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## BLAST FURNACE COKE QUALITY IN RELATION TO PETROLEUM COKE ADDITION

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### INTRODUCTION

The incorporation of petroleum coke as an additive in industrial coking coal blends is a practice often used by steel companies. A suitable blast furnace coke produced by replacing part of the coking coal blend with a suitable petroleum coke (addition of 5 to 15%), was made by Great Lakes Carbon Corporation [1] and successfully tested at several blast furnaces. This coke had lower reactivity, less ash and slightly higher sulphur content than coke made without the addition of petroleum coke.

In contrast with these results, it has been reported in a BCRA study [2] that additions of petroleum coke to a strong coking coal, above 5 wt%, increased coke reactivity. These differences may be explained on the basis of the coal or blend characteristics to which petroleum coke is added. Petroleum coke addition seems to give better results if the coal/blend has high fluidity.

Petroleum coke is one of the typical components of coking coal blends at Inland Steel [3] and has occasionally been used, depending mainly on economic considerations, at ARMCO [4], Dofasco [5], several Japanese Steel Companies [6] and Somisa (Argentina) [7]. High-sulphur petroleum coke is also used in Russia as a component of the coal charge for producing metallurgical coke for non-ferrous metallurgy and other non blast-furnace uses [8].

The percentage of petroleum coke used depends mainly on the coal/blend to which it is added. The

blending limit in Japan is considered to be about 5 wt%. This limit has been established as the quantity of petroleum coke added with which the fluidity of the coal/blend decreases to below 200 ddpm [6].

The maximum limit of petroleum coke addition for the production of acceptable coke quality has been reported in a work to be 20 wt% [9], although in another work carried out in Argentina, a petroleum coke addition of 40 wt% has been quoted [7].

The addition of petroleum coke to preheated charges has been studied by INCAR [10] and Inland Steel [11].

In two relevant studies that used a variety of petroleum cokes, it was found that metallurgical coke of better quality -lower reactivity to CO<sub>2</sub> and lower fines production in a microstrength test in one case [12] and higher CSR in the other [11]- were obtained, when petroleum coke of the highest volatile matter was used.

The present situation in Spain is favourable for the use of petroleum coke. So, a study to laboratory and semi-industrial scale was made to assess the possibility of using petroleum coke as an additive to the typical industrial coal blend coked by the Spanish Steel Company, ENSIDESA. The influence of the petroleum coke particle size was also studied to semi-industrial scale.

A method for improving the characterization of petroleum coke (with similar elemental and proximate composition) to be used as an additive to coking coals has been developed by INCAR [13].

### EXPERIMENTAL

Laboratory carbonization tests (400 g coal < 1 mm) were carried out following a procedure developed by INCAR [14,15]. The strength of laboratory coke was determined by means of the abrasion index, defined as the weight per cent of the initial sample < 1 mm after 3000 revolutions in a mini-Micum drum at 33 rpm [14].

Semi-industrial carbonization tests were carried out at the 6 t capacity oven of the INCAR Coking Test Plant [16]: 6.5 m length, 2.8 m height and 0.45 m width.

Control of the expansion and contraction of the coal blends was made using the Koppers-INCAR laboratory test [17]. To semi-industrial scale, internal gas pressure was measured using a probe placed through the ram side door 30 cm above the sole of the oven and below the charging hole of the ram side.

Coke samples were taken in the wharf exit, with minimum handling, as is common practice at INCAR.

Cold coke strength was assessed by the IRSID test following ISO standard procedure [18]. Coke reactivity (CRI) and post-reaction strength (CSR) were determined by the NSC method [19]. The ECE reactivity method recommended by the Economic Commission for Europe and modified by INCAR was also used [20].

Pore volume distribution in the range 7.4 to 15000 nm pore diameter was evaluated with a Carlo Erba 2000 mercury porosimeter. Surface areas were determined by CO<sub>2</sub> adsorption at 273 K, using the Dubinin-Radushkevich equation [21].

Total porosity of coke was measured according to ASTM standard procedure [22].

A study of the interfaces between metallurgical coke and the petroleum coke added was carried out, using polarised light microscopy. Interfaces were classified into four categories according to the type of contact present. A point counting technique was used to quantify interfaces [23]. The percentage of 'good' and 'poor' quality interfaces was calculated as a measure of the degree of bonding between the metallurgical coke matrix and the petroleum coke.

## RESULTS AND DISCUSSION

Characteristic data of coal blends and green petroleum cokes used are given in Table I. E1 and E2 are typical blends used by ENSIDESA, whose composition was calculated according to a mathematical model developed by this Company [24].

