ADIÇÃO DE AGREGADOS RECICLADOS DE AL_2O_3-SIC EM CONCRETOS REFRATÁRIOS PARA SIDERURGIA*

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Resumo

Refratários, materiais usados nos revestimentos de equipamentos industriais, estão associados a uma gama de problemas ambientais. O maior usuário de materiais refratários é a indústria siderúrgica. Os resíduos refratários são historicamente dispostos como resíduos em aterros industriais. O desenvolvimento de tecnologia de reciclagem de refratários após uso em processo siderúrgico foi avaliado a partir da adição de agregados reciclados do sistema Al_2O_3-SiC em concretos refratários do sistema Al_2O_3-SiC-C. De uma forma geral, os resultados do ensaio de escorificação dinâmica e testes industriais indicaram o potencial do emprego de agregados reciclados de panela de gusa, carro torpedo e placas de válvula gaveta.

Palavras-chave: Refratários, Reciclagem, Concretos, Meio Ambiente, Siderurgia.

ADDITION RECYCLED AGGREGATE AL_2O_3-SIC IN REFRACTORY CONCRETE FOR STEELMAKING

Abstract

Refractories, materials used industrial equipment, are associated with range of environmental problems. Refractory wastes are historically disposed of as waste in industrial landfills. However, some of the refractory materials used have the potential to be recycled, contributing to environmental and economic sustainability. The addition of recycled aggregates of system Al_2O_3-SiC on refractory concrete of the Al_2O_3-SiC-C system were evaluated for the development of refractory recycling technology after use. In general, the results of the dynamic slag test indicated the potential of the use of recycled aggregates of charging ladle, torpedo ladle car and slide gate plates.

Keywords: Refractory, Recycling, Concrete, Environment, Steelmaking.

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1 INTRODUCTION

The largest user of refractory materials is the steel industry, followed by the cement industry. Refractories used in each piece of equipment in each market segment are unique, with specific processing problems, such as impurities, quantities and generation frequency. Regardless of the application, part of the refractory after use has the potential for recycling. Shaped materials are generally easier to recycle than monolithic materials. The use of anchors, metallic fibers, etc., make monolithic materials more difficult to be recycled. Regardless of the type of refractory, it is essential that the material is as clean as possible, reducing processing costs and increasing the range of applications [1].

In Brazil, the decision about recycling or disposing of it in nature has been an economic one for most companies. Few steelmaking companies currently process refractories after use as a business, due to the distances between the producer and the user of the refractory, the cost of processing it and the low demand for this type of material. On the other hand, refractory companies have increasingly valued the possibility of recycling materials after use as raw materials in the compositions of their products [2]. Refractory materials after use represent an alternative source of raw material and can replace natural or artificial raw materials in some applications. The recycling of this type of material can represent an opportunity for the steel industry to reduce costs, reduce the difficulty in disposing of waste and obtain an image of an environmentally friendly company.

In this sense, this work aims to develop recycling technology for refractories, conformed class, obtained from the demolition of pig iron ladle, torpedo ladle car and separation of side gate plates allowing its addition in high performance refractory concrete. The residues were characterized after segregation and crushing to obtain recycled aggregates using internal resources from a national steelmaking company and, subsequently, the main properties and characteristics of specimens made using refractory concrete with and without the addition of recycled aggregates were evaluated.

1.1 Recycled aggregate technology

The Japanese steelmaking industry is a pioneer in the development of technologies to reduce the consumption of refractories, as well as recycling refractories. The following are some available literature on the subject. Researchers of Japan steelmaking companies have developed works in this area in recent years using 3R concepts for the reduction and recycling of refractory waste [3].

The main concepts of the 3R consumption reduction and recycling technology are:

- Reduce: control of process variables that increase the wear of refractories and implementation of repair techniques to prolong the life of the refractory lining.
- Reuse: apply refractories after use as raw materials for the process, eg slag conditioner.
- Recycle: reuse of refractories after use with some processing to incorporate new refractory products.

The refractory waste recycling starts with the pre-treatment of the waste according to the flow shown in figure 1 [3].

