coke reactivity

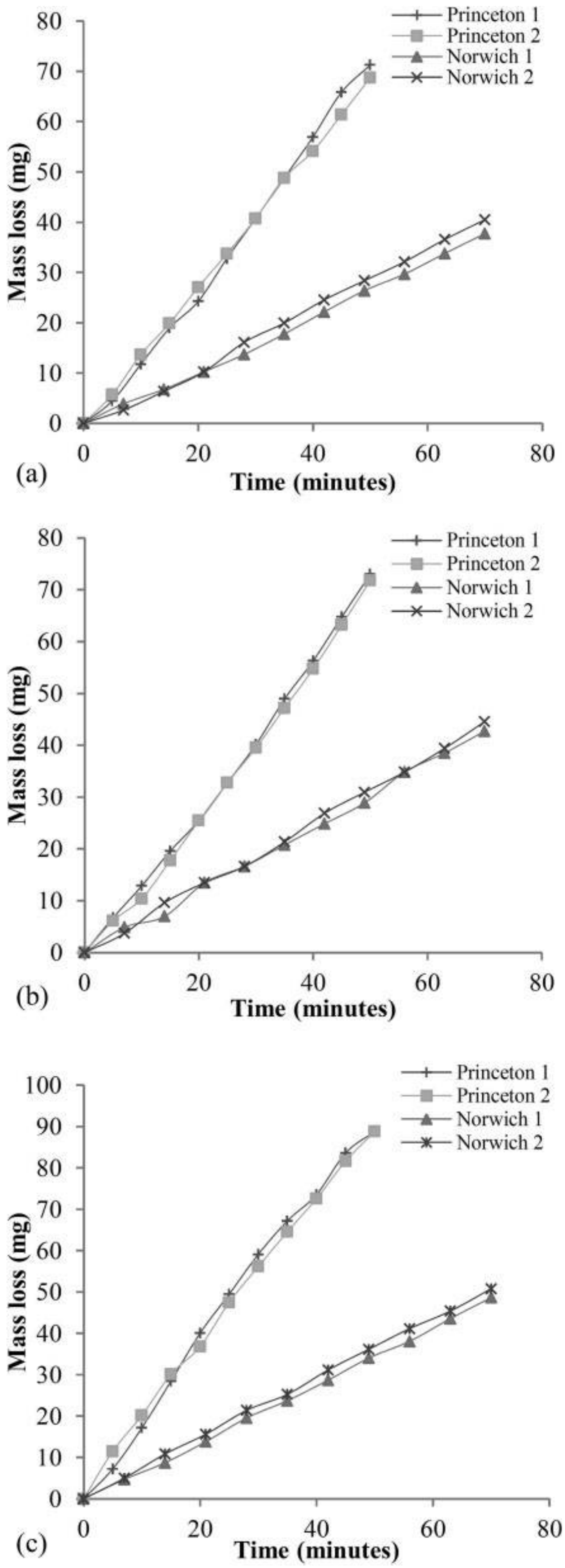
It is known that temperature, gas flow, structure, particle size and mineral composition affect coke reaction rate with CO_2.[16–23]

In this work, the effect of temperature and CO_2 flow has been studied using a thermal balance. First of all, temperature influence will be analysed. For this purpose, tests have been performed by duplicate using Princeton coke with a flowrate of 15 L h^{-1} CO_2 and varying the temperatures between 1100 and 1150°C, holding it for 50 min (Fig. 4).



4 Temperature effect on mass loss for Princeton coke with 15 L h^{-1} CO_2 flow

Norwich and Princeton cokes have been used for the study of the influence of the CO_2 flow value. Mass loss against time will be obtained at 1100°C in order to simulate the standard test in the vertical furnace, and varying flow rates of 2.15, 8 and 15 L h^{-1} will be used (Fig. 5). These results agree with those reported by Dlugsz *et al.*[17]



a 2.15 L h^{-1}; *b* 8 L h^{-1}; *c* 15 L h^{-1}

5 Gas flow effect CO_2 on mass loss line slope for Norwich and Princeton cokes with flows

Figure 6 shows the mass loss slope (MLS) for the Norwich and Princeton cokes with different CO_2 flows.

