

# Corrosion of structural steel in the metallic shell of hot stoves

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## Abstract

This study proposes to verify and clarify the main corrosion mechanisms in industrial regenerators or hot stoves, widely used in the steel industry, indicating actions for their monitoring and control. The corrosion mechanisms in the upper parts, internally, are associated with the formation of siderite ( $\text{FeCO}_3$ ) and sulfur, which also favor stress corrosion and the occurrence of cracks. Different corrosion mechanisms may be associated with the lower parts of the regenerators and may be accelerated by the presence of flue gas condensate and sulfur. Practical actions were proposed for the correct measurement and control of the good operating conditions of the regenerators.

**Keywords:** Corrosion, hot stoves, sulfur, fuel gas quality.

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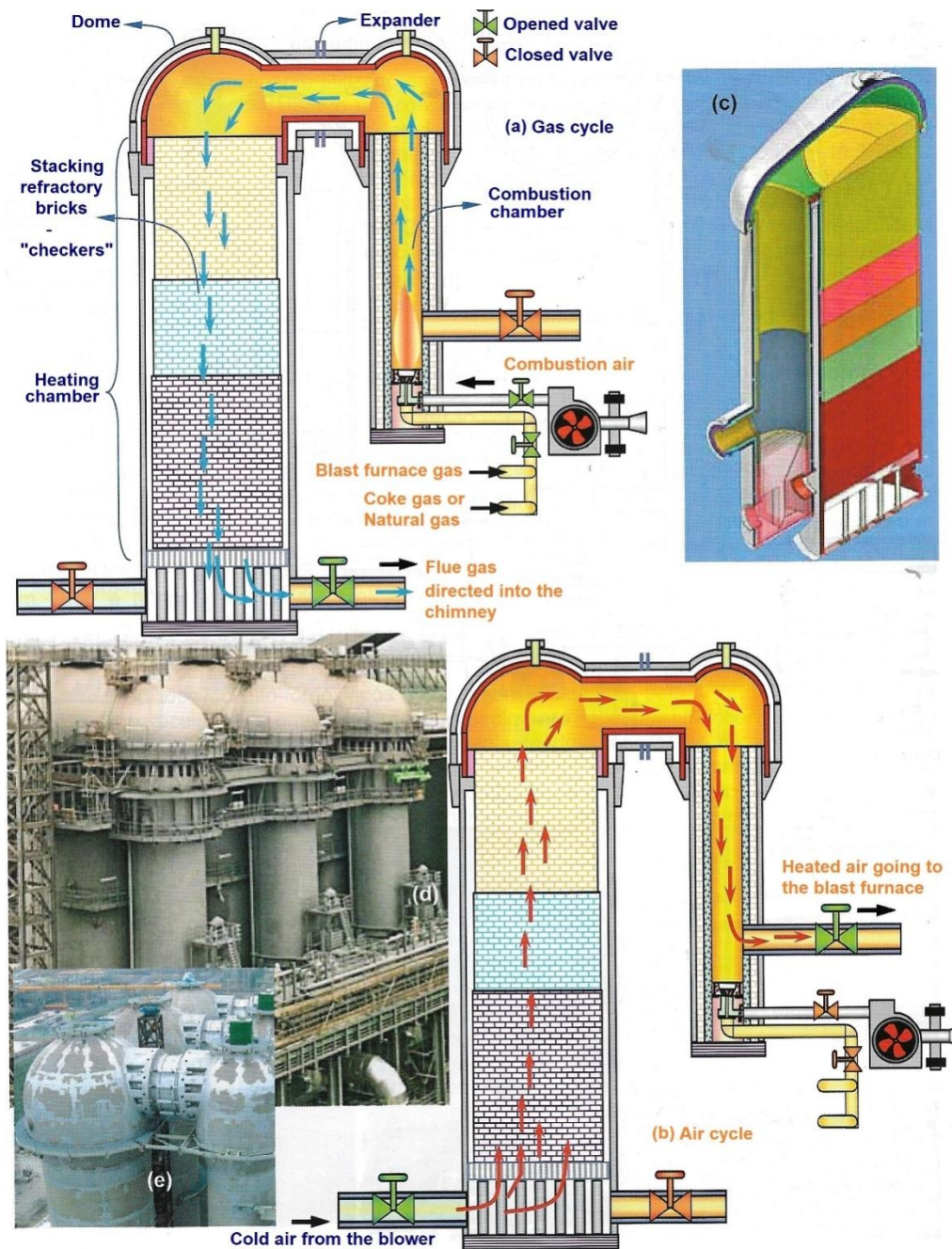
## I. Introduction

The Brazilian steel industry has evolved rapidly in its operational results using applied technology and technical-scientific knowledge to overcome the not so recent challenges of competitiveness, excess capacity, cost reduction and environmental issues, the latter being well contextualized by Fernandes [1], such as carbon dioxide emissions and energy efficiency. Within these industrial plants, in blast furnaces, the regenerators have a useful life cycle between 30 and 40 years and play an important operational and financial role for the proper functioning of these reactors.

