RELATION BETWEEN TEXTURE AND REACTIVITY IN METALLURGICAL COKES OBTAINED FROM COAL USING PETROLEUM COKE AS ADDITIVE

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Introduction

Reactivity to CO_2 is, perhaps, the most important quality parameter used to evaluate the performance of a metallurgical coke in the blast furnace [1]. A lot of effort has been made to study how it is influenced by the different physicochemical characteristics of metallurgical cokes [2]. On the other hand, petroleum coke (PC) is frequently used as an additive in cokemaking and it is well known that its addition has an important influence on the properties of metallurgical cokes [3]. However, in many cases, it is not clear how and why metallurgical coke properties are affected by the addition of PC. The aim of this work is to study how addition of PC affects the reactivity and textural properties of the resultant metallurgical cokes. Thus, it was observed that PC addition to coking blends causes a reduction in the micropore volume and reactivity of metallurgical cokes. A correlation between these two parameters was found.

Experimental

Two coals, one -W- with low volatile matter content (ca., 16.8 wt%) and low Gieseler fluidity (9 ddpm) and the other -A- with medium volatile matter content (ca., 23.4 wt%) and high Gieseler fluidity (1118 ddpm); and two green petroleum cokes -R1 and RD- were used. Proportions of 4, 10 and 20 wt% of both PCs were mixed with W, while coal A was only blended in percentages of 4 and 10 wt%. Fluidity of the mixtures was assessed, using the Gieseler plastometer (ASTM D2639-74). Coal/PC blends were carbonized in a laboratory oven of 400 g capacity. The main characteristics of this oven as well as carbonization conditions are given elsewhere [4]. Pore volume distribution of pores with a radius of between 3.7 nm and 7500 nm was evaluated by mercury porosimetry. The pore volume was divided into three ranges: micropores ($r_p < 3.7$ nm), mesopores (3.7 nm $< r_p <$ 25 nm) and macropores (25 nm $< r_p <$ 7500 nm). Micropore volume was calculated by subtraction of macro- and mesopore volumes (obtained by mercury porosimetry) from the total pore volume -Vp- (calculated from apparent -Hg- and true -He- densities). DR-micropore volume was also determined, in a Micromeritics® ASAP 200 apparatus, by CO_2 adsorption at 273 K, using the Dubinin Radushkevich equation. Take into account the low adsorption capacity of the metallurgical cokes, about 5 g of each sample were used in order to be able to work within a range of acceptable precision. Reactivity of the metallurgical cokes was evaluated, using the CEE-INCAR procedure, as described elsewhere [5].

Results and Discussion

Table 1 summarizes the Gieseler plasticity of the mixtures as well as the main textural properties and reactivities of the resultant metallurgical cokes. As was expected, addition of petroleum coke produces a decrease in the plastic characteristics of the mixtures. Furthermore, for the same amount of PC added, the differences in the plastic properties between the two PCs can be attributed to differences in their degree of 'chemical activity', as has been reported in previous works [4,6]. This reduction in rheological properties contributes to a higher densification of the resultant metallurgical cokes (i.e. a smaller pore volume) [6]. In fact, results in Table 1 show a decrease in the pore volume with increasing petroleum coke addition. However, it should be pointed out that, while in the case of macro- and mesopore volume there are some fluctuations, the micropore volume decreases systematically as the amount of PC added increases, independently of the technique used in its assessment and although the two techniques evaluate micropores of different size. At the same time, petroleum coke addition produces a decrease in the reactivity of the metallurgical cokes [4,6]. This decrease can not be attributed to the dilution of some of the catalytic oxides of the ashes existing in the metallurgical coke [7], because even with a 20 wt% addition of PC this potential catalytic effect should remain the same. Therefore, for a given series (i.e. W-series or A-series) the main differences among the metallurgical cokes obtained are those due to the variations in the micropore volume and, in consequence, this decrease in the microporosity must be the main factor responsible for the decrease in the reactivity of metallurgical cokes. Figure 1 shows the relation between the CO_2 reactivity and the micropore volume calculated following the two methods mentioned above. In both cases, a good correlation was found between these two parameters.

Conclusions

The addition of green petroleum coke to coking coals produces a decrease in the plastic properties of the blends. This in turn results in a decrease in the pore volume of the resultant metallurgical cokes, which is mainly due to the reduction of the micropore volume. The good correlation found between micropore volume and reactivity of metallurgical cokes suggests that the latter could be a consequence of the former.

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Table 1. Gieseler maximum fluidity of the Coal/PC mixtures and main textural properties and reactivity of metallurgical cokes.

	Fluidity	Vp	Macro	Meso	Micro	DR-Micro	Reactivity
Coal+wt%PC	(ddpm)			mm^3/g			(%)
W	9	143.1	104.1	6.5	32.5	5.8	14.3
W+4R1	5	137.1	99.6	7.2	30.2	4.9	13.6
W+10R1	3	118.8	88.1	4.4	26.3	3.1	12.2
W+20R1	2	106.9	91.1	3.7	12.1	2.5	10.7
W+4RD	6	132.8	99.2	5.8	27.8	3.9	13.0
W+10RD	4	106.9	86.7	4.5	15.6	2.8	12.0
W+20RD	3	94.3	77.3	5.5	11.5	2.0	10.1
A	1118	114.7	78.3	7.5	29.0	3.8	16.1
A+4R1	704	104.2	75.3	5.3	23.6	3.5	15.8
A+10 R1	444	87.9	78.1	4.4	5.4	3.3	15.2
A+4RD	800	101.4	80.5	7.0	14.0	3.3	15.6
A+10RD	582	78.0	68.5	6.1	3.5	2.8	15.0

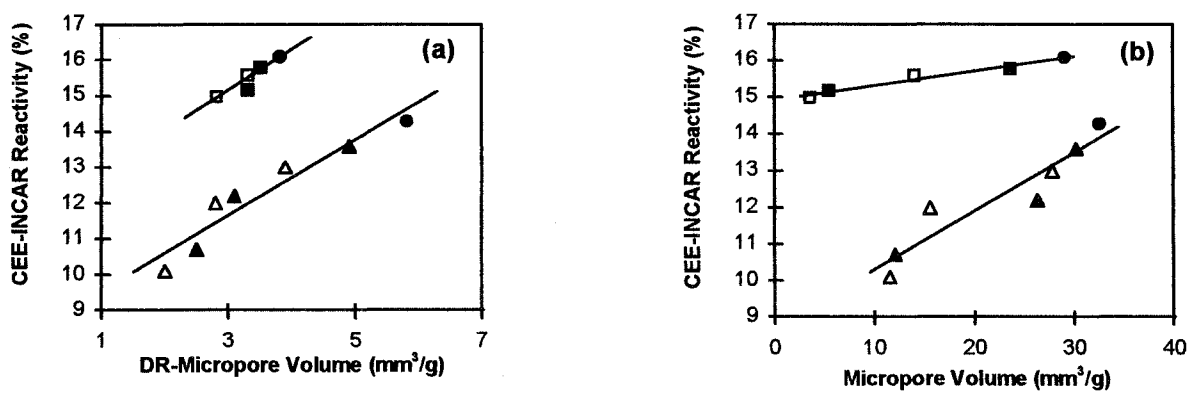

Figure 1. Relation between reactivity and micropore volume calculated **(a)** by CO_2 adsorption and **(b)** by mercury porosimetry and true (He) and apparent (Hg) densities. (■) A+R1; (□) A+RD; (▲) W+R1; (Δ) W+RD; (●) Coal with no PC addition.