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FOUNDRY COKE WITHOUT COAL: MORE THAN HALF-CENTURY OF PRODUCTION IN ARGENTINA[1]

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Abstract

A foundry coke industry is well established in Argentina, using blends of essencially petroleum coke and coal tar pitch for the production of cupola coke in non-recovery oven batteries. The paper includes a detailed discussion of the raw materials base (including coal tar pitch substitutes that have been used at some time), the criteria followed for the blend design, the main features and operation of the coke ovens, the coke quality obtained and the specificities of the behavior of this coke in the cupola.

Key words: Coke; Non-recovery oven; Petroleum coke; Coal tar pitch; Cupola; Recarburization.

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1 INTRODUCTION

Although massive coke production for blast furnace is carried out in conventional slot by-products batteries, using imported coals, foundry coke is produced in Argentina in non-recovery ovens with local raw materials, without using coal at all.
This way to produce coke was developed as a substitute for coke imports, in the sixties. Main raw materials are petroleum coke, produced at four domestic refineries, and coal tar pitch also produced locally, based on tar from the already mentioned slot coke ovens.
A typical blend includes 80% pet coke, 17% coal tar pitch and 3% coke fines. Coking time is in between 72 and 96 hours.
This paper describes the development of this particular coke production regarding raw materials, blend design, coke oven operation, coke quality and behavior in the cupola.

2 RAW MATERIALS

The base of the blends used in this industry is petroleum coke. A sketch of a typical plant is shown in figure 1 [1]. The delayed coker unit processes the vacuum residue and produces coke and coker gasoil [2]. These units are introduced in the oil refineries not only because of the flexibility in processing cheaper, heavier oils but because of profits for conversion of residual fractions into valuable fuel [3].
The process consists of heating a residual oil feed to its thermal cracking temperature in a furnace with multiple parallel passes. This cracks the heavy, long chain hydrocarbon molecules of the residual oil into coker gas oil and petroleum coke. Cracking begins in the furnace, continues in the transfer line, and finishes in the coke drum.

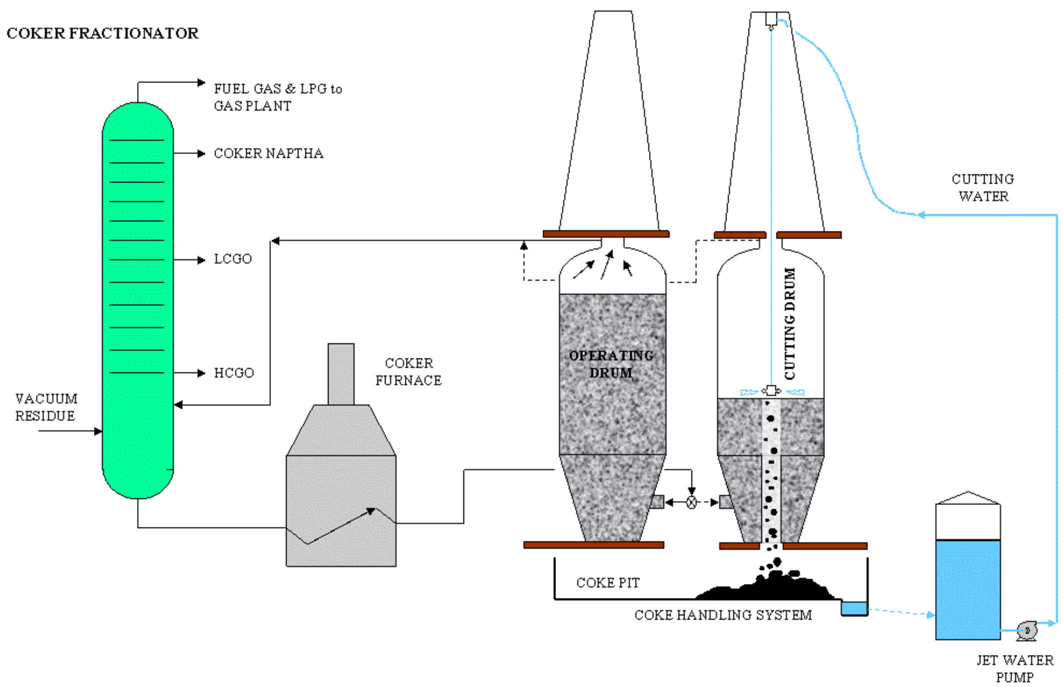

Figure 1. Typical delayed coker installed in an oil refinery, producing coker gasoil, and petroleum coke as a by-product [1].