The present study is divided into two parts:

- 1) Coal blend E1 and petroleum coke A were used and carbonizations to laboratory and semi-industrial scale were carried out.
- 2) Coal blend E2 and petroleum coke B were used. In this case, as the study was focused on the influence of petroleum coke size, only carbonizations to semi-industrial scale were carried out.

As can be seen in Table I, blends E1 and E2 are very similar.

### Industrial blend E1 + Petroleum Coke A

#### Laboratory tests

Figure 1 shows the variation of the abrasion index with petroleum coke addition up to 20 wt%. There is a

Table I. Characteristics of blends (E1 and E2) and petroleum cokes (A and B) as received.

	E1	E2	A	B
<b>Proximate analysis</b>				
Moisture (wt%)	7.9	8.8	1.1	0.7
Ash (wt% db)	7.9	8.4	0.4	0.6
Volatile matter (wt% db)	25.8	25.4	12.7	12.5
<b>Ultimate analysis</b>				
S (wt% db)	0.80	0.65	4.57	1.33
C (wt% db)	83.5	83.4	88.2	90.1
H (wt% db)	4.7	4.6	3.9	4.3
N (wt% db)	1.5	1.6	1.6	2.2
O* (wt% db)	1.6	1.4	1.3	1.5
Gieseler maximum fluidity (ddpm)	666	721	--	--
<b>Petrographic analysis</b>				
Mean reflectance -R <sub>0</sub> - (%)	1.09	1.10	--	--
St.deviation of R <sub>0</sub>	0.19	0.20	--	--
Vitrinite (vol%)	73.0	69.9	--	--
Exinite (vol%)	6.0	4.6	--	--
Semifusinite (vol%)	6.6	8.8	--	--
Fusinite (vol%)	14.3	16.7	--	--
<b>Particle size analysis</b>				
> 3 mm (wt%)	10.6	14.8	0.0	29.5
< 2 mm (wt%)	77.3	77.3	0.0	56.0
< 1 mm (wt%)	56.0	59.5	98.5	27.6
< 0.5 mm (wt%)	39.5	42.4	97.8	16.5

\* Calculated by difference

clear tendency for this index to decrease as the amount of petroleum coke increases. As can be seen in Figure 2, ECE-INCAR reactivity follows the same trend as the abrasion, decreasing as the amount of petroleum coke increases.

Pore volume distribution, using mercury porosimetry, was determined in cokes prepared at laboratory scale with industrial blend E1 and different amounts of petroleum coke A. Figure 3 shows how the total volume of pores decreases as the amount of petroleum coke increases. Regarding the pore size distribution presented in Figure 3, it can be seen that the decrease in total pore volume is mainly due to the reduction in the micropores, while the volume of macro and mesopores remains almost constant.

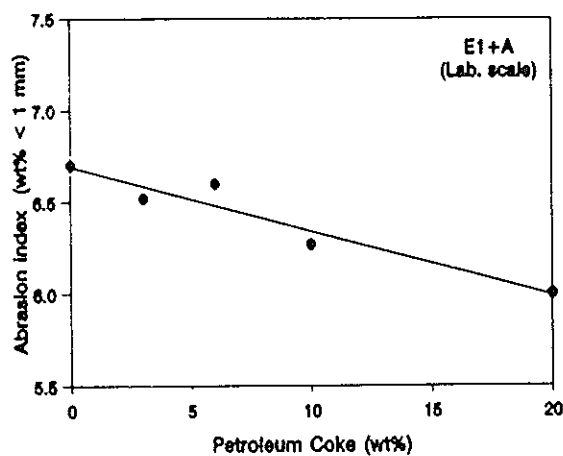


Figure 1. Variation of abrasion index with petroleum coke addition.

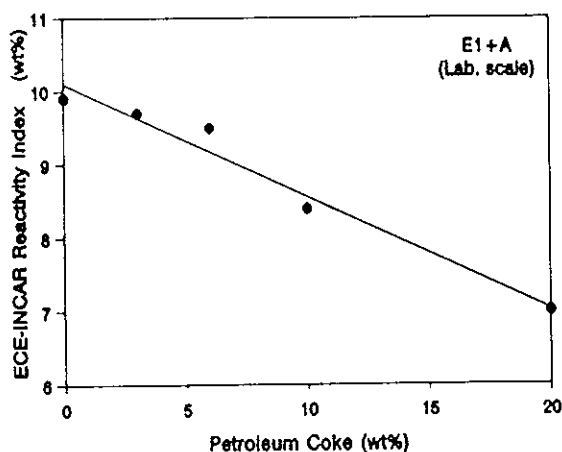


Figure 2. Variation of ECE-INCAR reactivity index with petroleum coke addition.