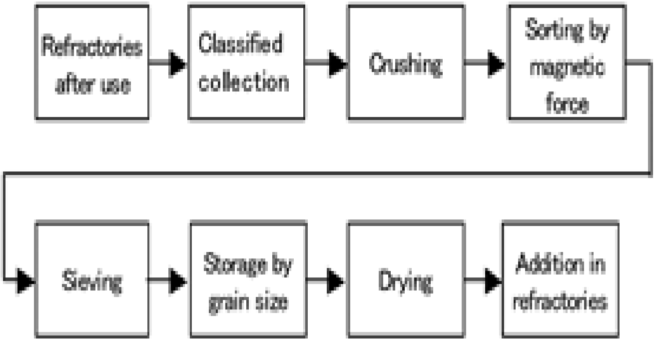

Figure 1. Flux addition of recycled aggregates in refractories [3].

Right after demolition and / or disposal of the refractories after use, it is necessary to separate and select the parts containing slag and metal from the process. This step is important and requires special care to avoid low efficiency of the recycling process. The next step is the crushing of refractory waste to suitable granulometry for addition as recycled aggregates in refractory concrete. For this operation, different types of crushers can be used according to the size and characteristics of the refractory residues.

Upon completion of the crushing of refractory waste, temporary storage of aggregates in different bays is necessary in order to maintain segregation of refractory families to ensure compatibility with the final application.
According to the literature [3], refractory residues with characteristics compatible with new refractory products have the potential to be used as recycled aggregates incorporated in thicker granulometry in an adequate percentage (Figure 2).

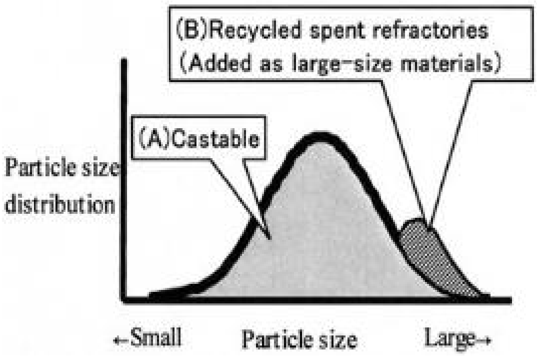

Figure 2. Particles distribution of refractory concrete and recycled aggregates [3].

The diagram below proposed by Hanagiri et al., [3] illustrates the potential for using high quality refractory residues such as Al2O3, MgO and SiC refractories. On the other hand, refractories containing considerable silica content usually have less potential of incorporation to refractories due to the concentration of impurities that deteriorate the quality of the refractory (Figure 3).

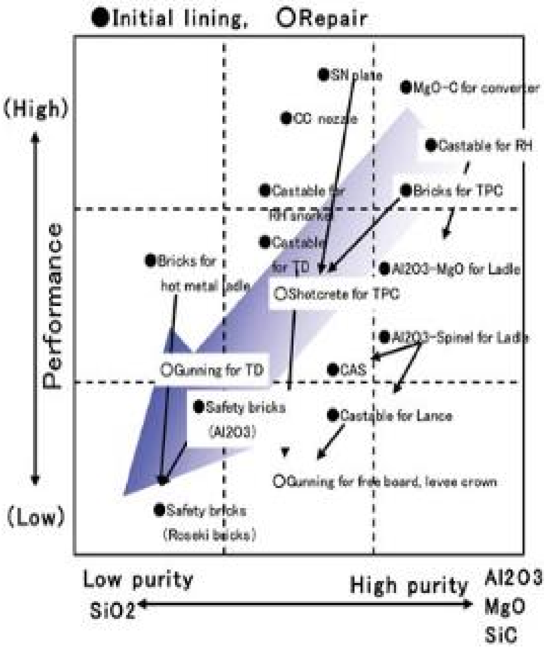

Figura 3. Potential use of spent refractories [3].