Understanding of the main mechanisms of corrosion of the metallic casing of the regenerators is of utmost importance so that operation and maintenance engineers and technicians can periodically monitor these components and define the best strategies for conservation and use of this equipment, to avoid failures or prolonged and early interruptions of production for revamps that have a relevant impact on the master plan of the companies in the steel segment. As the few works related to regenerators have focused mainly on refractories or stress corrosion mechanisms [2-4], the objective of the present paper is to present an overview of the corrosion mechanisms of the metal casing and correlate them to the process conditions and failures commonly found in this equipment.

Hot stoves or Cowpers regenerators, which in this paper will be referred to only as regenerators, are widely used equipment for heating the air used in blast furnaces, operationally reaching temperatures between 1,150 and 1,200 °C of blast air. To perform their function, the regenerators work both as pressure vessels and heat exchangers in alternating cycles with air and gas. Each regenerator is formed by a metallic casing, normally made of structural steel, refractory materials, and a set of special valves, with the function of facilitating heat exchange in a low-pressure system (normally between 3 and 5 bar, gauge pressure).

As can be seen in Figure 1, a burner, which can be of ceramic or metallic type, combusts a mixture of blast furnace, coke oven gas or natural gas with air in the combustion chamber. Then, the combustion gases transfer energy and heat the stacking of the checker chamber (refractory bricks whose stacking generates many smaller diameter ducts to maximize the heat exchange area), before exiting through the smoke channel. In the air cycle, combustion is stopped, the smoke channel is also closed, and then the blowing air supply is opened and heated by the previously heated checker chamber and directed to the blast furnace. Typically, a blast furnace has a configuration of three to four regenerators, which work in alternation in these gas/blow cycles, producing a repeatability of thermal and mechanical oscillations in the entire assembly during the life of the equipment [5-7].



**Figure 1** – Cowper regenerator with external combustion chamber in two stages of operation: a) cycle with gas or heating, b) cycle with wind or blowing, c) another option for the dome, d and e) images of industrial installations, adapted from[5]

## II. Experimental

To remove the sample from the top, a 63.5 mm diameter (2 ½) STARRET rapid steel cup saw and a magnetic base drilling machine with variable rotation were used. The equipment was done at a relatively low speed, aiming to preserve the microstructural characteristics of the steel.

The TM510-SE equipment was used to measure the steel thickness by ultrasound according

to the internal reference standard PT016 ME (like the current NBR16616 of 07/2017), measuring head angle of 0° and grease as coupling. The SEM analysis of the oxide layers was performed using a ZEISS EVO MA10 Scanning Electron Microscope. Typical flue gas compositions as a function of the percentage of oxygen in the air used in combustion and main regenerator operation parameters can be seen in Table 1.

**Table1** – Operating conditions of a regenerator and flue gas composition

	Unit	Normal air	22% O <sub>2</sub>	23% O <sub>2</sub>	24% O <sub>2</sub>	25% O <sub>2</sub>
<b>O<sub>2</sub> in air+O<sub>2</sub></b>	Vol.-%	20.7	22.0	23.0	24.0	25.0
<b>Air</b>	Vol.-%	100.0	98.3	97.0	95.8	94.5
<b>O<sub>2</sub></b>	Vol.-%	0	229.4	392.2	547.4	695.4
<b>O<sub>2</sub> flow</b>	Nm <sup>3</sup>	1412	1445	1469	1491	1512
<b>Flame temperature</b>	°C	17.0	17.5	17.9	18.2	18.6
<b>Flue gas flow(C6)</b>	kNm <sup>3</sup> /h	31.8	31.6	31.5	31.4	31.3
<b>Power</b>	MW	18.0	18.6	19.0	19.4	19.7
<b>Air+O<sub>2</sub> flow (C6)</b>	kNm <sup>3</sup> /h	14.0	13.6	13.2	12.9	12.6
<b>Flue gas flow</b>	kNm <sup>3</sup> /h	28.4	28.4	28.4	28.4	28.4
<b>Flue gas/(BFG+NG)</b>	-	1.68	1.63	1.59	1.56	1.53
<b>Flue gas analysis</b>						
<b>CO<sub>2</sub></b>	Vol. %	24.1	24.8	25.4	25.9	26.4
<b>N<sub>2</sub></b>	Vol. %	66.5	65.5	64.8	64.1	63.4
<b>O<sub>2</sub></b>	Vol. %	0.7	0.7	0.7	0.7	0.7
<b>H<sub>2</sub>O (as vapour)</b>	Vol. %	8.7	9.0	9.1	9.3	9.5
<b>Fire time C6</b>	Vol. %	105.9	102.1	99.6	97.3	95.2