#### Semi-industrial scale

In order to check the results obtained at laboratory scale, another set of tests was carried out using the same blend E1 with 2, 4 and 6 wt% of the petroleum coke A, respectively. Table II presents the relevant characteristics of the blends and the coking conditions of these tests. The ash and volatile matter content of the blends decreases slightly as the petroleum coke increases. At the same time sulphur content increases, 6 wt% of petroleum coke being the maximum limit that permits sulphur percentages in the blend below 1 wt%. Maximum Gieseler fluidity, measured as ddp<sub>m</sub>, decreases significantly as the amount of petroleum coke in the blend increases.

Blends of E1 and different amounts of petroleum coke A were subjected to the Koppers-INCAR test in

Table II. Main properties of the blends and coking conditions (E1 + A).

	Petroleum Coke (wt%)			
	0	2	4	6
<b>Characteristics of the blends</b>				
Moisture (wt%)	7.9	7.6	8.0	6.5
Ash (wt% db)	7.9	7.8	7.3	7.2
Volatile matter (wt% db)	25.8	25.5	25.1	24.7
Sulphur (wt% db)	0.80	0.87	0.96	1.01
Gieseler max. fluidity (ddpm)	666	413	392	390
<b>Coking conditions</b>				
Bulk Dens. (kg/m <sup>3</sup> db)	717	713	702	712
Coking time (h)	18	18	18	18
Mean Flue Temp. (°C)	1259	1243	1249	1255
Internal Gas Press. (mbar)	112	60	44	34

order to study the variation of expansion and contraction, with the increase of petroleum coke in the blend. Figure 4 shows that as the amount of petroleum coke increases from 0 to 20 wt%, the contraction expressed in mm varies from -17 to -23, supporting the fact that petroleum coke has the effect of decreasing coking pressure. The values of the maximum internal gas pressure measured in the coking test carried out to semi-industrial scale are given in Table II. There is a noticeable decrease in maximum pressure as petroleum coke increases in the blend. These data are in agreement with the results obtained using the Koppers-INCAR test.

Mechanical strength to semi-industrial scale was measured using the IRSID test. Figure 5 shows the variation of both indices,  $I_{20}$  and  $I_{10}$  as the amount of petroleum coke increases in the blend. Mechanical strength increases, up to 4 wt% of petroleum coke in the blend, then diminishes for 6 wt% addition, although the values of the indices for cokes obtained from a blend containing 6 wt% petroleum coke are better than for those with no additive. Regarding mechanical strength, a 4 wt% addition of petroleum coke can be considered to be an optimum percentage for this blend.

Figures 6 shows the decrease in ECE-INCAR metallurgical coke reactivity with increasing amounts of petroleum coke addition. A similar trend is found for the reactivity index CRI, as can be seen in Figure 7. The increase of the CSR index is also shown in this figure.

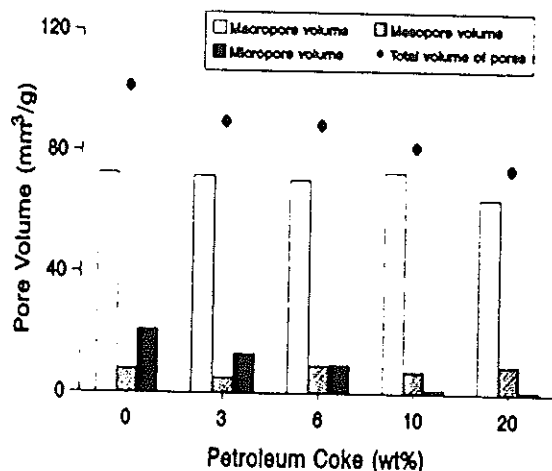


Figure 3. Pore volume distribution of metallurgical cokes obtained from blends E1 + Petroleum coke A.

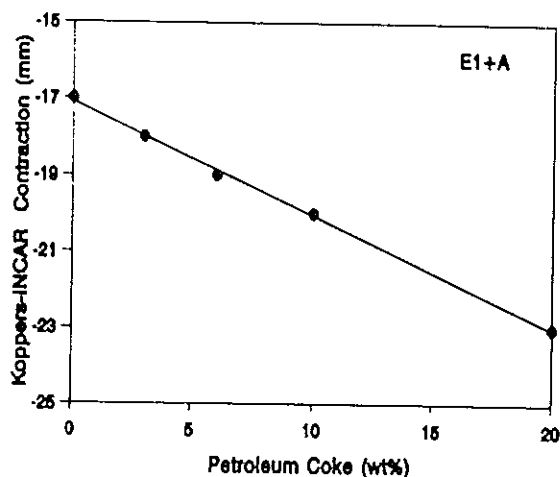


Figure 4. Variation of the Koppers-INCAR contraction with the addition of petroleum coke.

