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## Original Article

# Evaluation of spent pot lining (SPL) as an alternative carbonaceous material in ironmaking processes

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## ABSTRACT

Integrated ironmaking plants equipped with blast furnaces utilize several types of carbonaceous materials for hot metal production. Among them, coal is used for cokemaking and PCI, being the most expensive raw material for primary iron production. Due to high costs, ironmaking plants are constantly searching for alternative carbonaceous materials. Spent pot lining (SPL) is a carbonaceous waste from primary aluminum production which could potentially participate in the ironmaking with consolidated raw materials. With that in mind, a SPL first cut sample was characterized aiming its application in the ironmaking industry. Proximate, sulfur and calorific value determinations were carried out, as well as ash chemical (XRF) and mineralogical (XRD) compositions. In addition, the material's density, HGI, cold mechanical strength (breakage, abrasion and compression), reactivity and hot mechanical strength were assessed. The results obtained were compared with ironmaking most common carbonaceous materials and its potential and difficulties were discussed.

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## 1. Introduction

Carbonaceous materials are considered essential in the ironmaking industry, especially for integrated metallurgical works, which are equipped with blast furnaces. In light of that, coal is the main carbon source, used either as fuel in pulverized coal injection or as metallurgical coke, obtained by

carbonizing an appropriate coal blend at temperatures up to 1100 °C.

In recent years, international coal market has experienced considerable volatility giving rise to a notorious variability in coal prices and problems related to supply [1]. For that reason, the search for alternative carbon sources to partially substitute coals and coke are encouraged. This is particularly important for countries such as Brazil, which fully depend on coal imports to supply its ironmaking industry demands. Some known coal alternatives are natural gas injection and mini blast furnaces (charcoal based), the latter being relatively common in Brazil. Besides of that, upcoming technologies focusing on alternative sources of carbon are being developed, such as

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adding biomasses and plastics to cokemaking [2–4], pulverized coal injection (PCI) [5,6] and new reduction reactors [7]. In this scenario, ironmaking plants usually show potential and interest in incorporating alternative carbonaceous materials throughout its production processes, including cokemaking, iron ore sintering and blast furnace.

In ironmaking industry, carbonaceous materials can have different roles depending on its application. They can be used as fuel, reducing agent, permeable support or a combination of these, e.g., metallurgical coke. To attain high performance, these materials must achieve a set of quality parameters regarding each process, such as carbon and ash content, calorific value, reactivity and physical characteristics (mechanical strength, density and porosity).

In primary aluminum production, alumina is converted to metallic aluminum by electrolytic reduction in Hall-Héroult cells. In this process, electrical current enters the cell through carbon anodes and passes through the electrolyte bath before being collected by carbon cathodes at the bottom of the cell. The electrolyte is essentially a solution that contains alumina ( $\text{Al}_2\text{O}_3$ ) dissolved in cryolite ( $\text{Na}_3\text{AlF}_6$ ), held in temperatures around  $960^\circ\text{C}$  [8]. Over time, the cathode carbon blocks become impregnated with fluoride containing salts and other chemicals used in the alumina reduction process. Eventually, the cell fails after 3–8 years of operation and the carbon cathode “potlining” is removed and the shell is re-lined. The resulting waste material is called SPL (spent pot lining), which can be easily separated in two well-defined fractions [9,10]: a carbon rich fraction constituted of old cathode (1st cut) and a non-carbon fraction mainly constituted of old refractory, insulating bricks and ramming paste (2nd cut). The SPL first cut is of main interest for this work, although its compositions usually present inorganic compounds such as  $\text{Na}_3\text{AlF}_6$ ,  $\text{NaF}$ ,  $\text{CaF}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{NaAl}_{11}\text{O}_{17}$  [11]. Besides of that, due to the presence of cyanide compounds and soluble fluorides, SPL first cut is classified as a hazardous waste by United States Environmental Protection Agency (EPA – D088 [12]). According to Courbariaux et al. [13], cyanides can react with water to form highly toxic hydrogen cyanide and a caustic solution containing dissolved cyanides. In the meantime, reactions occurring inside SPL result in the emission of hydrogen and methane, which in unventilated areas can lead to explosions. Moreover, on a long-term basis, leaching of fluoride can translate into the contamination of rainwater runoff if left uncontrolled.

According to Pawlek [14], it is estimated that world's aluminum smelters generate about a million tons of SPL annually, which is commonly disposed in landfills with risk of soil contamination due to leaching [15]. Regarding SPL reutilization, some studies have focused in using it in clinker production to reduce cement works energy costs [16–18]. In addition, Von Krüger [9] presented promising results to use SPL first cut as an auxiliary reducing agent, with additional fluxing characteristics, in ferro silicon manganese smelting. Lazarinos et al. [19] have also investigated SPL first cut gasification in a pilot scale plant, reporting that cyanides were totally destroyed during combustion and the conversion achieved was approximately 21%. However, industrial applications for this residue are still relative restricted.