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As cracking continues in the drum, gas oil and lighter components are generated in vapor phase and separate from the liquid and solids. The drum effluent is vapor only except for any liquid or solids entrainment, and is directed to a fractionation column where it is separated into the desirable boiling point fractions. Solid coke is deposited in the drum in a porous structure that allows flow through the pores. All solids and uncracked residual liquid produced from the vapor and liquid feed are intended to remain in the drum (figure 2).

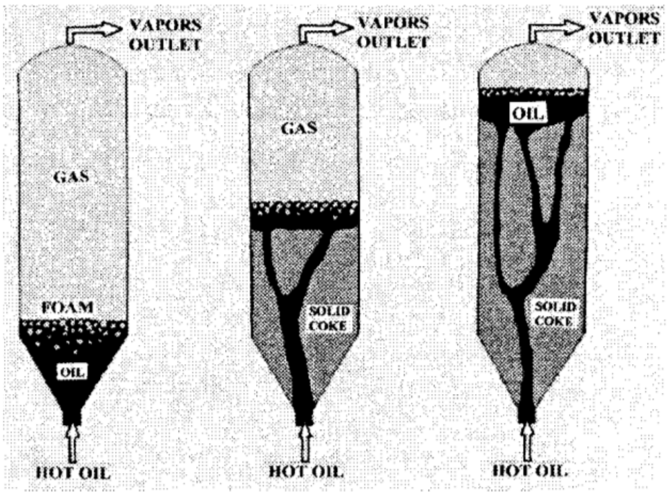

Figure 2. Delayed coking process advancing in one coking drum [4].

After the drum is full of the solidified coke, the hot mixture from the furnace is switched to a second drum. While the second drum is filling, the full drum is steamed to further reduce hydrocarbon content of the petroleum coke, and then water quenched to cool it. The top and bottom heads of the full coke drum are removed, and the solid petroleum coke is then cut from the coke drum with a high pressure water nozzle, where it falls into a pit for reclamation to storage.
World pet coke production was of some 100 Mt in 2008 (75 Mt in 2004). The production is dominated by the USA, but with an important production in Latin America (table 1).

Table 1. World production of petroleum coke in 2004 by region [5]

Region	Production (Mt/year)	% total
North America	46	61
Latin America	11	15
Asia (except China)	6	8
Europe	5	7
Middle East/Africa	2	3
China	5	7
Total	75	

Worldwide, most of the petroleum coke is used as a raw material for production of anodes for the primary aluminum industry; other uses include combustion (at cement plants), metallurgical coke production, Soderberg paste, graphite electrodes.
Four oil refineries have delayed coker in Argentina: YPF in Lujan de Cuyo, Mendoza and La Plata, Buenos Aires (0.93 Mt/year); Esso in Campana, Buenos Aires (0.35 Mt/y), and Shell in Avellaneda, Buenos Aires (0.2 Mt/year) [6]. So, annual production is in the order of 1.5 Mt. Due to the crude oil quality, pet coke sulfur content is usually low (between 0.5 and 1%). Foundry coke producers must compete

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with other industries for the supply: the conventional slot oven batteries at Ternium Siderar, San Nicolas, Buenos Aires, using up to 40% petroleum coke in the coal blend [5]; Copetro, a coke calciner for the production of anodes for the aluminum industry; producers of ferroalloys, for use as a reductant at submerged arc furnaces, and other smaller markets [6].
A typical analysis of current pet coke analysis for Lujan de Cuyo oil refinery is presented in table 2 [7].

Table 2. Typical Lujan de Cuyo oil refinery petroleum coke analysis [7]

Variable	Value
Moisture, %	5
Volatile matter, %	12.7
Ash, %	0.3
Fixed carbon, %	87
Sulfur, %	1.2
Calorific Power, kCal/kg	8,500
Hardgrove Index	50

The second raw material is coal tar pitch. It is produced in Carboquimica del Parana, Ramallo, Buenos Aires, departing from coal tar supplied by Ternium Siderar steel plant (www.carboquimicadelparana.com). The production process is summarized in the right part of figure 3. Tar is heated to temperatures up to 400^{o}C in specially designed distillation stills. This removes moisture, naphthalene, light creosote oil and heavy creosote oil from the coal tar. The resultant product is the coal tar pitch.