Test definition in thermal balance

The previous studies have served to determine the best parameters that will define the test by the new method:

(i) carbon dioxide flowrate: 15 L h^{-1}
(ii) heating rate up to 1100°C: 6–7°C min^{-1}, higher heating rates would cause greater difficulties in reaching the 'plateau'
(iii) sample weight: ~200 mg
(iv) sample particle size: between 1 and 2 mm
(v) CO_2 flow sample submission time: between 35 and 65 min, depending on the needed time to get a reliable parameter of slope
(vi) total test time: 3 h approximately.

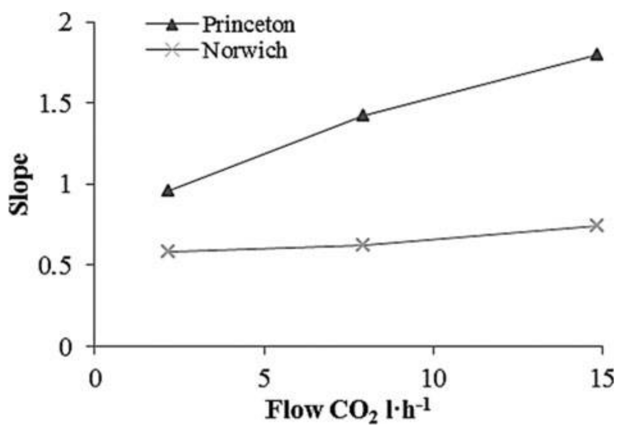
Calculation of coke reactivity

Mass losses were obtained for some standard samples supplied by INCAR; also other mass losses were obtained from industrial samples tested (Fig. 7*a*) in the designed CRI furnace (taking into account ISO 18894 standards descriptions). Once the thermal balance is calibrated with those standards, 11 overall, results were plotted in a graph obtaining a wide range of reactivities/ slopes (Fig. 8). For calculating the reactivity of a new coke, using the thermal balance, the mass loss straight line obtained is represented in the graph and the reactivity is assessed.