Figure 4 shows the influence of the addition of recycled aggregates on the main properties of refractory concrete, such as water content for mixing, apparent porosity and resistance to corrosion. In general, percentages of addition between 10 and 20% do not negatively affect the properties of the materials. Additions above 20% show a tendency to reduce important properties of refractories, especially the corrosion rate [3].

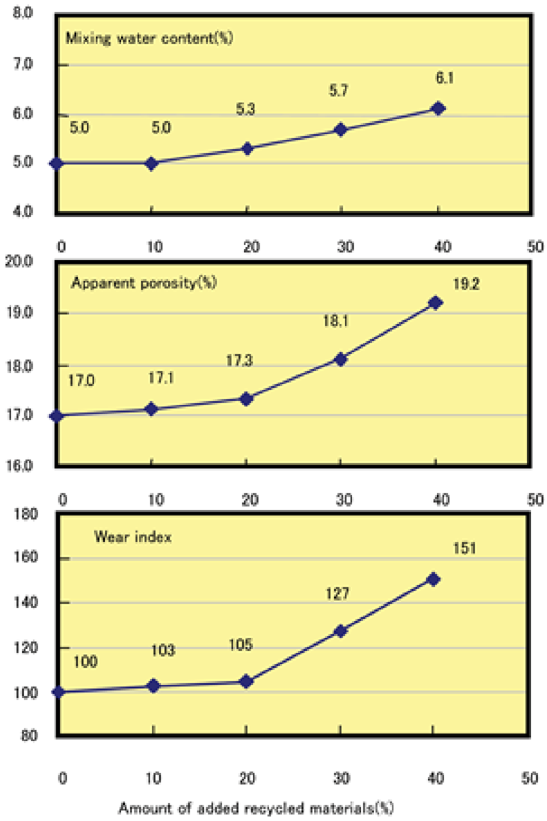

Figure 4. Influence of the addition of recycled aggregates on the properties of refractory concrete [3].

In the mid-1980s, with the development of new steelmaking techniques, different processes for treating liquid metal were improved and / or incorporated into steelmaking activities, such as: dissiliation, dephosphorization and desulfurization. Due to the strict demands imposed, the performance of traditional Al_2O_3-C refractories, used at the time, was considerably affected. Among the different modalities, the materials of the Al_2O_3-SiC-C system started to play an important role as refractory lining [4].

During industrial use, Al_2O_3-SiC-C refractories experience significant structural changes along their thickness, which give these materials a dynamic or mutant character when considering their properties. Although, in principle, these changes can be beneficial, the biggest challenge in this field is to understand and control these changes, which are influenced by several factors and / or variables, such as:

- Raw materials;
- Processing;
- Metallurgical process variables (time, temperature e atmosphere).

Al_2O_3-SiC-C refractories are essentially composed of alumina (fused and / or sintered), carbon (graphite), silicon carbide and metallic antioxidants, and the handling and transport resistance is provided by the phenolic resin or tar, which acts as a binder. The purpose of each component can be seen in the schematic representation shown in figure 5.

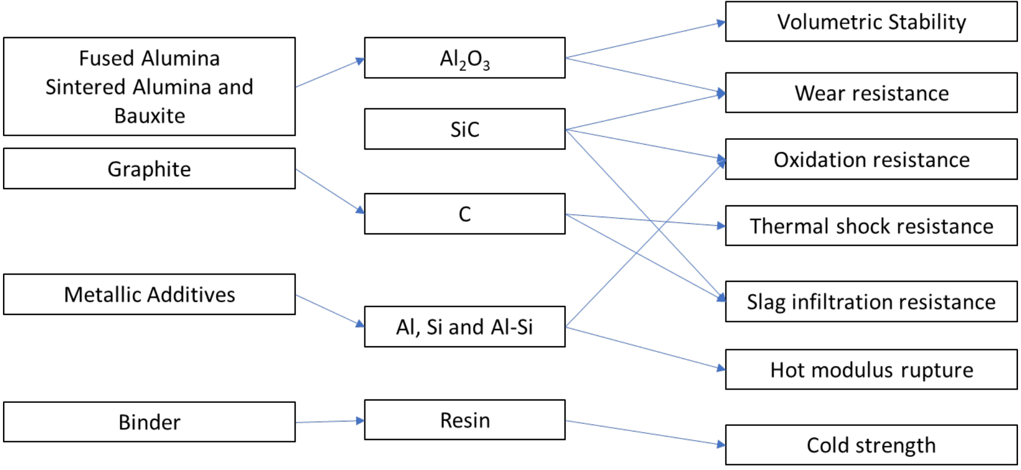

Figure 5. Schematic representation showing the purpose of the different components of the Al_2O_3-SiC-C system [5].