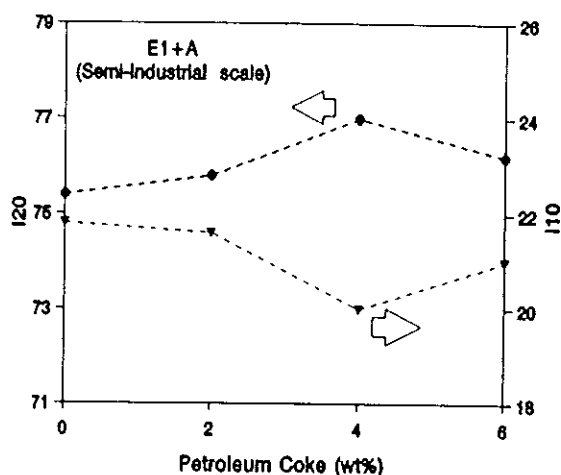


Figure 5. Variation of IRSID indices,  $I_{20}$  and  $I_{10}$ , with the addition of petroleum coke. Semi-industrial scale.

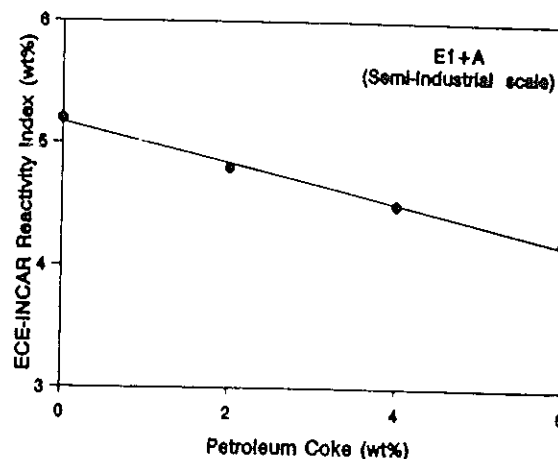


Figure 6. Variation of ECE-INCAR reactivity index with increasing amounts of petroleum coke added. Semi-industrial scale.

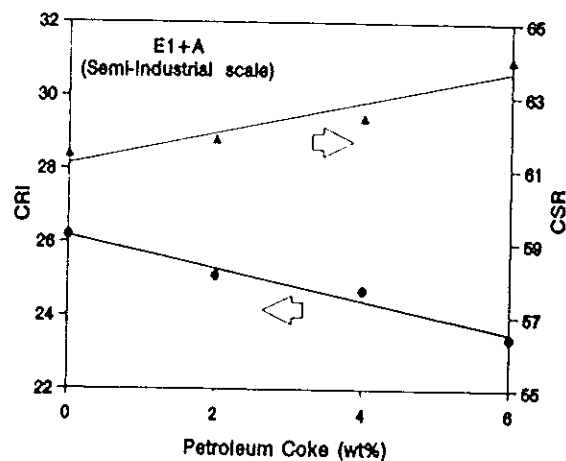


Figure 7. Variation of CSR and CRI with the addition of petroleum coke. Semi-industrial scale.

Total porosity for coke obtained to semi-industrial scale with petroleum coke addition, measured with water pycnometry [22], decreases slightly as the amount of petroleum coke increases, as can be seen in Figure 8.

In order to investigate the variation of the pore size distribution, mercury porosimetry was carried out on coke samples obtained from blends of E1 and petroleum coke A. The results obtained are shown in Figure 9. There is a reduction in the total volume of pores with little change in macro and mesopore volume and, as with cokes obtained to laboratory scale, a clear reduction of micropore volume is observed.

#### Industrial blend E2 + petroleum coke B

One of the factors known to influence most the incorporation of more or less inert additives to the

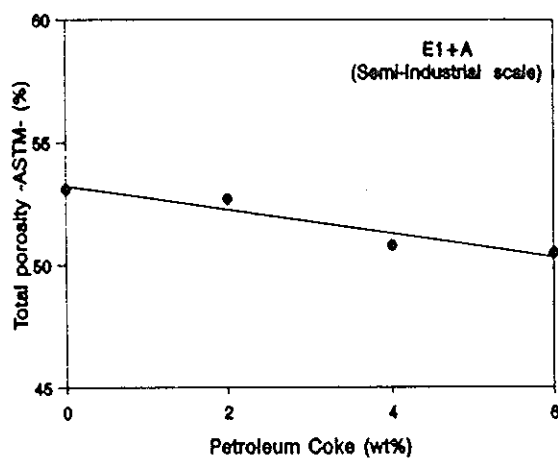


Figure 8. Variation of porosity with petroleum coke addition. Semi-industrial scale.