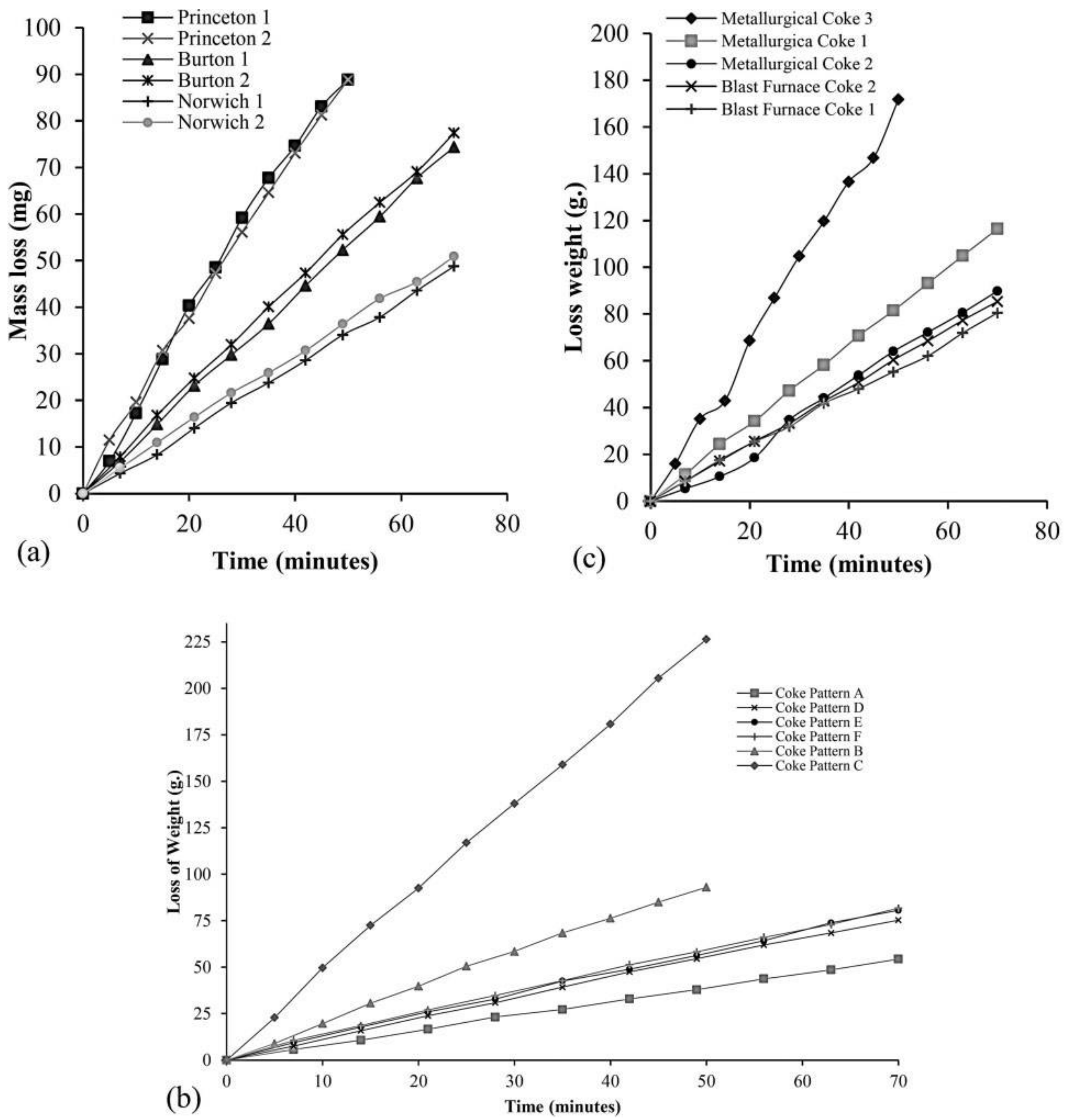
Tested coke's reactivities in Fig. 7*b* and *c* are the 11 cokes referred in Table 3, with the exception of the last two corresponding to petroleum cokes. In Table 6, the slope and the reactivity of the 11 cokes are considered together.

Cokes were tested at standardised parameters, and the MLS was calculated. Figure 8 shows the relationship between the coke's reactivity and the slope on the mass loss straight lines in thermal balance, according to the method proposed in this work. A polynomial type relationship with a high correlation coefficient was found.

With this values, a functional relationship between CRI (%) and slope can be established. A polynomial



6 Mass loss slopes for Norwich and Princeton cokes with three flows



7 ***a*** **mass loss for Princeton, Norwich and Burton cokes with flow of 15 L h^{-1},** ***b*** **mass loss for coke patterns with flow of 15 L h^{-1} and** ***c*** **mass loss for industrial cokes with flow of 15 L h^{-1}**

type expression was discovered to relate the MLS and coke's reactivity

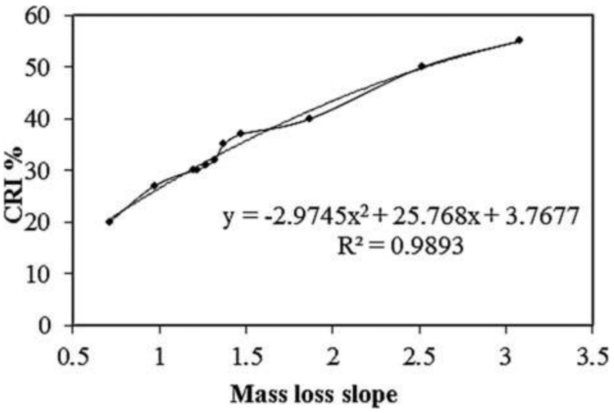
$$CRI = -2.9745MLS^2 + 25.768MLS + 3.7677; R^2 = 0.9893 \ \mathrm{R}$$