Taking into consideration Brazilian companies' strong dependence on imported coals, the potential of absorption of

carbonaceous materials by integrated ironmaking plants and the need to find sustainable ways to reutilize SPL, the study of this residue aiming its use in the ironmaking industry is convenient. This work carried out the characterization of the first cut of a SPL sample from the Brazilian aluminum industry, aiming its application into ironmaking processes. SPL capabilities regarding its use for blast furnace, cokemaking, PCI and iron ore sintering was discussed in comparison with the commonly carbonaceous materials used in ironmaking.

## 2. Methods

### 2.1. Raw materials

In order to access SPL chemical, physical and metallurgical properties as a carbonaceous material for the ironmaking industry, a sample of SPL's first cut was obtained from a Brazilian aluminum industry. The first cut, which is rich in carbon, was separated from the refractory rich fraction by common dismantling practices and crushed after to a particle size between 75 and 25 mm. After that, the material was simply random sampled accordingly to standard procedure in order to obtain a sample of approximately 15 kg. This sample was crushed to a maximum size of 25 mm using a laboratory jaw crusher, homogenized and further prepared according to each analysis requirements. Details regarding each characterization technique are presented next.

### 2.2. Chemical characterization

The reducing gas and energy generation potentials of any carbonaceous material are closely related to its chemical composition. Thus, determining SPL components and proportions is essential in order to evaluate its applicability regarding ironmaking processes requirements. In that sense, proximate analysis (ASTM D3172), sulfur analysis using a Leco SC 132 (ASTM D4239), calorific value (ASTM D5865) and ash composition were conducted. The ash chemical and mineral compositions were obtained by X-ray fluorescence spectroscopy (XRF) (ASTM D4326) and X-ray diffraction, respectively. The latter was realized in a Siemens D5000 diffractometer using Cu source, scanning goniometry interval of 1 second for  $0.02^\circ$  of degree from  $4$  to  $74^\circ$ , respectively. The ash samples were obtained from the SPL first cut combustion using a muffle furnace at  $1000^\circ\text{C}$ .

### 2.3. Physical characterization

In order to evaluate the application of SPL first cut in industrial scale it is imperative to know its physical and mechanical characteristics to proper understand the material behavior regarding its handling, preparation and utilization.

SPL first cut porosity was indirectly measured through apparent and real density (ASTM D167), both determined by picnometry for samples with particle size between 4 and 7 mm and under  $75\ \mu\text{m}$ , respectively. Since carbonaceous materials are usually crushed or grinded in order to obtain suitable particle size ranges, SPL first cut hardgroove grindability index (HGI) was determined according to ASTM D409. The mechanical

properties of SPL first cut were evaluated via compression and drum tests. The compression experiments were carried out in a hydraulic press utilizing cylindrical specimens (10 mm in diameter and height). The drum test was realized according to ASTM D3402 in order to evaluate SPL first cut resistance against impact and abrasion. After tumbling, both stability and hardness factors were obtained by the percentage of remaining material over 25 and 6.3 mm, respectively.

#### 2.4. Metallurgical characterization

In counter current reduction reactors, such as the blast furnace, the reducing agent needs to act as fuel, reducing gas generator and permeable support, being the only solid material that supports the iron bearing burden and provides a permeable matrix necessary for slag and metal to percolate and for the hot gases to flow upwards. For that, carbonaceous materials demand adequate mechanical strength at high temperatures and reducing atmospheres. To evaluate those properties, CRI (coke reactivity tests) and CSR (coke strength after reaction) are the most used techniques and were carried out according to ASTM D5341. Coke reactivity index measures the weight loss of a sample reacting with CO<sub>2</sub> at 1100 °C for 2 h. The reacted residue is submitted to tumbling and the remaining material above 9.5 mm determines the material's strength after reaction.

### 3. Results

#### 3.1. Chemical characterization

The results regarding SPL first cut proximate, sulfur and calorific value analysis are shown in Table 1. The results obtained were within the ranges usually found in the literature [10]. From the data obtained by proximate analysis, it is notable that the material is comprised mainly by fixed carbon and ashes, with very little amount of volatile matter.

In ironmaking, fixed carbon is related to the material capacity to produce energy and reducing gases. In that sense, most of the processes require carbonaceous materials with high fixed carbon. SPL first cut presents fixed carbon and calorific value of 74.3% and 6408 kcal/kg, respectively. In addition to that, the ash content of the material was 23.3%, which according to Shi Zhong-ning et al. [11] can vary up to 50% depending on electrolytic cell conditions. In comparison to that, virgin cathode blocks present higher values of fixed carbon and calorific value, since its ash content is usually below 3% due to electrical and thermal conductivity needs [20]. The first cut significant higher ash comes from liquid electrolyte infiltration into the pores of carbon blocks during operation [21].