2 DEVELOPMENT

2.1 Materials and Methods

The effects of adding recycled aggregates in refractory concrete from the Al_2O_3-SiC-C system were evaluated through laboratory tests. Table 1 shows the main properties and characteristics of the recycled aggregates and studied refractory concrete, according to the technical data sheet of the producer of the refractories. Refractory concrete was named as CRF, and recycled aggregates from the replacement and demolition of refractories were named as: API (Aggregates Pig Iron Ladle), ATC (Aggregates Torpedo Ladle Car) and ASG (Aggregates Side Gate Plate).

Table 1. Composition and properties of all materials.

Materials	CRF	API	ATC	ASG
Al_2O_3 (%)	56,0	73,0	60,0	77,0
SiC (%)	19,8	10,0	9,0	9,5
ZrO_2 (%)	---	---	---	4,8
Density (g/cm^3)	2,67	2,89	2,93	3,07
Porosity (%)	14	7,0	6,5	8,0
CCS (MPa)	30	45	55	200

CCS = Cold Crushing Strength.

2.1.1 DRX

The mineralogical characterization was carried out aiming to identify the crystalline phases present in the refractory concrete, as well as, in the studied recycled aggregates. The technique used was the qualitative analysis of phases by X-ray diffraction, using X-ray diffractometer from the Laboratory of the Physics Department of the Federal University of Ceara, Brand: PANAlytical, Model: XPert Pro MPD, Operation: 40kV x 40mA, Radiation: Co (Kα1).

2.1.2 Slag Test

In order to determine the relative resistance of a refractory to the presence of slag or metal in an industrial application, several scoring tests have been developed. Among the most used are the static test and the dynamic tests with the rotary furnace. The test methodology was based on the NBR 8830 standard. The slag used in the test can be a synthetic slag or the slag itself formed during the production process.

The dynamic scoring evaluation consists of the slag attack test using a rotary kiln containing a crucible assembled with specimens of the studied materials.

The test with the rotary furnace is widely used, being a dynamic type test. A steel cylinder is coated with 8 test samples, in rhombohedral format (figure 6). A burner is used to heat the samples to the test temperature and the slag is fed periodically. After testing, the samples are cut along their length, and the volume of material lost from the original sample is determined. The advantages of this method are its dynamic nature and the continuous slag renewal.

The dynamic scoring of specimens made with free refractory concrete and containing added recycled aggregates in a percentage of 20% was evaluated, as shown in table 2.

Table 2. Specimen configuration.

Specimen	Addition Recycled
CRF	0%
CRF+API	20%
CRF+ATC	20%
CRF+ASG	20%

To prepare the specimens, mixing and humidity parameters were used according to the manufacturer's recommendations, performing the following steps: (i) curing in metallic form for 24h, (ii) curing in air (24h), (iii) drying in an oven 110 ° C (24h).

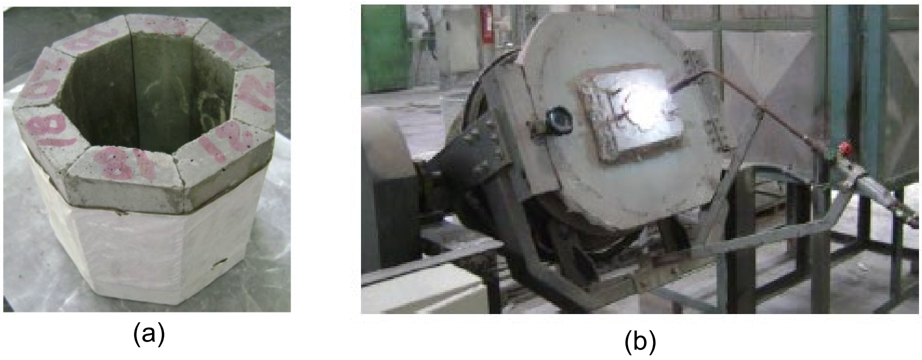
(a) (b)

Figure 6. Slag test: (a) specimen set and (b) slag test device.