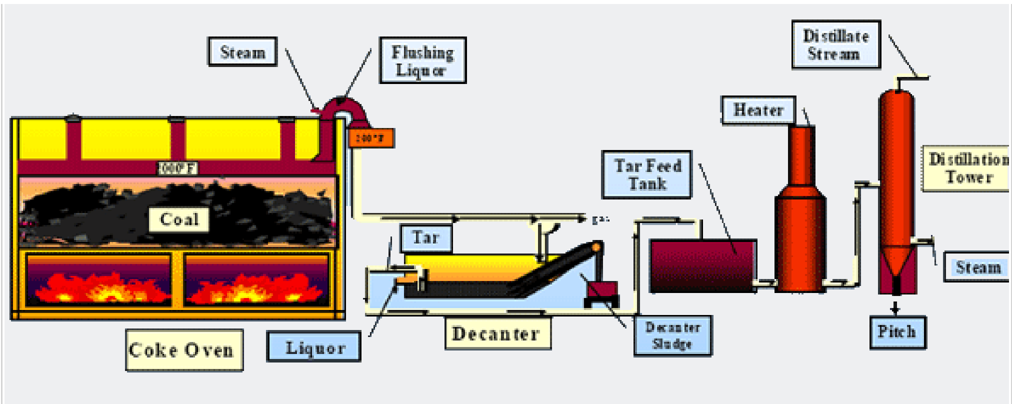

Figure 3. Sketch of a typical plant for production of coal tar pitch from coking coal [8].

A typical proximate analysis of coal tar pitch is presented in table 3.

Table 3. Proximate analysis of coal tar pitch

Variable	Value
Moisture, %	5
Volatile matter, %	79.20
Ash, %	5.27
Fixed carbon, %	15.53

In periods where coal tar pitch supply was scarce, the search for substitute materials was strong. Coal tar pitch from Colombia, supplied in 200 l drums, was the easiest substitution, although with additional preparation work. Other have been oxidized

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asphalt 120/5, produced in batch reactors where hot liquid asphalt was air injected and the dumped to a pool, where it was cut after solidification. That asphalt was cut into pieces in a special machine and then incorporated to the blend, before grinding. A typical specification of asphalt for coke production is presented in table 4 [9].

Table 4. Specification of oxidized asphalt for metallurgical coke production [9]

Variable	ASTM Standard	Value
Compliance point (ring and sphere), oC	D36	120-125
Penetration to 25 °C, 100 g, 5 s, 1/10 mm	D5	3-6
Ignition point (Cleveland V.A.), °C (minimum)	D92	370
Relative density, 25/25 °C, (minimum)	D70	0.990
Solubility in C_2S, % (minimum)		99
Heating loss (5Hs, 163 oC), % (maximum)	D6	0.1

Also, asphaltite mined in Mendoza or Neuquen provinces has been added to the blend, as a coal tar pitch substitute. This is a naturally occurring, hard, solid bitumen whose chief constituents, asphaltenes, have very large molecules. Though related to asphalts, asphaltites differ from them chemically and physically in some ways. Unlike asphalts, asphaltites do not fuse readily. A typical analysis of asphaltite of Minacar Mine, Mendoza, is presented in table 5.

Table 5. Analysis of asphaltite from Los Castanos Mine, Mendoza, Argentina [10]

Variable	Value
Moisture, %	0.5
Fixed Carbon, %	62.4
Ash, %	3.7
Upper Calorific Power (cal)	8,890
Sulfur, %	3

Coke fines are recovered and recycled to the coal blend to improve coke size by acting ion the fissures estructure.
Finally, for certain cast iron producers asking for lower recarburization power in the cupola to obtain hot metal with lower carbon content, in some cases imported coking coals; domestic high-ash Rio Turbio steam coal; sand or soil have been added.

3 BLEND DESIGN

As mentioned, the most common blend design is in the order of 80% petroleum coke, 17% coal tar pitch and 3% coke breeze. Being the most expensive raw material, it is always desirable to decrease coal tar pitch content in the blend, but with lower values the decrease in mechanical strength is significant.
For the aforementioned blend, taking into account the proximate analysis in table 1 and 2, the calculated blend proximate analysis is presented in table 6. Compared with standard coal-based coking blends, the ash content is much lower, fixed carbon is higher and volatile matter is in the same order.