**Table 1 – SPL first cut chemical characterization.**

	Ash (wt. % db)	VM (wt. % db)	FC (wt. % db)	Sulfur (wt. % db)	Calorific Value (wt. % db)
SPL	23.3	2.5	74.3	0.1	6409

db, dry basis; VM, volatile matter; FC, fixed carbon.

Generally, in ironmaking, high content of inorganic matter is associated with inferior energetic yield and formation of higher slag volume.

The SPL volatile matter yield (2.5%) is very low, since cathode carbon blocks are usually manufacture at temperatures of 1200 °C (depending on the type of cathode, up to 2800 °C, if graphitization is necessary), besides of being utilized in temperatures up to 900 °C during years of operation [11,20]. It is known that volatile matter has great influence on the reactivity of carbonaceous materials, since its release can significantly increase the surface area available for reaction. Among the processes used in ironmaking, the volatile matter yield of carbonaceous materials varies significantly depending on its applications.

Sulfur content obtained for SPL first cut was 0.1%. This value is considered small, being justified by the low sulfur in the raw materials used for cathode manufacture, as well as cell operational conditions. This characteristic is valuable for iron and steelmaking, since sulfur is a deleterious element for steel properties and its elimination in the blast furnace and hot metal refining processes are expensive.

Ash composition and mineralogy are shown in Table 2 and Fig. 1, respectively. From Table 2, it can be observed that SPL first cut mineral matter is majorly comprised of compounds containing fluorine, sodium, aluminum and calcium, which accounts for 94% of its total inorganic constituents. In what regards ash mineralogy, the following mineral phases can be observed (Fig. 1): sodium fluoride (NaF), calcium fluoride (CaF<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), aluminum carbide (Al<sub>4</sub>C<sub>3</sub>) and albite (NaAlSi<sub>3</sub>O<sub>8</sub>). As expected, the presence of such compounds indicates that SPL inorganic matter is mainly derived from electrolyte infiltration, as already commented.

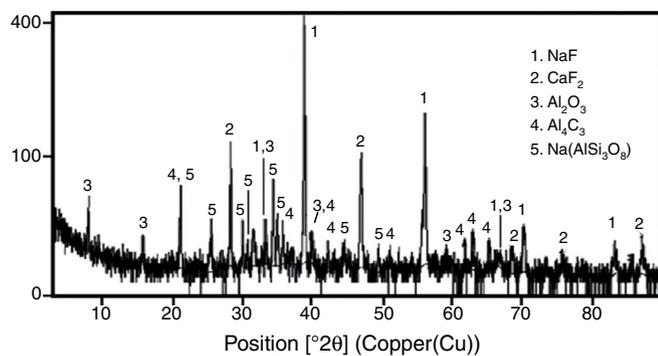
#### 3.2. Physical characterization

Table 3 shows the results regarding the SPL first cut physical characterization. The results obtained were similar to those presented by Tschöpe [10]. From the results, it can be observed that the material has similar apparent and real densities of 2.19 and 2.22, respectively, which reflects in a relatively low porosity (1.52%). According to Yurkov [20] and Tschöpe [10], virgin cathode carbon blocks present apparent and real densities in the ranges of 1.54–1.73 and 1.94–2.24 g/cm<sup>3</sup>, respectively, and porosities from 16 to 28%. The cathodes original porosity is reduced as cell operation goes by, due to the infiltration of molten salts into blocks' open porosity [20]. The apparent density and porosity of the carbonaceous materials utilized in ironmaking can be commonly related to mechanical properties and reactivity.

An HGI index of 33 was obtained to SPL first cut, which is considered low in comparison to the coals usually observed in ironmaking. This indicates that this material is very hard and difficult to grind. The stability and hardness factors obtained from the ASTM tumbler test were relatively high and showed that SPL does not undergo significant size degradation due to breakage and abrasion forces, respectively. Furthermore, as presented in Table 3, compression strength tests shown that the material under study is capable to withstand loads up to 3.7 kN. This value is considerably high, considering that

**Table 2 – SPL first cut ash chemical composition determined by X-Ray fluorescence spectroscopy.**

Equivalent compound	F	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	MgO	K <sub>2</sub> O	MnO	P <sub>2</sub> O <sub>5</sub>	Cl
Content (wt. %)	42.9	28	15.4	8	2.8	1.28	0.5	0.28	0.19	0.17	0.041	0.04

**Fig. 1 – SPL first cut ash X-ray diffractogram.****Table 3 – SPL first cut physical and mechanical properties.**

Property	SPL
Apparent density (g/cm <sup>3</sup> )	2.19
Real density (g/cm <sup>3</sup> )	2.22
Porosity (%)	1.52
Hardgroove grindability index (HGI)	33
Stability factor (%)	79.9
Hardness factor (%)	80.3
Compression rupture strength (kN) [MPa]	3.7 [54.1]

compressive strength of metallurgical cokes found in the literature majorly vary between 2 kN [22] and 3.5 kN [23].