### III. Corrosion in regenerators

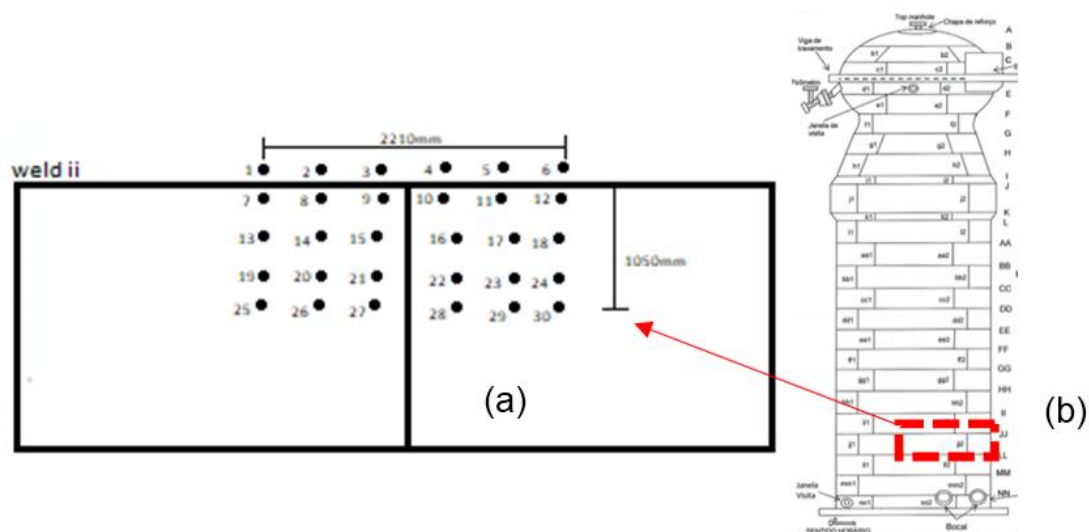
Schaub et al. [2] divided the attack on the metal casing of regenerators mainly into two corrosion groups. The first mechanism of attack on the metallic casing leads to a reduction in the thickness of the metallic casing of the regenerator. Figure 2 and Table 2 show an example of a field ultrasonic measurement of the lower region of a regenerator's metallic casing with thickness reduction (uniform corrosion), the plate being 26 years old and 20 mm thick in the original design. In point 2, there was the greatest loss of thickness in the period, a 63% reduction of the original thickness of the plate, or 0.48 mm/year. Points 2 to 4 presented the highest steel corrosion rates. At point 12, the lowest thickness loss of only 0.06 mm/year occurred.

Corrosion on metallic casings in Cowpers type regenerators in structural steels, such as ASTM 242 and similar steels built in the 80s and earlier, has an average corrosion rate expected in design in a range of 0.35-0.40 mm/year (depending on the design and the standard of the country of

origin used for pressure vessels - source: author), especially keeping in mind that the working and environmental conditions to which this equipment is submitted are similar to the design.

These differences in corrosion rates can be explained due to the presence or not of flue gas condensate in some parts of the internal face of the plate, which eventually crosses an eventual failure of the refractory lining and, when condensation occurs, forms an electrolyte, even if temporary during return in operation after shutdowns, for example.

The lower regions of the regenerators (Fig.2 and Fig.3) are also the ones with the lowest temperature of the shell, where the moisture of the combustion gases from the mixture of fuel gases and combustion air can be partially in liquid phase, especially on the cold face of the refractory and its interface with the shell. For this, it is sufficient that the flue gas temperature be lower than the gas dew temperature, which according to Kassas et al. [3] has been estimated at 180°C.