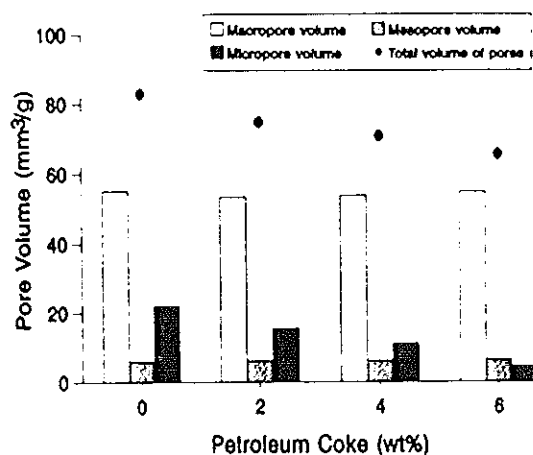


Figure 9. Variation of pore size distribution (mercury porosimetry) of cokes obtained from blends of E1+A. Semi-industrial scale.

metallurgical coke matrix is the particle size. In this section the addition of petroleum coke of different sizes is investigated. Due to the procedure used for the laboratory test, only tests to semi-industrial scale were carried out. Figure 10 illustrates the three particle size distributions used (termed: fine, medium and coarse).

Table III shows the coking conditions and the main characteristics of the mixtures of the industrial blend E2 plus 3 and 6 wt% petroleum coke. Characteristic data of blend E2 are included in Table I. As the measurement of Gieseler fluidity is carried out under standard conditions (particle size < 0.425 mm) the study of the influence of the particle size of petroleum coke on the plastic properties of the blends should be considered with caution. Table III shows the decrease in the internal gas pressure as the amount of petroleum coke increases in the

blend, but no effect of the particle size is observed in these values. These results are in agreement with those of semi-industrial tests using the mixture of blend E1 and petroleum coke A.

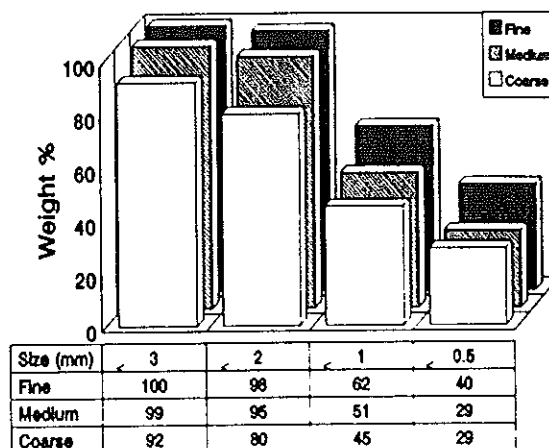


Figure 10. Particle size of the petroleum cokes used.

Koppers-INCAR tests were carried out on samples of the blend E2 with 3 and 6 wt% of petroleum coke B. As was said before for Gieseler fluidity, the particle size in this test is established (< 1 mm), so only one set of results is presented in Figure 11. The value of the contraction decreases with the addition of petroleum coke in agreement with the results presented above.

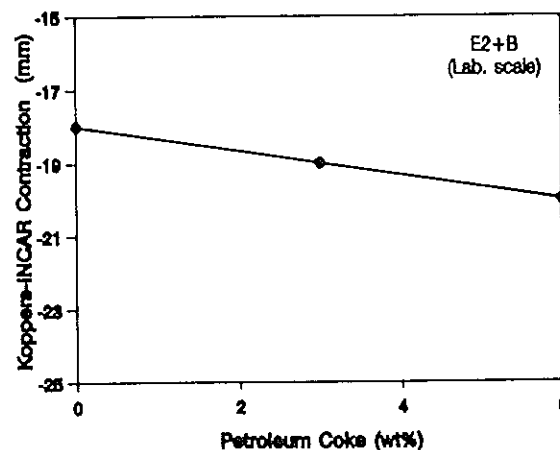


Figure 11. Variation of Koppers-INCAR contraction with the addition of petroleum coke.