Table 3 shows the chemical composition of the slag used in the dynamic scoring test. The chemical composition was determined by the X-ray fluorescence technique, using a fused tablet.

Table 3. Chemical composition of slag.

CaO	**SiO_2**	**MgO**	**MnO**
38,36%	14,01%	2,05%	0,61%
Al_2O_3	**S**	**TiO_2**	**K_2O**
3,67%	1,79%	0,20%	0,92%
C	**P_2O_5**	**Na_2O**	**T-Fe**
5,39%	0,21%	0,03%	12,64%

2.1.3 Industrial Trial

In order to evaluate the industrial performance of the use of recycled Al_2O_3-SiC aggregates, the concreting of a special part used in the KR process, called Impeller KR, was carried out. The entire process of mechanical preparation and application of refractories for this part was carried out at the Precast Plant CSP installed inside the Companhia Siderurgica do Pecem plant, located in São Gonçalo do Amarante City – Ceara State (figure 7).

The recycled aggregates with controlled granulometry were previously obtained after segregation and crushing using the Company's internal resources. Then, big bags were prepared with a weight equivalent to 20% of the total amount of refractory concrete of the Al_2O_3-SiC-C system required for concreting the Impeller KR.

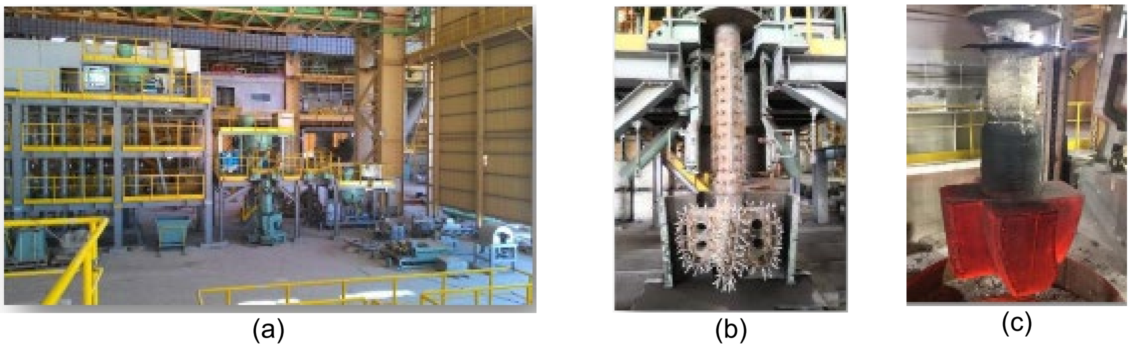
(a) (b) (c)

Figure 7. Precast Plant CSP: (a) overview plant (b) molding process and (c) Impeller KR after 1 heat.

2.2 Results and Discussion

2.2.1 DRX

The results of the mineralogical characterization are shown in table 4. The results indicated that the phases Al_2O_3, SiO_2 and SiC are common for all samples. The API and ATC samples showed some similarity in terms of mineralogical composition. The sample of aggregates of gate valve plates (ASG) presented ZrO_2 and Si. In turn, the Mullite phase [$Al_4Si_2O_9$], was identified for all samples of recycled aggregates. In general, the mineralogical composition of the samples of recycled aggregates revealed ceramic compatibility for the use of these residues as raw material for refractory products. In other words, the results showed no restriction for incorporating these materials in refractory concrete.

Table 4. DRX Results.