Table 6. Calculated proximate analysis of a blend with 80% pet coke, 17% coal tar pitch and 3 % coke breeze

Variable	Value
Volatile matter, %	24.2
Ash, %	1.04
Fixed carbon, %	74.76

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For coal tar pitch substitution, oxidized asphalt was added but in higher proportion, 27% for the case without any coal tar pitch at all. Oven operation was to be watched more carefully when using all-asphalt as a binder, because volatiles tended to burn faster, thus influencing fissuring pattern and giving a smaller coke size as a result.
As already mentioned, asphaltite took part in the blend to replace coal tar pitch, but its addition was limited to some 5%, due to the high sulfur content. A particular blend that have been used for coke consumed in calcium carbide production through submerged arc furnace had 30-35% asphaltite, 5-10% coal tar pitch and the balance was pet coke [10].

4 COKE OVEN OPERATION

There are six plants, belonging to five companies. Two of them are located in Lujan de Cuyo, Mendoza; Las Parejas, Santa Fe; Quilmes, Buenos Aires, General Rodriguez, Buenos Aires and Tandil, Buenos Aires (figure 4). The companies involved are Las Palmas S.R.L. (www.laspalmas.com.ar); Mecaf Argentina S.R.L. (www.mecafargentina.com.ar); Sidymetal S.A. (www.sidymetal.com.ar); Minera Lujan S.R.L. (www.mineralujan.com.ar) and Procamet S.A. Besides coke, some of them produce recarburizers for the steel and foundry industry and carbonaceous material for sand molds (sea coal substitutes).

Figure 4. Location of the six non-recovery foundry coke facilities in Argentina.

The ovens are of the non-recovery type, with rectangular plant view and arched roof, built in low alumina refractories (figures 5 and 6).

ISSN 2176-3135

Figure 5. Typical non-recovery coke oven design [7].

Figure 6. General views of one of the plant [7].

The total number of ovens could be estimated in 120. Four of them are of the heat-recovery type, with sole heating by off gas. Supposing continuous four-day operation and four metric tons of coke per oven, annual capacity would be around 40,000 t. Some production is exported to Chile, Uruguay and Brazil.

In figure 7 a scheme of the process is presented. The blend of petroleum coke and coal tar pitch, with some coke fines, is mixed, milled and transported to a charging hopper. Charging is usually carried out through a hole in the top of the oven. The leveling is carried out manually. If necessary, the charge is lighten with the help of fuel, volatiles combust and the coking process starts.

The process may take three to four days (two days in ovens with sole heating through heat recovery from off-gas). During it, it is important to keep a regulation of combustion through the management of air input to the oven, through an opening in the front door. The aim is to obtain a high quality coke, without incurring in combustion losses.

ISSN 2176-3135

Coke is quenched partially inside the oven and partially outside, one manually extracted. Before dispatching to customers, screening through 50 mm screen is often carried out.
Oven control is carried out manually, by moving (opening or closing) plate valves located at the back of the oven, to manage air input. One typical problem, common to other horizontal non-recovery oven operations, is combustion loss. As air comes in contact with coke, if not properly controlled, some loss may happen. This is generally estimated by oven builders as 3 to 5%.