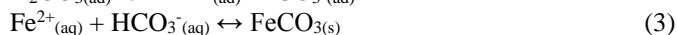
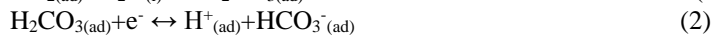
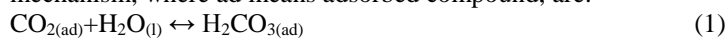


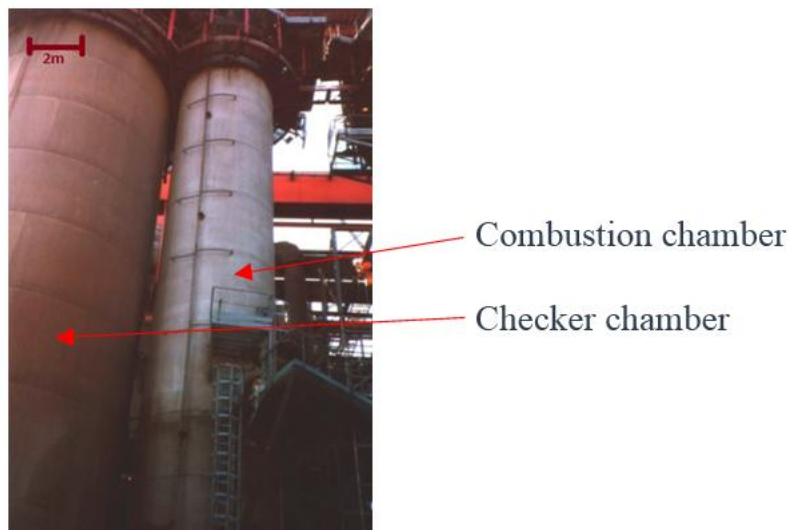
**Figure 2-** Loss of thickness of the metallic housing of a regenerator measured by ultrasound (a) detailed view and (b) general view of hot stove

**Table2** – Ultrasonic thickness measurements as already detailed in the experimental part

Point	Thickness (mm)	Point	Thickness (mm)
1	11.2	16	17.8
2	7.4	17	17.1
3	8.4	18	10.3
4	9.5	19	12.3
5	13.7	20	10.3
6	11.2	21	16.8
7	11.5	22	16.8
8	11.3	23	13.3
9	11.1	24	12.4
10	15.6	25	13.2
11	17.3	26	11.4
12	18.4	27	15.8
13	10.8	28	16.7
14	11.8	29	17.3
15	17.3	30	16.8

The corrosion of carbon steel in environments containing CO<sub>2</sub> generates a corrosion product called siderite (FeCO<sub>3</sub>) that can form a passive layer or not, depending on the chemical conditions of the electrolyte such as pH, carbonate concentrations [8,9] and oxygen saturation, among other factors. The reactions involved in this mechanism, where ad means adsorbed compound, are:





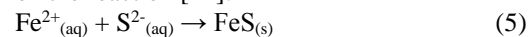
**Figure 3-** External plating of the checker chamber(left) and combustion chamber (lower parts) for a regenerator with external combustion chamber

Corrosion due to the presence of sulfur [10-13] usually occurs in small, localized regions on the metal surface, forming pits. It occurs on carbon steel and on metals or alloys that passivate or form films of corrosion products on the metal surface. Behind the flue gas condensate electrolyte, an electrochemical cell of the localized type initiated with small anodic and large cathodic areas is formed, thus constituting a system that locally allows and/or favors material penetration.

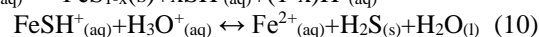
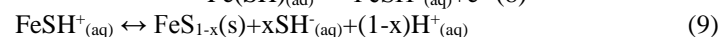
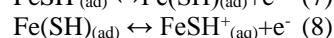
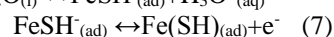
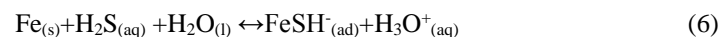
It can be stated that, the lower the pH the higher the probability of sulfur corrosion. The formation and/or precipitation of ferrous sulfide (FeS) in the vicinity of the pitting regions can be explained by the increased concentration of OH<sup>-</sup>

ions that promote, consequently, the increase of the pH value and the alkalization of the reaction [12]:  
 $\text{SH}^-_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{S}^{2-}_{(\text{aq})}$  (4)

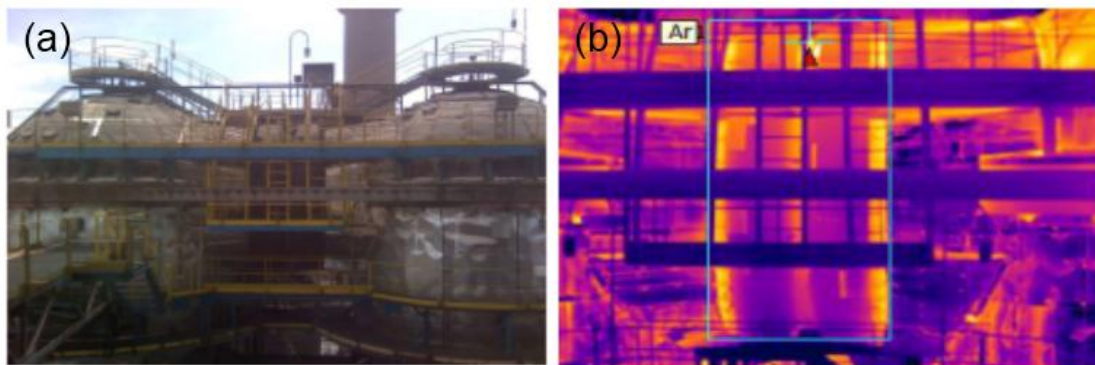
The concentrations of [Fe<sup>2+</sup>] and [S<sup>2-</sup>] reach the saturation limit of these ions in the medium and promote the precipitation of ferrous sulfide based on the reaction [11]:



Zimer [14] states that the effect of H<sub>2</sub>S on the corrosion of carbon steel also consists of the galvanic cell formed between the cementite and ferrite phases. The heterogeneous deposition of FeS on the steel surface does not produce an efficient passivation layer. In this case, the following reactions can occur [14]:

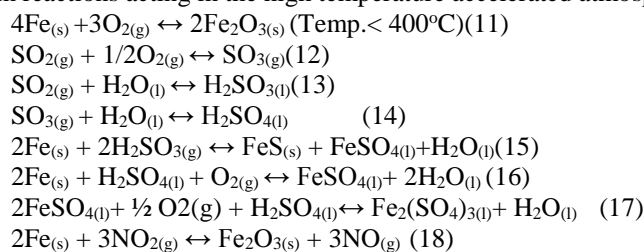


In the upper parts of the regenerators (Fig. 4), there is the chemical or dry oxidation of the metal housing first externally with the industrial atmosphere (air contaminated with NO<sub>2</sub> and SO<sub>2</sub>) and then internally with the combustion gases (CO<sub>2</sub>, CO, O<sub>2</sub>, and H<sub>2</sub>O), with the kinetics most favored by the higher temperatures.

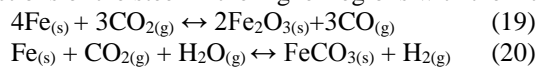


**Figure4-** The interconnection between the combustion chamber and the dome (upper parts) for a regenerator with external combustion chamber: (a) general view and (b) thermographic detail view

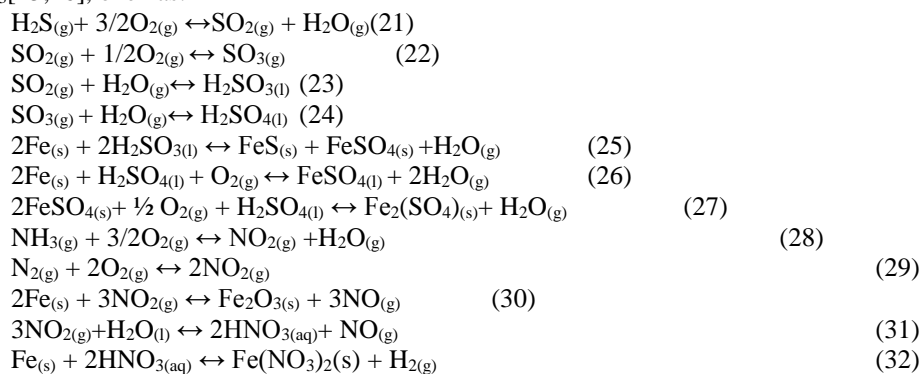
The main reactions acting in the high temperature accelerated atmospheric corrosion reaction are:



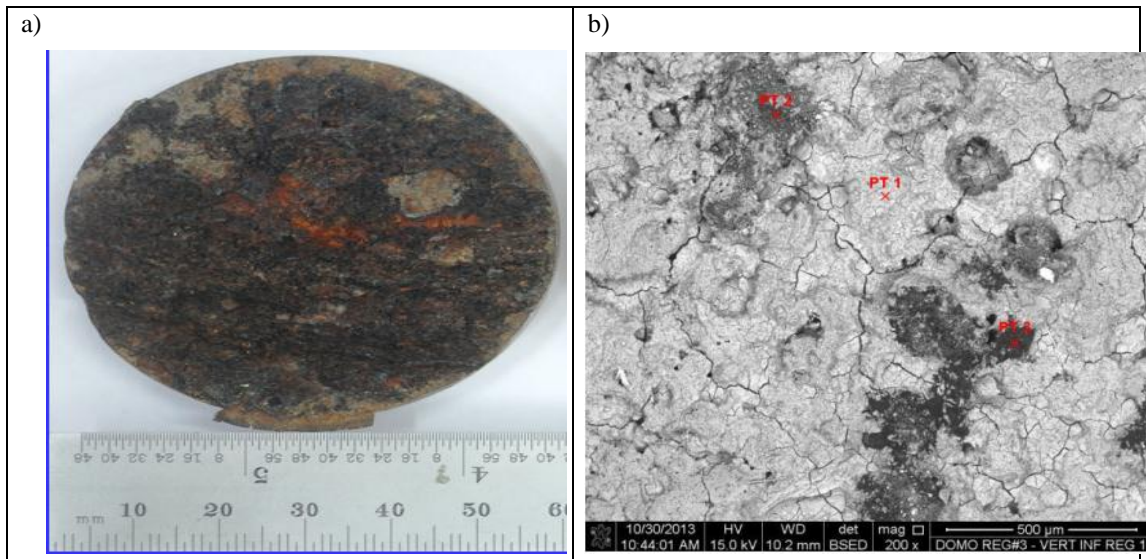
The reactions of the steel in the higher regions with the internal environment of the regenerator are [15,16]:



Considering the presence of  $\text{NO}_2$  and  $\text{SO}_2$  from coke oven gas combustion typically with the presence of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  [15,16], one has:



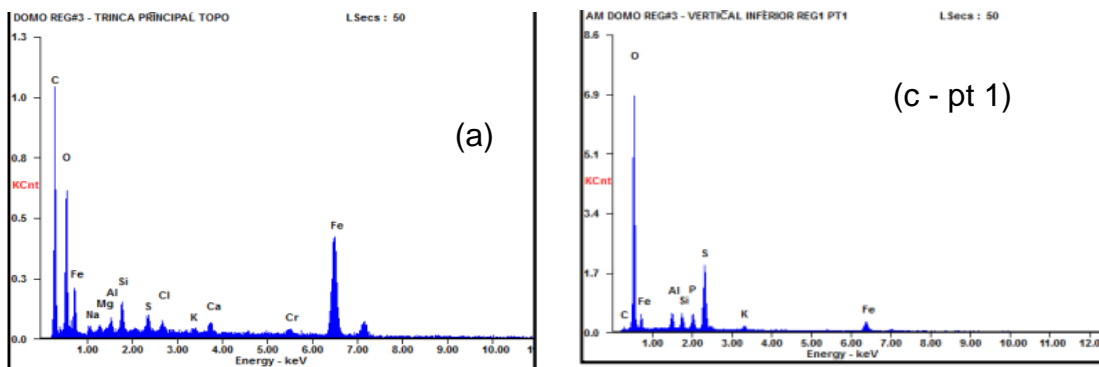
A sample was taken from the metal casing of a regenerator in the dome part, showing the uniform corrosion appearance of the inner surface of the sample (Fig. 5a), and by scanning electron microscopy, the micrograph shows different phases of corrosion products and fouling, referenced by points 1, 2 and 3 (Fig. 5b).