Detected Phases	**CRF**	**API**	**ATC**	**ASG**
Aluminum Oxide [Al_2O_3]	P	P	P	P
Aluminum Silicon Oxide [Al_4SiO_9]	P	---	---	---
Silicon Carbide [SiC]	P	P	P	P
Silicon Oxide [SiO_2]	P	P	P	P
Calcium Iron Silicate [$CaFe(Si_2O_6)$]	P	---	---	---
Silicon [Si]	---	---	---	P
Aluminum Silicate [Al_2SiO_5]	---	P	---	P
Zirconium Oxide [ZrO_2]	---	---	---	P
Mullite [$Al_4Si_2O_9$]	---	P	P	P
Carbon [C]	---	P	P	---

Label:
P = Present Phase

2.2.2 Slag Test

The main requirement for refractory concrete during operation is resistance to chemical attack due to contact with liquid slag at high temperatures.

The slag attack refers to the chemical reactions that corrode the surface of the refractory lining in service and the reactions that take place between the molten slag, the refractory and the fluxing agents that have been infiltrated. Refractory erosion often accompanies the corrosion process. In many industrial applications, the refractory is in contact with the slag or metal during use and a chemical reaction often occurs between them. Some reaction products can be extremely harmful to the life of the refractory, while other reactions can result in little or no variation in your campaign.

Figure 8 shows the appearance of the specimens after the slag test.

Sample	**Specimen Photo**
CRF	
CRF	
CRF+API	

CRF+API	
CRF+ACT	
CRF+ATC	
CRF+ASG	
CRF+ASG	

Figura 8. Specimen after slag test.

Table 5 shows the wear results of the specimens after the scoring test.

Table 5. Slag test results.

Sample	Index Wear (%)	Average Index Wear (%)
CRF	23,1	21,9
CRF	20,6	
CRF+API	20,5	20,6
CRF+API	20,7	
CRF-ATC	15,2	17,6
CRF+ATC	20,0	
CRF+ASG	19,5	19,1
CRF+ASG	18,7	

The average wear rate for non-recycled specimens was 21.9%. The specimens of the CRF + ATC sample, on the other hand, presented an average of 17.6%, in other words, it performed better in terms of resistance to corrosion by slag. Then, the specimens of the CRF + ASG and CRF + API configurations exhibited intermediate wear rates of 19.1% and 20.6%, respectively.

In general, the addition of recycled aggregates containing silicon carbide (SiC) and with a relatively higher density than the original raw materials for refrATCory concrete represents a contribution of SiC to the refractory system and greater stability of the microstructure due to its lower porosity.

SiC is one of the important elements in preventing carbon oxidation up to approximately 1525°C, by reducing CO (g) to C (s), according to equation 1. As a result of this reaction, the carbon formed fills the corroded area of SiC and, subsequently, according to equation 2, SiO (g) combines with the remaining CO (g) to form C (s) and SiO_2 (s). Finally, as a result of equations 1 and 2, SiC reduces CO (g) to C (s) forming SiO_2 (s) (equation 3) [8]:

$$SiC_{(s)} + CO_{(g)} \leftrightarrow SiO_{(g)} + 2C_{(s)} \qquad (1)$$

$$SiO_{(g)} + CO_{(g)} \leftrightarrow SiO_{2(s)} + C_{(s)} \qquad (2)$$

$$SiC_{(s)} + 2CO \leftrightarrow SiO_{2(s)} + 3C_{(s)} \qquad (3)$$

In this case, it is believed that the protection of carbon is basically due to the formation of SiO_2 (s) and secondary precipitation of C (s) from the oxidation of SiC, which leads to an expansion of the solid phase of approximately 3,4 times when considering the density of cristobalite (2,2 g/cm^3). The increase in volume and the resizing of pores, in turn, can reduce the permeability of the refractory, contributing to delay the oxidation of carbon. The pertinent literature suggests that, under industrial conditions, along the length of the Al_2O_3-SiC-C bricks, these reactions promote a reduction in porosity on the hot face, contributing to increase the compressive strength and the elasticity modulus in this region of the brick. Figure 9 shows the behavior of SiC, apparent porosity and resistance to compression at room temperature over an Al_2O_3-SiC-C brick [5, 7].