Considering the results of all different physical and mechanical tests carried out, it is possible to say that the carbon fraction of SPL has good mechanical properties (compression, breakage and abrasion) in comparison to other carbonaceous materials commonly used in ironmaking. While virgin cathode blocks already present good mechanical properties (compressive strength around 28 MPa [20] in comparison to 54.1 MPa for the SPL, see Table 3), the carbon matrix densification due to thermal treatment and electrolyte infiltration over the years may eliminate structural defects, improving SPL mechanical characteristics.

### 3.3. Metallurgical characterization

Concerning metallurgical properties of carbonaceous materials for blast furnace, the most accepted method of analysis consists in measuring at which extent the material reacts with carbon dioxide at 1100 °C (Coke Reactivity Index – CRI) and its posterior mechanical strength (Coke Strength after Reaction – CSR). Both CRI and CSR indexes are fundamental and worldwide used to evaluate the quality of reducing agents in counter current reactors. If the carbonaceous material react excessively (high reactivity/CRI) with the oxidizing gas the material will weaken and will be degraded into smaller particle. Excessively degradation leads to reduction of permeability

in counter current reactors, impairing its performance and productivity.

For SPL first cut, CRI and CSR results were 9.2% and 82.4%, respectively. In comparison, metallurgical coke is the most used reducing agent in the ironmaking industry and have usual quality requirements for CRI in the range of 20 to 30% and CSR above 60% [23]. Thus, it is possible to infer that SPL presents low reactivity toward CO<sub>2</sub> and consequently high mechanical strength after reaction. SPL first cut low CRI may come from its low porosity and highly graphitized carbon structure. The low porosity and high ash content decreases the surface area available for reaction, leading to low reactivity. Furthermore, the formation of a white powder covering the cathode particles was observed after CRI tests, similar to that reported by Lazarinos et al. [19]. According to the authors, the layer is formed from the salts infiltrated in the cathodes during years of operation, mainly composed of sodium and calcium fluorides. The layer formed acts as a barrier for gas diffusion, contributing to the low reactivity of SPL first cut.

## 4. Discussion

Table 4 allows a comparative analysis between SPL first cut and other commonly used carbonaceous materials from ironmaking industry, such as metallurgical coke, coking coals, PCI coals and coke breeze. Coking coals and metallurgical coke are the most required and expensive raw materials in ironmaking [24,25]. PCI coals are coals with no or very weak rheological properties and are used for pulverized coal injection in blast furnaces with the objective of partially substitute coke as fuel. Coke breeze are the fines generated from coke stabilization due to handling and transportation and are used as fuel in iron ore sintering plants. From the characterization obtained for the SPL first cut, it is possible to discuss its potential for application in the processes observed in the ironmaking industry.

### 4.1. Blast furnace reducing agent

As can be seen from Table 4, SPL presented high values of stability and hardness factors, compression strength and high temperature strength (CSR). Those indices in conjunction with its low reactivity toward CO<sub>2</sub>, shows that the SPL is stronger and less reactive than the usual metallurgical coke. In light of that, SPL first cut have potential to partially substitute metallurgical coke in blast furnaces. This could lower the costs for blast furnace raw materials, although its size would need to be adjusted to be similar to that of metallurgical coke, between 40 and 80 mm [38].

However, SPL first cut reactivity is less than half that of usual metallurgical coke. This could cause an increase in the temperature of thermal reserve zone (TRZ) of blast furnace. A possible way to contour this problem could be the addition of nut coke, metallurgical coke under 40 mm, into the ferrous