Results for petroleum cokes have not been included as the mass loss does not follow a straight line but rather has an 's' shape. The reasons for this are due to losses arising from pyrolysis and volatiles that produce cracks and increase the grain porosity. Moreover, this effect is enhanced because the release of volatiles occurs in an explosive manner as it was detected in some cases. Therefore, this method is not considered to be suitable for determining petroleum coke's reactivity, as received.

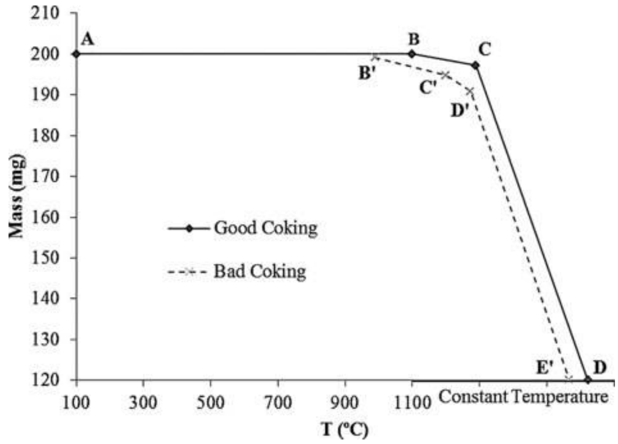
The reasons that show the high interest of the thermal balance test compared with the vertical furnace, from the standard, are as follows:

(i) it is possible to determine the mass loss during sample heating in an N_2 atmosphere before reaching 1100°C, detecting if subcoking has taken place

(ii) with this equipment, only the MLS, when reacting with CO_2, is taken into account in order to estimate reactivity; it does not take into account possible losses in mass during heating due to poor coking; this is an advantage over the vertical furnace as, in this case, these weight losses, before the introduction of carbon dioxide, are attributed to the reaction of coke with it; therefore, for badly coked coals, semicokes, the ISO



8 Relationship between TGA and %CRI mass loss slope



9 Example of mass loss curves for well coked and badly coked cokes

Table 6 Estimated reactivities and slope in thermal balance for tested cokes

Coke	CRI/%	Slope
Coke pattern A	20	0.71
Coke pattern B	40	1.87
Coke pattern C	55	3.08
Coke pattern D	27	0.97
Coke pattern E	30	1.22
Coke pattern F	35	1.37
Blast furnace coke 1	30	1.20
Blast furnace coke 2	31	1.27
Metallurgical coke 1	37	1.47
Metallurgical coke 2	32	1.32
Metallurgical coke 3	50	2.52

18894 standard produces wrong measurements with a higher value of reactivity.

In the thermal gravimetric mass loss line, only the straight part of the same is considered because, at the beginning, when CO_2 is introduced, there is a short curved section that is characteristic of each coke, becoming straight immediately afterwards.

Interpretation of thermal gravimetric graphs

Thermal gravimetric loss weight lines follow two patterns for the blast furnace and metallurgical cokes, as they are well or badly coked. These two behaviours are outlined in Fig. 9.

Well coked cokes

Three segments appear in the curve for well coked cokes (good coking curve, Fig. 9):

(i) segment AB: heating up the sample to 1100°C takes place without loss of mass
(ii) segment BC: keeping the temperature constant at 1100°C, CO_2 begins to be introduced; in this transition segment, the mass loss does not follow any pattern until it stabilises when reaching the point C
(iii) segment CD: the coke begins to lose mass at a constant rate as it is shown in the graph, so the slope in this segment can be taken for reactivity estimation.