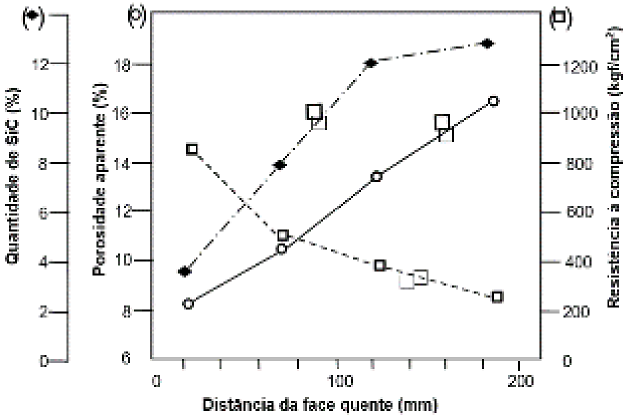

Figure 9. Behavior of SiC, apparent porosity and resistance to compression at room temperature over an Al2O3-SiC-C brick after 613 heats.

Additionally, SiC gives extra advantages to the refractory, such as: high resistance to corrosion and high resistance to thermal shock damage [8].

It is believed that the increase in mechanical strength for Al_2O_3-SiC-C refractories at high temperatures is partially related to the formation of needles in the form of needles, called “whiskers”. These crystals have high mechanical resistance and are mainly manifested in the porosity of the refractory. Thus, there is a reduction in pore size and the mechanical strength and corrosion resistance of the refractory is effectively improved [4].

Therefore, the addition of recycled aggregates containing SiC favors the enrichment of the refractory concrete microstructure. A better understanding of the interactions of recycled aggregates with the original raw materials of concrete will be explored in further studies to investigate the effects on the microstructure and other properties of refractory castables in the Al_2O_3-SiC-C system.

In terms of operational performance, the Impeller KR molded with the addition of recycled aggregates of Al_2O_3-SiC presented promising results through a campaign of 430 heats whose campaign target for this piece is 310 heats.

Figure 10 shows the monitoring performed during the industrial test. The refractory lining did not show marked wear during the campaign until reaching 430 heats.

100 heats 200 heats 300 heats 430 heats

Figura 10. Record of Impeller KR industrial test containing added recycled aggregates.

In figure 11, the final aspect of the refractory lining is shown, showing that the recycled aggregates were intact in the composition of the refractory lining. In general, the results of the industrial test confirmed that the addition of recycled Al_2O_3-SiC aggregates does not have negative effects on the resistance to corrosion by metal and liquid slag from the refractory lining.

These results allow us to infer that the use of recycled aggregates of Al_2O_3-SiC obtained from refractories after use in the steelmaking process has great potential as a strategy to reduce costs and contribute to the environmental sustainability of the process, minimizing the disposal of waste in controlled landfills.

(a) (b)

Figura 11. Post-mortem: (a) Impeller KR after 430 heats and (b) recycled aggregates of Al_2O_3-SiC preserved on refractory concrete.

3 CONCLUSION

In general, the laboratory and industrial results indicated the potential of using recycled aggregates of Al_2O_3-SiC obtained from the segregation and crushing of refractory residues from the demolition of refractories applied to the pig iron ladle (API), torpedo ladle car (ATC) and the replacement of side gate plates (ASG). The wear index of the specimens with the addition of 20% recycled aggregates from the Al_2O_3-SiC system was lower compared to the wear index of the non-recycled specimens. The post-mortem analysis of Impeller KR after 430 heats containing the addition of recycled aggregates to the composition of the refractory concrete indicated that the recycled aggregates were preserved so that there were no negative effects on the properties and characteristics of the refractory lining. In short, these results are important to foster the development of refractory recycling technologies. In addition, they point to new perspectives for the use of these refractory wastes whose intrinsic quality allows direct use in refractory products and, above all, from the perspective of sustainability for refractory wastes that, historically, are disposed of in controlled landfills generating environmental and economic impacts for suppliers. and consumers of refractories.

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