**Table 4 – Quality parameters for SPL first cut and ironmaking most used carbonaceous materials.**

Properties	SPL	Metallurgical coke	Coking coal	PCI coal	Coke breeze
Fixed carbon (wt. % db)	74.3	87–91 [23]	50–85 [28]	45–85 [30]	74 [31]–87 [32]
Volatile matter (wt. % db)	2.5	<1 [23]	15–40 [28]	10–40 [30]	1.5 [32]–5.22 [31]
Ash (wt. % db)	23.3	8–12 [23]	<10	<10 [30]	11.5 [33]–20.5 [34]
Sulphur (wt. % db)	0.1	0.5–0.9 [23]	<1	0.5–1 [30]	0.5–0.9 [23]
Calorific value (kcal/kg)	6409	6800–7300	n.a.	5975–8100 [30]	5980 [34]–7968 [32]
Apparent density (g/cm <sup>3</sup> )	2.19	0.85–1.30 [25]	1.28–1.35 [29]	1.28–1.35 [29]	0.85 [35]
Real density (g/cm <sup>3</sup> )	2.22	1.80–2.10 [26]	n.a.	n.a.	1.36 [35]
Porosity (%)	1.52	42–63 [22]	n.a.	n.a.	30 [36]–60 [37]
HGI	33	n.a.	40–100	40–70 [30]	n.a.
Stability factor (%)	79.9	>60 [27]	n.a.	n.a.	n.a.
Hardness factor (%)	80.3	>70 [27]	n.a.	n.a.	n.a.
Compression strength (kN)	3.7	2[17]–3.5 [22]	n.a.	n.a.	n.a.
CRI (%)	9.8	20–30 [23]	n.a.	n.a.	n.a.
CSR (%)	85.5	>60 [23]	n.a.	n.a.	n.a.

n.a., not available.

burden, a common technique in modern blast furnaces. The addition of small amounts of nut coke contributes to better gas permeability, enhanced reduction kinetics, lower TRZ temperature and good softening melting properties of the ferrous burden [38].

Moreover, in comparison with coke, SPL first cut has higher ash content, which would generate more slag per ton of hot metal, affecting blast furnace productivity. It is also known that fluorine and alkalis are detrimental to blast furnace operation as it may cause refractory damage and productivity problems [27,39]. On top of that, according to Courbariaux et al. [13], SPL particles agglomerate and stick at temperatures around 800 °C due to aluminum and sodium fluorides melting, which could cause burden descent and permeability problems to the furnace. The presence of fluorides in the blast furnace top gas is also believed to be an environmental concern [40].

It is also well known that SPL first cut usually presents cyanide amounts over those accepted by the environmental and health organization [9,11–14]. The cyanides comprised in SPL first cut are formed by reactions between the nitrogen in the air, the carbon in the cathode and the sodium in the electrolyte, producing NaCN. During SPL storage, NaCN is converted to (Fe(CN)<sub>6</sub>)<sup>4-</sup> complexes, which are quite stable [19]. The remaining cyanides are highly soluble in water, leading to storage, handling and transport difficulties. According to Lazarinos et al. [19], for SPL stored for long periods of times, 90% of the cyanides are in ferricyanides form. Cyanide formation in the blast furnaces can be highly toxic and deleterious on human health and the environment [41], thus its levels need to be controlled with caution. The pre-treatment of SPL first cut by leaching or other processes capable of removing cyanides could improve its potential of use.

#### 4.2. Additive in cokemaking

Since SPL presents high fixed carbon content and low reactivity toward CO<sub>2</sub> and volatile matter, it could be interesting to use this material for coke production. In contrast to coking coals, SPL does not soften when heated, being classified as an inert material, such as petroleum coke and coke breeze. Those additives are commonly used by the industry aiming

to reduce coal blend cost [42], depending on market availability at lower prices, and also to control coking pressure levels [28,43,44], increasing coke oven battery campaign.

According to Loison et al. [28], the effect of inerts addition over coking pressure will depend on the type of inert material used (nature and particle size), the coking conditions and the properties of the coal blends. In what concerns coke quality, inerts can impair coke properties, especially mechanical strength. Arima [45] emphasizes that inerts particle size is one of the main factors to be controlled. According to Loison et al. [28] and Kubota et al. [46], coke and inert materials have different thermal expansion coefficients, which lead to the formation of cracks during the coke resolidification. The size of the cracks formed is equal to or less than the size of the inert added, being 1.5 mm the critical size above which coke quality is significantly impaired. Thus, SPL first cut particle size must be controlled in a way to limit its impact in coke quality. Besides the problems regarding blast furnace application commented before, the high amount of ash present in SPL first cut could impair coke yield, while its composition could create refractory problems due to the presence of fluorine and alkalis. Similar to the blast furnace, the presence of cyanides at cokemaking temperatures could be highly problematic and hazardous.

#### 4.3. Blast furnace auxiliary fuel injection

In regard to SPL first cut as an auxiliary fuel for blast furnace injection, Table 1 shows that its fixed carbon and calorific value are within the ranges of PCI coals. In contrast to that, SPL presents low volatile matter yield and reactivity. Although the reactivity and volatile matter yield of SPL are low, blends for injection containing such characteristics have been reported in the literature and used in industrial cases [30]. SPL carbon fraction low HGI indicates that this material is difficult to grind, which could increase operating and maintenance costs. Additionally, ash content for PCI coals is usually required to be under 10%, against 23.3% observed for the material in this study. High ash contents could increase pulverizer wear, impairing its performance, besides of increasing slag volume and flux requirements for the blast furnace [30].