Figures 12 and 13 show the variation of the IRSID indices,  $I_{20}$  and  $I_{10}$ , with the addition of the three different particle sizes of the petroleum coke used. Mechanical strength increases for 3 wt% addition and then, decreases for 6 wt% when coarse and medium petroleum coke particle sizes are used. For the particle size termed fine, there is an improvement for 3 wt%

addition and then mechanical strength is slightly lower for 6 wt% than for 3 wt% although it is better than the initial blend without petroleum coke addition.

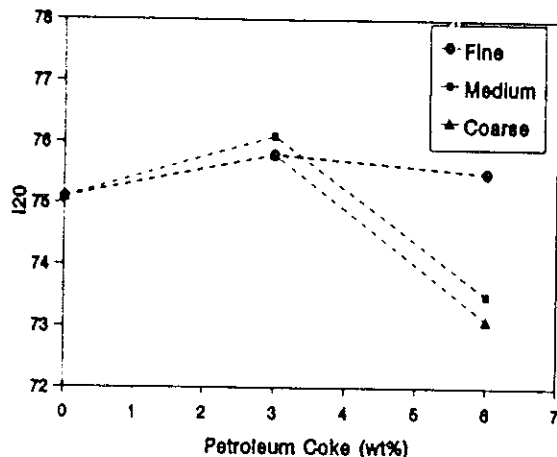


Figure 12. Variation of  $I_{20}$  with the addition of petroleum coke with three particle sizes. E2+B. Semi-industrial scale.

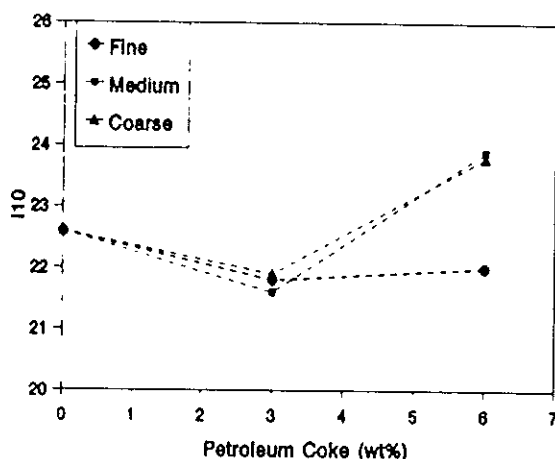


Figure 13. Variation of  $I_{10}$  with the addition of petroleum coke with three particle sizes. E2+B. Semi-industrial scale.

Coke reactivity was tested using both, ECE-INCAR and NSC methods. Figure 14 shows the variation of the ECE-INCAR reactivity index with the addition of increasing amounts of petroleum coke and for coarse and fine particle size. For 3 and 6 wt% of fine petroleum coke addition, there is a steady reduction in reactivity to  $\text{CO}_2$ . On the other hand, when coarse particle size petroleum coke is added, after remaining nearly constant for 3 wt% addition, it increases for 6 wt%. The results from the NSC test are shown in Figures 15 and 16. Figure 15 shows that there is a clear decrease in CRI index with fine petroleum coke addition, this value being the lowest for 6 wt%. In the case of coarse and medium

petroleum coke addition, 3 wt% hardly affects the CRI (slightly higher values than with fine addition) and 6 wt% clearly impairs the CRI in both cases.

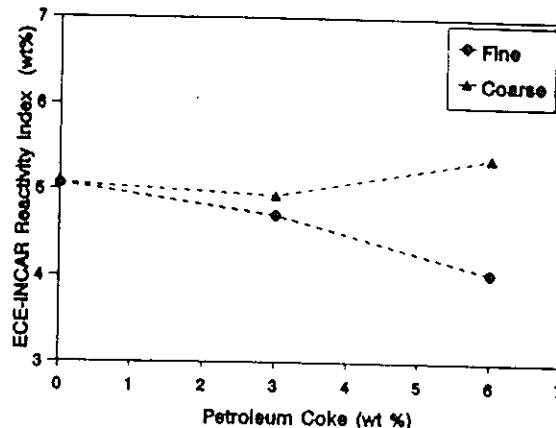


Figure 14. Variation of ECE-INCAR reactivity index with the addition of petroleum coke of different particle sizes.

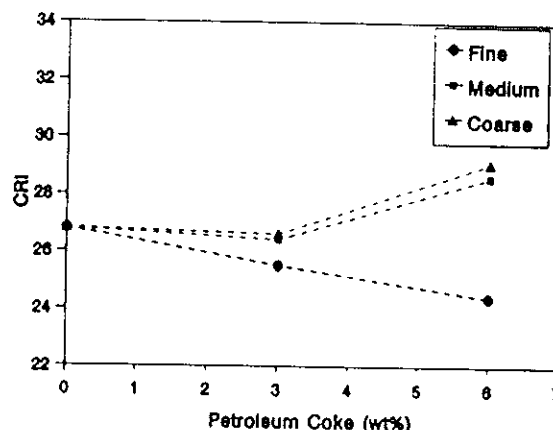


Figure 15. Variation of CRI with the addition of petroleum coke of different particle sizes.