Badly coked cokes

For badly coked cokes (semicokes), four segments instead of three appear in the curve (bad coking curve, Fig. 9). A mass loss occurs: B'C' segment, at temperature lower than 1100°C. This mass loss denotes the subcoking, and the temperature at which this occurs depends on how it has been coked (temperature defect on heating). The weight loss that occurs in this testing part, when using the ISO 18894 standard, should be badly attributed to coke reactivity.

With the method proposed in this paper, it is possible to determine the reactivity of coke (CRI) avoiding the possible errors that the ISO 18894 standard presents for badly coked cokes (semicokes), which is a very important circumstance when producing ferroalloys, as the use of different cokes is a common practice not used in the blast furnace pig iron production, which uses normally good quality cokes. Once CRI is obtained from the thermal balance, the degradability (CSR) of the coke is obtained by the related formula.

Repeatability of thermal balance test

The test was repeated three times in the thermal balance to estimate the test's repeatability (Table 7).

It can be seen that the error ranges from 0.07 to 3.3%. The average value of all errors is 2.2%, but even the highest error value, 3.3%, is less than was expected to be when calculating CRI following the ISO 18894 standard.

Table 7 Slope test repeated values, difference between extremes and error

Slope				
Valor 1	Valor 2	Valor 3	Difference	Error/%
0.71	0.71	0.69	0.02	2.8
0.97	0.96	0.96	0.01	1.0
1.20	1.18	1.17	0.03	2.5
1.22	1.21	1.20	0.02	1.6
1.27	1.24	1.23	0.04	3.1
1.32	1.3	1.28	0.04	3.0
1.37	1.33	1.32	0.05	3.6
1.47	1.46	1.46	0.01	0.7
1.87	1.82	1.81	0.06	3.2
2.52	2.46	2.42	0.1	4.0
3.08	2.92	2.91	0.17	5.5

Conclusions

Using coke patterns provided by the INCAR, equipment that allows the calculation of CRI and CSR used in the electric furnace, i.e. blast furnace, metallurgical and petroleum cokes, has been developed based on ISO 18894 standards.

The obtained CRI (%) and CSR (%) relationship is

$$CSR = -1.4953CRI + 103.42$$

A method for determining the reactivity of the blast furnace and metallurgical cokes via thermal gravimetric analysis has been developed using mass loss straight line slope in standardised conditions, which has a high reliability, which may be an alternative to the ISO 18894 test. This new test allows detecting bad produced cokes, semicokes, not detected with ISO 18894 standards. It also prevents the use of the CRI index in those cases in which it should be an erroneous value because, for semicokes, this parameter is increased by the lack of coking (10% in some cases).

As the particle size of the new method is 1–2 mm (in the future, it could be the size required for industrial facilities to reduce specific consumptions, but it must be proved in the ferroalloys production electric furnaces), CRI can be determined in industrial cokes in the market with <20 mm size, not able for the ISO 18894 standard.

Petroleum cokes cannot give a CRI acceptable value as it behaves as a semicoke. Prior pyrolysis of petroleum cokes before being tested may not improve the result as it generates a significant amount of porosity and probably size degradation (explosions), and this alters reactivity.

A polynomial type expression was discovered that relates the MLS to the reactivity of coke (Fig. 8)

$$CRI(\%) = -2.9745MLS^2 + 25.768MLS + 3.7677$$

The differences between CRI values with the new method and the ones that can be found using the ISO 18894 standards are below the error of the ISO 18894 method.

The proposed method is not suitable to determine the reactivity of petroleum coke, as at the moment that the CO_2 is introduced, mass lose does not take place evenly; thus, its reactivity cannot be determined by its slope.

We obtained a criterion that allows us to determine the quality of cokes used in manganese metallurgy electric furnaces.

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