Considering the unfavorable properties of SPL first cut in comparison to PCI coal properties, blending can be used to optimize the relative strengths of each carbonaceous material used, diluting unfavorable properties, and reducing costs since cheaper alternatives can be incorporated. Vamvuka et al. [47] showed the potential of using inorganic rich materials (66.6% ash content) from the automobile industry. The authors reached blend additions up to 30% with a single coal, maintaining the combustion levels required to the blast furnace. Also, Gao et al. [48] and Yu et al. [40] demonstrated through thermodynamic and mathematical simulation that SPL first cut could be promisingly used as an auxiliary fuel in blast furnaces even in high percentages. The simulations indicated a combustion temperature capable do destroy all cyanide components (reducing environmental damage) and that blast furnace slag would absorb the majority of fluorides contained in the ash [48]. Nevertheless, the authors indicate that kinetic issues need to be better evaluated and suggest the use of natural gas or oxygen enrichment to improve SPL first cut combustion efficiency.

#### 4.4. Iron ore sintering fuel

A frequently possibility of using solid residues rich in iron or carbon is in the iron ore sintering. In the sintering process, solid fuels have the objective to produce heat leading to the formation of a melt phase and consequently iron ore sintering. For that, coke breeze and anthracite are the most common fuels observed in the industry. From Table 4 it can be seen that SPL first cut has fixed carbon, volatile matter, ash and calorific value within the ranges usually observed for coke breeze. However, coke breeze is usually used with particle size under 3 mm. Thus, SPL first cut would need to be grinded to obtain such particle size. Once more, due to the material high hardness and mechanical strength, its comminution could be difficult and costly. Furthermore, SPL ash contains problematic compounds comprised of fluorine and alkalis, which can cause environmental and operational problems to the sintering process, besides of impairing sinter quality, due to liquid phase interactions. Additionally, the effect of combustion for the destruction of cyanides, similar to those observed in PCI, could occur during sintering. However, no studies concerning this effect were found in the literature, making it difficult to estimate the extent of cyanides destruction.

#### 4.5. General considerations about SPL usability

Alternative routes to utilize SPL first cut in the steel industry can be intended as reducing agent in alternative reduction reactors (Corex, Tecored and others) and foaming agent in electric arc furnaces. However, it is believed that, due to SPL first cut nature and characteristics, especially ash mineralogy and cyanide content, its potential use without previous treatment is limited. SPL additions would only be possible in relatively small percentages with known carbonaceous materials and in applications with the capacity to eliminate cyanides and minimize fluorides problems, causing little impact to the processes. Considering that, SPL first cut appears to have more potential to be used as an auxiliary fuel for injection into blast furnaces.

On the other hand, studies aiming to separate SPL first cut inorganic species from carbon through leaching or froth flotation can already be found in the literature. A wide range of processes focusing on SPL cyanide removal is also observed [13]. Shi Zhong-ning [11] achieved in a laboratorial study, from a sample with carbon content of 49%, through a two-step alkaline-acidic leaching, final carbon purity of 96.4%. Although researches indicate that SPL beneficiation with high efficiency is possible, the establishment of an industrial and economically viable process is still far away. The high amounts of SPL already in storage in the aluminum industry and its high generation, its considerably high energy content, the growing scarcity of fossil fuels and the demand for sustainable alternatives in the ironmaking industry encourage further researches aiming SPL first cut beneficiation and application.

## 5. Conclusion

In this work, the first cut of spent pot lining (SPL), a carbonaceous residue from the aluminum industry, was characterized aiming to evaluate its possible applications in the ironmaking processes. In general, SPL first cut presented acceptable energy potential for various ironmaking applications. Also, it is very low sulfur content when compared to others common carbonaceous materials, brings benefits in terms of SO<sub>x</sub> emissions and economy in the refining stages of hot metal and steel.

The material high mechanical strength against abrasion, breakage and compression favors its use as granulated material in reduction reactors, as well as its transport and handling, since the formation of fines is not significant. On the other hand, if small particle size is needed, its comminution can be costly.

The high ash content present in the material could be detrimental depending on its application, however, its main problem is its cyanide content and ash composition, the latter rich in fluorides and alkali compounds. Its inorganic constituents could sharply harm the performance and integrity of industrial machines and the quality of its products. Moreover, cyanides can be very toxic and deleterious on human life and to the environment and should to be dealt with care.

Considering SPL first cut properties and the processes available in the ironmaking industry, its application without beneficiation looks more promising as an auxiliary fuel for blast furnaces. However, there is no literature available about industrial scale tests or using PCI simulators, which could better elucidate this application.

## Conflicts of interest

The authors declare no conflicts of interest.