Data for CSR clearly shows the same trend as for CRI (Figure 16). There is a clear improvement for the fine additions. The CSR index does not seem to change for the 3 wt% addition of medium and coarse particle size and clearly impairs for 6 wt% petroleum coke addition.

Figures 17 and 18 show the variation of porosity, calculated using helium and mercury picnometry and water picnometry, with the addition of petroleum coke with fine and coarse particle size. Both Figures display the same trend: lower porosity than industrial blend E2 when 3 and 6 wt% of fine sized petroleum coke, and 3 wt% of coarse particle size is added. On the other hand porosity is higher for E2 plus 6 wt% petroleum coke with coarse particle size.



Table III. Main properties of the blends and coking conditions (E2 + B).

Petroleum Coke (wt%)	E2	Coarse		Medium		Fine	
	0	3	6	3	6	3	6
<b>Characteristics of the blends</b>							
Moisture (wt%)	8.8	8.8	8.4	8.8	8.1	8.7	8.4
Ash (wt% db)	8.5	8.2	8.5	8.3	8.3	8.3	8.0
Volatile matter (wt% db)	25.5	24.9	24.7	25.2	24.7	24.9	24.2
Sulphur (wt% db)	0.66	0.65	0.69	0.66	0.70	0.68	0.71
Gieseler max. fluidity (ddpm)	721	464	380	534	391	588	446
<b>Coking conditions</b>							
Bulk density (kg/m <sup>3</sup> db)	712	703	712	702	717	696	703
Coking time (h)	18	18	18	18	18	18	18
Mean Flue Temperature (°C)	1252	1267	1248	1265	1250	1248	1249
Internal Gas Pressure (mbar)	60	40	4	44	4	48	4

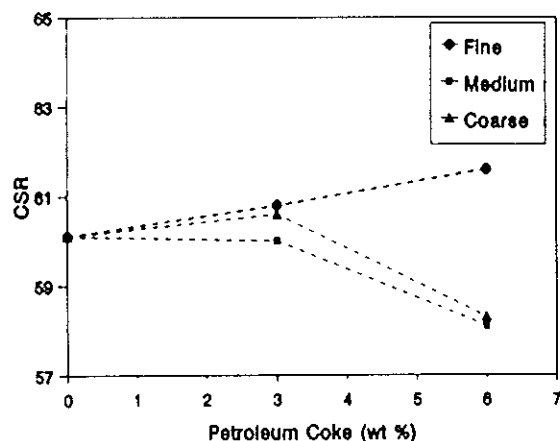


Figure 16. Variation of CSR index with the addition of petroleum coke of different particle sizes.

Metallurgical cokes obtained from mixtures of the industrial blend E2 and petroleum coke B with fine and coarse particle sizes were subjected to mercury porosimetry to determine pore volume distribution. These results can be seen in Figure 19. The most significant differences are due to micropore volume. For fine particle size petroleum coke, micropore volume decreases, but when coarse particle size is added there is a marked contrast between 3 and 6 wt% addition. In the first case, micropore volume decreases and in the second it has a higher value than the original sample. As was seen before for porosity, at 3 wt% level addition, there is no difference in the pore volume distribution with fine and coarse particle size petroleum coke addition. For 6 wt%, there is an increase in the micropore volume.

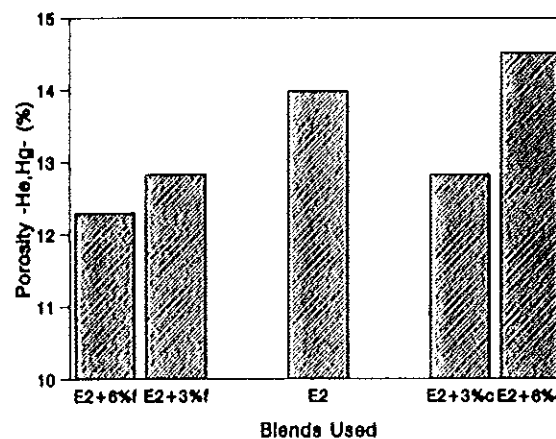


Figure 17. Variation of porosity (helium and mercury picnometry) with the addition of petroleum coke with different particle sizes.