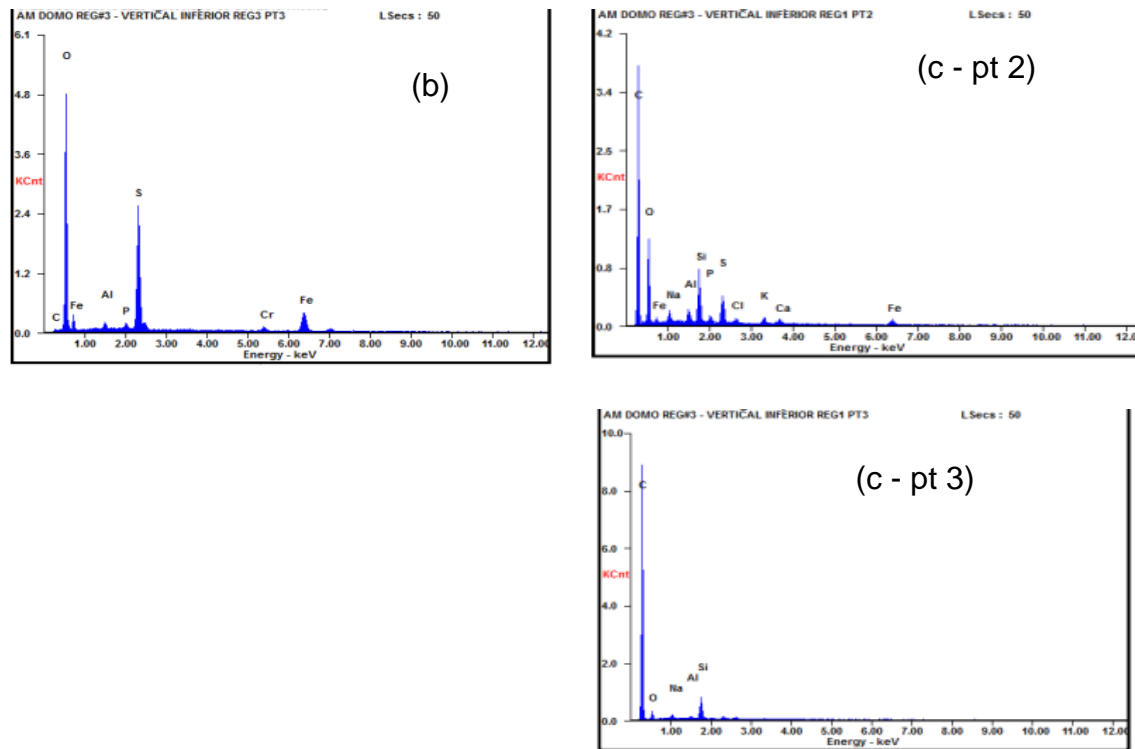


**Figure5** – Macro (a) and micrographic (b) visualization of the oxidation products of the upper part of the metallic housing of a regenerator

As a complement to the analysis and based on the selected points in Fig. 5b, the qualitative chemical composition of each phase of the corrosion products is presented in Fig. 6. The formation of siderite ( $\text{FeCO}_3$ ) and sulfides (Fig. 6) can be verified, correlating these oxidation compounds for the first time in the literature with this type of equipment. In Fig. 6b, the presence of sulfides and oxides of iron, aluminum and chromium can be visualized. Fig. 6c, at point 1, indicates the presence of sulfides and oxides of Al, Si, P, and Fe.

The spectrum of Fig. 6c, referring to point 2 indicates the presence of sulfides, iron carbonate, potassium and calcium, and oxides of aluminum, silicon, and phosphorus. The spectrum of Fig. 6c, point 3, shows a high carbon content, but without the presence of oxygen and iron, and with the presence of Si, Al, and Na.



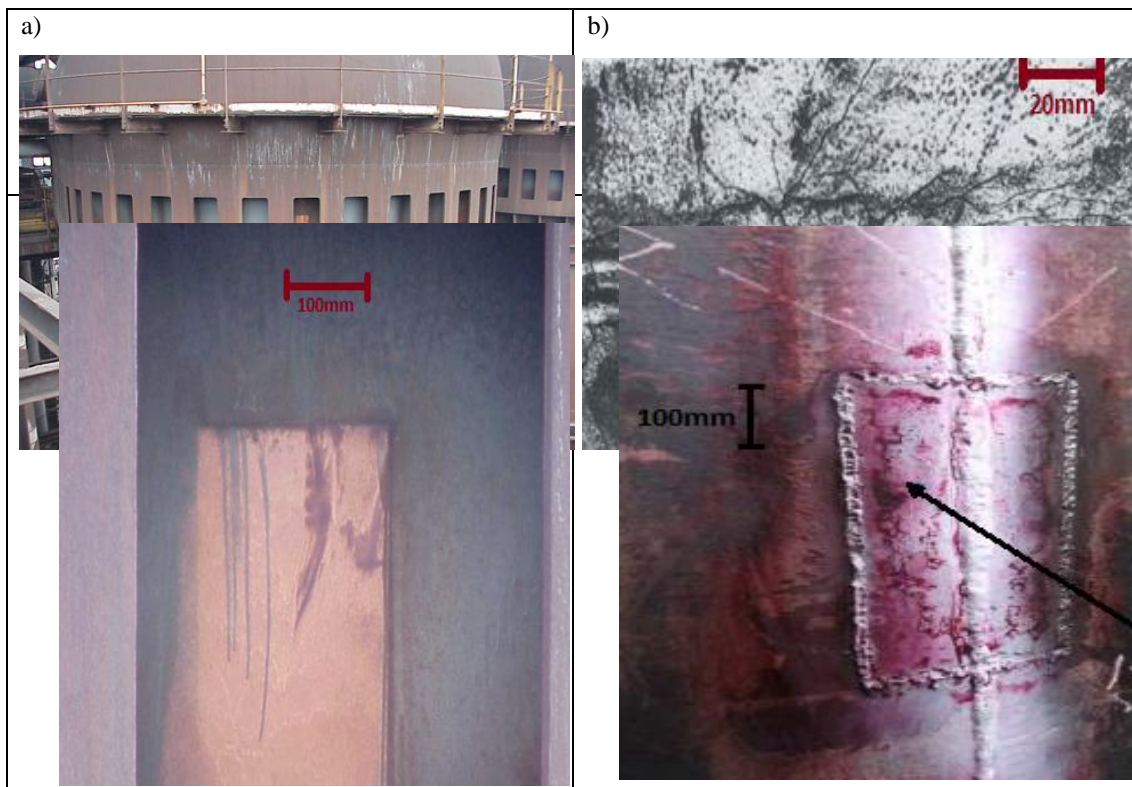


**Figure6** – Energy dispersive spectroscopy results of oxidation products of the internal part of the regenerators:(a and b) typical results from upper parts, (c) points 1,2 and 3 showed at figure (6b)