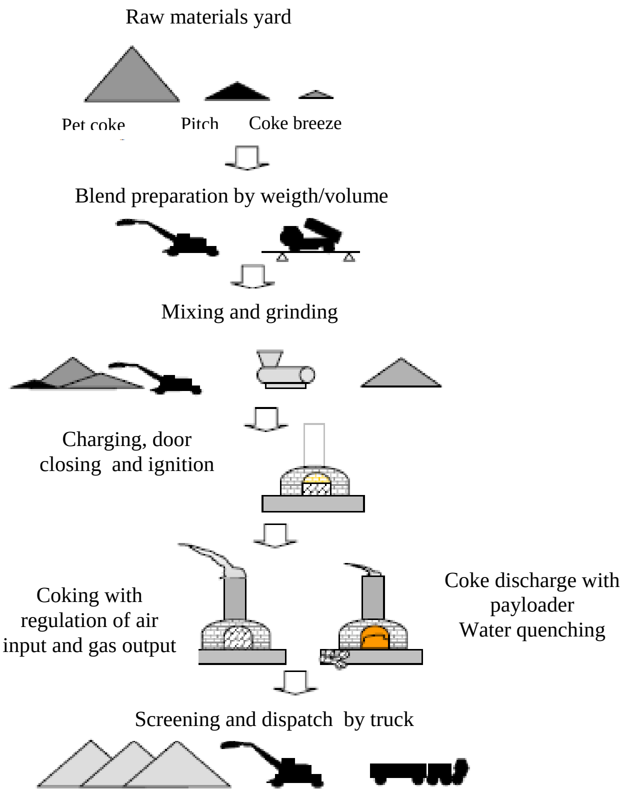

Figure 7. Scheme of the process for foundry coke production without coal in Argentina [11].

5 COKE QUALITY

As already mentioned, the raw materials let assure a coke with very low ash content. A typical specification is presented in table 7 [12].

Table 7. Specification of coke quality of one of the domestic suppliers [12]

Product	Volatile matter (%)	Ash (%)	Moisture (%)	Sulfur (%)	Fixed carbon (%)	Size >70 mm (%)
High recarburization/Low S	1.7	1.5	4	0.6	96 min	95
Medium recarburiz./Low S	2.5	5	4	0.6	93 min	95
Low recarburization	2.5	9	4	0.7	89 min	95
Medium recarb./Medium S	2.5	5	4	1.0	93 min	95

ISSN 2176-3135

These plants control coke mostly by size, moisture, ultimate analysis, sulfur and in some cases, ATSM tumbler tests. Occasionally, MICUM tests and reactivity determinations have been carried out by third parties [11].
Most foundries evaluate this coke based on visual aspect and behavior during cupola operation; some of them request ultimate analysis to commercial labs. Just the larger ones, dedicated to the automotive industry, carry out some testing (moisture, ultimate analysis, sulfur).
Regarding the coking mechanism, it should be somewhat different from that of coal-based coking. Coal tar pitch softens at temperature well below the softening range of coking coals. The binding process should have similarities with what occurs in Soderberg paste for submerged arc furnace electrodes, common in the ferroalloy industry, or with artificial graphite electrodes for electric arc furnaces and ladle furnaces used in the steel industry, as these processes are also based on petroleum coke and coal tar pitch.
Some light on the mechanisms involved could be taken also from the studies of steel companies using a high proportion of petroleum coke in their coking blend [4, 13-14].

6 COKE BEHAVIOR IN THE CUPOLA

The most interesting feature presented by this coke from the point of view of cupola operation is the negligible ash content. It is well known that carbon pick-up by liquid iron is limited by the viscous film of molten ash surrounding the coke in the bed [15]. This is not the case with this coke; so, recarburization occurs in faster and deeper way than with conventional foundry cokes. This was what brought about the existence of so called low, medium and high recarburization cokes, as in table 1, a classification which does not exists in other markets.
The way to make low or medium recarburization coke was to add to the blend imported coking coal, domestic Rio Turbio high ash sub bituminous high-volatile coal, sand or just soil. These ways gave completely different results in cost and quality of the coke. Soil addition was the cheapest one, and chemistry was not very different from coal ash; but mixing must be watched closely. Sand was easier to distribute, but a much more acid slag was obtained. The addition of sub-bituminous coal was limited because abrasion strength was affected (and most probably, coke reactivity, too). Use of imported coking coal was at times requested by customers, not only to regulate ash content/recarburization behavior, but for other reasons, related with graphite inheritance and defects in some castings (probably not justified). Here the problem was the low production volume, which meant that shipments have to remain in the coal yard for very long time, submitted to weathering, with the well known result of degradation in coking properties.
Another consequence of the absence of ash is the use of a smaller proportion of limestone in the charge, to obtain the same slag chemistry as with conventional coke.
From time to time, this coke competes with imported coke, usually produced departing from bituminous coal blends. At times, coke produced at the already mentioned slot oven battery at the steel plant is also in the market, too. In both cases, cupola practice must be changed to fulfill the aimed sulfur and carbon in the hot metal, as well as to have the right slag chemistry and hot metal temperature.
For instance, in figure 8 the evolution of slag basicity with coke ash content is presented for a coke with a 50% SiO_2 content in the ash, and a constant addition of limestone [11].