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## REFERENCES

- [1] Montiano MG, Díaz-Faes E, Barriocanal C. Partial briquetting vs direct addition of biomass in coking blends. *Fuel* 2014;137:313–20.
- [2] Flores BD, Flores IV, Guerrero A, Orellana DR, Pohlmann JG, Diez MA, et al. Effect of charcoal blending with a vitrinite rich coking coal on coke reactivity. *Fuel* 2017;155:97–105.
- [3] Montiano MG, Díaz-Faes E, Barriocanal C. Influence of biomass on metallurgical coke quality. *Fuel* 2014;116:175–82.
- [4] Kato K, Nomura S, Uematsu H. Development of waste plastics recycling process using coke ovens. *ISIJ Int* 2002;42:S10–3.
- [5] Norgate T, Langberg D. Environmental and economic aspects of charcoal use in steelmaking. *ISIJ Int* 2009;49(4):587–95.
- [6] Asanuma M, Ariyama T, Sato M, Murai R, Nonaka T, Okochi I, et al. Development of waste plastics injection process in blast furnace. *ISIJ Int* 2000;40(3):244–51.
- [7] Hasanbeigi A, Arens M, Price L. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: a technical review. *Renew Sustain Energy Rev* 2014;33:645–58.
- [8] Gunasegaram DR, Molennar D. Towards improved energy efficiency in the electrical connections of Hall-Héroult cells through finite element analysis (FEA) modeling. *J Clean Prod* 2015;93:174–92.
- [9] Von Krüger P. Use of spent potlining (SPL) in ferro silico manganese smelting. In: Lindsay SJ, editor. *Light metals* 2011. Hoboken: John Wiley & Sons; 2011. p. 275–80.
- [10] Tschöpe K [Thesis] Degradation of cathode lining in Hall-Héroult cells. Trondheim: Norwegian University of Science and Technology; 2010.
- [11] Shi Z, Li W, Hu X, Ren B, Gao B, Wang Z. Recovery of carbon and cryolite from spent pot lining of aluminium reduction cells by chemical leaching. *Trans Nonferrous Met Soc China* 2012;22:222–7.
- [12] Chanania F, Eby E. Best demonstrated available technology (bdat) background document for spent aluminum potliners – K088. *Environ Protect Agency* 2000.
- [13] Courbariaux Y, Chaouki J, Guy C. Update on spent potliners treatments: kinetics of cyanides destruction at high temperature. *Ind Eng Chem Res* 2004;43:5828–37.
- [14] Pawlek RP. Spent potlining: an update. In: Suarez CE, editor. *Light metals* 2012. Hoboken: John Wiley & Sons; 2012. p. 1312–7.
- [15] Scott BS, Brett DT, Scott WS. Kinetics of fluoride removal from spent pot liner leachate (SPLL) contaminated groundwater. *J Environ Chem Eng* 2015;3:2580–7.
- [16] Venâncio LCA, Souza JAS, Macedo EN, Nazareno J, Quaresma N, Paiva AEM. Residues recycling: reducing costs and helping the environment. *JOM* 2010;62(9):41–5.
- [17] Gomes V, Drumond PZ, Neto JOP, Lira AR. Co-processing at cement plant of spent potlining from aluminum industry. In: Tomsett A, Johnson J, editors. *Essential readings in light metals: electrode technology for aluminum production* (4). Hoboken: John Wiley & Sons; 2013. p. 1057–63.
- [18] Renó MLG, Torres FM, Silva RJ, Santos JJCS, Melo MLNM. Energy analyses in cement production applying waste fuel and mineralizer. *Energy Convers Manag* 2013;75:98–104.
- [19] Lazarinos JGC, Moura FJ, Cardoso AB. Characterization and treatment of spent potliner. *Tecnol Metal Mater* 2009;5:127–32.
- [20] Yurkov A. Refractories and carbon cathode materials for aluminium reduction cells. In: Yurkov A, editor. *Refractories for aluminium: electrolysis and the cast house*. Springer International Publishing; 2014. p. 65–208.
- [21] Schønning C, Grande T, Siljan OJ. Cathode refractory materials for aluminium reduction cells. In: Tomsett A, Johnson J, editors. *Essential readings in light metals, volume 4, electrode technology for aluminum production*. Springer International Publishing; 2016. p. 849–56.
- [22] Amanat N, Tsafnat N, Loo BCE, Jones AS. Metallurgical coke: Na investigation into compression properties and microstructure using X-ray microtomography. *Scr Mater* 2009;60:92–5.
- [23] Diez MA, Alvarez R, Barriocanal C. Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking. *Int J Coal Geol* 2002;50:389–412.
- [24] Coelho RJ, Silva OJ, Alves MT, Andrade LA, Assis PS. Modelos de previsão de qualidade metalúrgica do coque a partir da qualidade dos carvões individuais e do coque obtido no forno piloto de coqueificação. *REM* 2004;57:27–32.
- [25] Benk A, Talu M, Coban A. Phenolic resin binder for the production of metallurgical quality briquettes from coke breeze: Part I. *Fuel Process Technol* 2008;89:28–37.
- [26] Sato H, Patrick JW, Walker A. Effect of coal properties and porous structure on tensile strength of metallurgical coke. *Fuel* 1998;77(11):1203–8.
- [27] Geerdes M, Toxopeus H, Vliet CVD. *Modern blast furnace ironmaking: Na introduction*. Amsterdam: IOS Press; 2009.
- [28] Loison R, Foch P, Boyer A. *Coke: quality and production*. England: Butterworths; 1989.
- [29] Riley JT. *Manual 57: routine coal and coke analysis: collection, interpretation and use of analytical data*. USA: ASTM International; 2007.
- [30] Carpenter AM. *Injection of coal and waste plastics in blast furnaces*. USA: IEA Clean Coal Centre; 2010. <https://www.uea.org/publication/injection-coal-and-waste-plastics-blast-furnaces-ccc166>, [http://www.iea-coal.org.uk/documents/82343/7523/Injection-of-coal-and-waste-plastics-in-blast-furnaces-\(CCC/166\)](http://www.iea-coal.org.uk/documents/82343/7523/Injection-of-coal-and-waste-plastics-in-blast-furnaces-(CCC/166)).
- [31] Cheng Z, Yang J, Zhou L, Liu Y, Wang Q. Characteristics of charcoal combustion and its effects on iron-ore sintering performance. *Appl Energy* 2016;161:364–74.
- [32] Zhong Q, Yang Y, Jiang T, Li Q, Xu B. Xylene activation of coal tar pitch binding characteristics for production of metallurgical quality briquettes from coke breeze. *Fuel Process Technol* 2016;148:12–8.
- [33] Benk A, Coban A. Investigation of resole, novalac and coal tar pitch blended binder for the production of metallurgical quality formed coke briquettes from coke breeze and anthracite. *Fuel Process Technol* 2011;92:631–8.
- [34] Cheng Z, Yang J, Zhou L, Liu Y, Guo Z, Wang Q. Experimental study of commercial charcoal as alternative fuel for coke breeze in iron ore sintering process. *Energy Convers Manag* 2016;125:254–63.
- [35] Ahmaruzzaman M, Sharma DK. Adsorption of phenols from wastewater. *J Colloid Interface Sci* 2005;287:14–24.
- [36] Ri DW, Chung BJ, Choi ES. Effects of anthracite replacing coke breeze on iron ore sintering. In: *ATS international steelmaking conference*. 2007. p. 248–54.
- [37] Benk A, Talu M, Coban A. Phenolic resin binder for the production of metallurgical quality briquettes from coke breeze: part I. *Fuel Process Technol* 2008;89:28–37.
- [38] Gavel DJ. A review on nut coke utilization in the ironmaking blast furnaces. *Mater Sci Technol* 2017;33(4):381–7.
- [39] Tung-hsin Y, Chu-kung K. Wear and tear of refractories in blast furnaces when melting fluorine-containing iron ores. *Foreign Sci Technol* 1960;1(7):297–302.
- [40] Yu D, Mamakkam V, Li D, Chattopadhyay K, Gao L. Alternative applications of APL: testing ideas through experiments and mathematical modeling. In: *Ratvik AP*,