The surface area was determined by CO<sub>2</sub> adsorption at 273 K. Figure 20 presents a comparison of the results obtained for 6 wt% fine and coarse petroleum coke addition. In agreement with the results referring to micropore volume, the highest surface area corresponds to 6 wt% coarse petroleum coke addition.

In order to explain the results obtained using petroleum coke of different particle sizes, a study of the interfaces between metallurgical coke and petroleum coke was carried out. Figure 21 shows the results of the quantitative interface study of coke samples obtained from E2 plus 6 wt% of fine and coarse petroleum coke. When coarse particle is used, there is an obvious increase in the percentage of fissured interfaces giving rise to 'poor' bonding and as a result more sites for cracks or CO<sub>2</sub> attack.

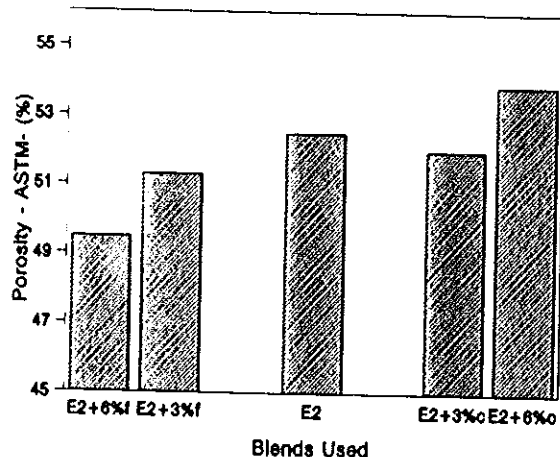


Figure 18. Variation of porosity (water picnometry) with the addition of petroleum coke with different particle sizes.

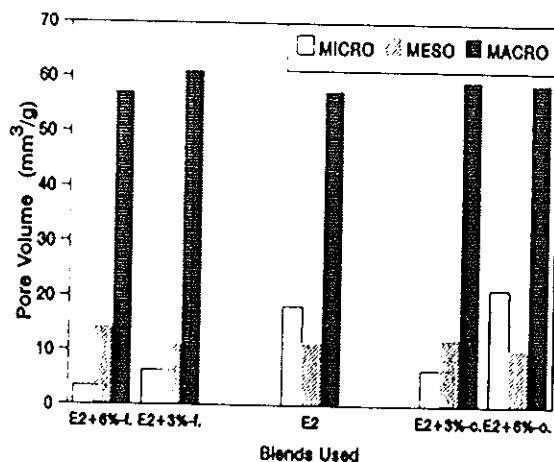


Figure 19. Variation of pore volume distribution with the addition of petroleum coke of different particle sizes.

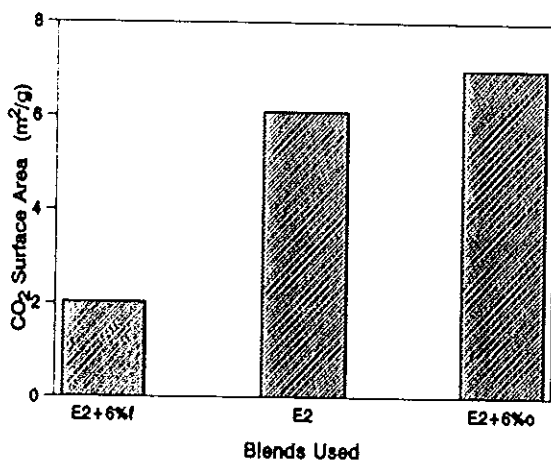


Figure 20. Comparison of the surface area obtained with 6 wt% fine and coarse petroleum coke addition.

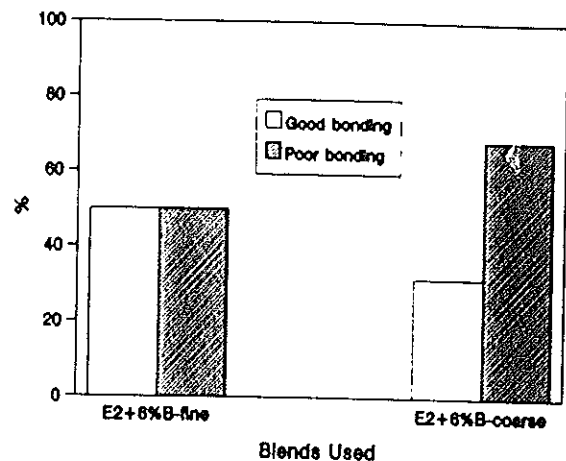


Figure 21. Quality of bonding between petroleum coke, fine and coarse particle size, and metallurgical coke.

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