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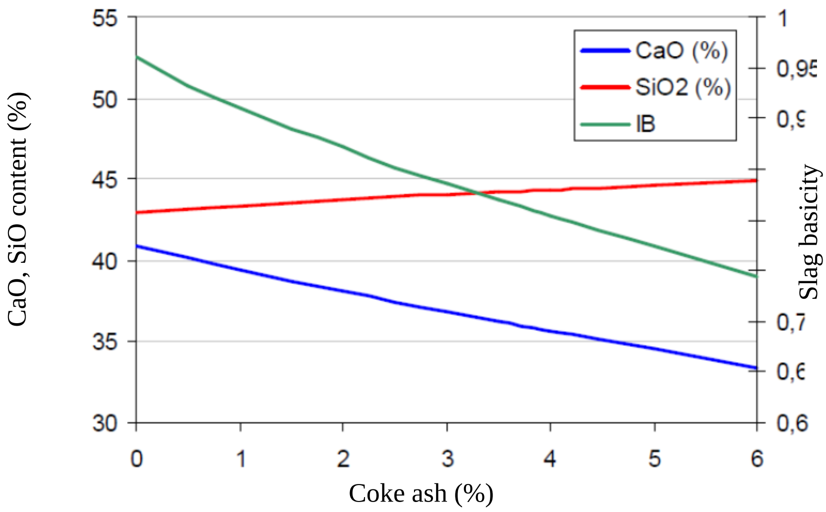

Figure 8. Evolution of slag basicity with coke ash content, for a constant limestone addition, and 50% SiO_2 in coke ash [11].

This change in slag basicity implies a change in slag viscosity, which influences recarburization, and in its desulfurization ability, as presented in figure 9. A problem occurring at times when using so called “low recarburization” (higher ash) coke was that if for any reason, recarburization was lower than expected, and the countermeasure was to add more coke, not only recarburization did not improve, but desulfurization started to worsen (limestone addition was not modified).

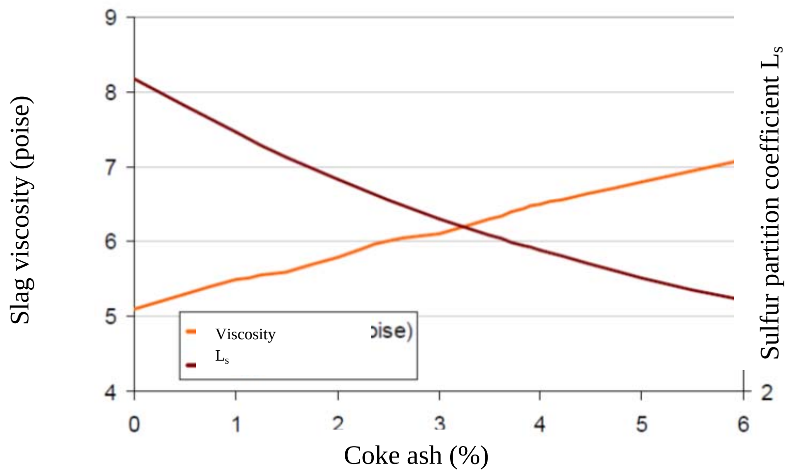

Figure 9. Evolution of calculated slag viscosity and calculated sulfur partition coefficient with coke ash content, for a constant limestone addition, and 50% SiO_2 in coke ash [11].

7 CONCLUSIONS

Due to the local availability of a high quality petroleum coke and of coal tar pitch, as well as the lack of domestic supply of coking coal, the foundry coke industry in Argentina is producing coke without using coal since more than a half century. This coke is produced at six sites, and is consumed locally and exported to neighbor countries like Chile and Brazil. Coke batteries are of the non-recovery type; some ovens are equipped with heat recovery.
Coking mechanism should be different from what is known from normal coking operation with coal. Pitch softens at much lower temperatures than coking coals.

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A particular aspect to be taken into account with this coke is the very low ash content. This is of course advantageous, but its influence on recarburization rate must be taken into account. Coke is divided in low, medium and high recarburization rate. To obtain that low or medium recarburization rate, additions are made to the blend, following different strategies.

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