- editor. Light metals 2017. Hoboken: John Wiley & Sons; 2017. p. 579–86.
- [41] Petelin AL, Yusfin YS, Travyanov AY. Possibility of cyanide formation in blast furnaces. *Steel Transl* 2008;38(1):5–6.
- [42] Alvarez R, Pis JJ, Díez MA, Barriocanal C, Canga CS, Menéndez JÁ. A semi-industrial scale study of petroleum coke as na additive in cokemaking. *Fuel Process Technol* 1998;55:129–41.
- [43] Fernández AM, Barriocanal C, Alvares R. The effect of additives on coking pressure and coke quality. *Fuel* 2012;95:642–7.
- [44] Nomura S, Arima T. The effect of volume change of coal during carbonization in the direction of coke oven width on the internal gas pressure in the plastic layer. *Fuel* 2001;80:1307–15.
- [45] Arima T. The effect of defects on surface-breakage strength of coke. *Tetsu-to-Hagane* 2001;87:274–81.
- [46] Kubota Y, Nomura S, Arima T, Kato K. Effects of coal inertinite size on coke strength. *ISIJ Int* 2008;48(5):563–71.
- [47] Vamvuka D, Schwanekamp G, Gudenau HW. Combustion of pulverized coal with additives under conditions simulating blast furnace injection. *Fuel* 1996;75(9):1145–50.
- [48] Gao L, Mostaghel S, Ray S, Chattopadyay K. Using SPL (spent pot-lining) as an alternative fuel in metallurgical furnaces. *Metall Mater Trans E* 2016;3(3):179–88.