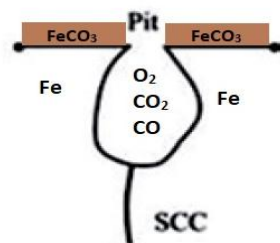
The second group of corrosive attacks to regenerator metal casings classified by Schaub et al. [2] are stress corrosion cracking (SCC) which is very common in regenerators, especially near weld regions in the heat affected zones (Fig.7).

The cyclic operation for heating the air affected the temperature oscillation on the regenerators' casing, generating mechanical stresses on the equipment's casing and the corrosiveness of the environment, mainly internal, predominantly acid, with the presence of sulfur and CO<sub>2</sub>. When the siderite (FeCO<sub>3</sub>) layer collapses, either by mechanical stress or chemical dissolution, it can lead to exposure of the steel substrate and promote localized corrosion such as pitting corrosion [7,9], as can be seen in Fig. 8. As pitting corrosion generates stress concentrators, cracks can be nucleated and propagated by different mechanisms.





**Figure7** – Typical occurrences of cracking in the metal casing of regenerators caused by SCC: (a) general view, (b, c, and d) detailed view.



**Figure8**–Mechanism of SCC formation after siderite ( $\text{FeCO}_3$ ) removal and pitting formation, adapted from [13]

In the 1980s, stress corrosion cracking (SCC) was identified to occur when regenerators unprotected from coatings were operated at dome temperatures exceeding  $1,300^\circ\text{C}$  and at high pressures [4]. Studies have revealed that the formation of  $\text{NO}_x$  from nitrogen in air increases exponentially when the temperature is above  $1300^\circ\text{C}$  [4]. Therefore, the formation of nitric acid ( $\text{HNO}_3$ ) occurs, which is a very aggressive condensate produced in the electrolyte in contact with the regenerator housing, attacking especially areas of high tensile stress concentrations, such as: the thermally affected zones adjacent to the housing weld seams and the weld seams themselves. This leads, over time, to progressive corrosion damage, continued crack formation, and ultimately to the failure of the regenerator as a

pressure vessel. The main reactions involved in this mechanism are equations (29), (30), (31) and (32).

In general, the amount of  $\text{NO}_x$  generation increases dramatically between  $1,450$  and  $1,500^\circ\text{C}$  [4]. In terms of regenerator operation, the increased  $\text{NO}_x$  generation leads to a greater possibility of SCC in the metal casing, and therefore the dome temperature must be controlled to limit the phenomenon [4]. The lagging ceramic burners installed in conventional regenerators usually have low mixing properties for fuel gas and combustion air, compromising this control.

Because of this, when the regenerator is operated at a temperature higher than  $1400^\circ\text{C}$ , even if below the theoretical range, localized regions of high temperature are generated in the combustion chamber, resulting in a large amount of  $\text{NO}_x$ , as

shown in Fig. 9. For this reason, the dome temperature is limited to 1400°C.

The mechanism of stress cracking in the presence of regenerator sulfur involves SO<sub>2</sub> from flue gas condensate, which forms sulfurous acid (H<sub>2</sub>SO<sub>3</sub>) that can be oxidized and form H<sub>2</sub>SO<sub>4</sub>, particularly when O<sub>2</sub> is present, as verified in equations (25), (26), and (27). As the condensate medium becomes acidic, generation of atomic hydrogen produced near the pitting and/or crack regions can occur by cathodic reduction of hydrogen ions.

Part of the generated atomic hydrogen, due to its small dimension, can penetrate through a pitting or a crack in the crystalline structure of the steel, going to lodge near the dislocations of the atomic structure, micro-cracks, inclusions, or voids.

The presence of dissolved atomic hydrogen in the ferritic or martensitic matrix facilitates the movement of dislocations in the crystal structure of the material (4,7). Atomic hydrogen can be adsorbed on the crack surface, decreasing its surface energy, and contributing to crack propagation [15].

There are several factors that affect the likelihood of stress corrosion occurrence in metallic materials, such as H<sub>2</sub>S concentration, temperature, total pressure, pH, exposure time, total applied stress, material properties (chemical composition, tensile strength, hardness, heat treatment, microstructures, etc.), and impurities and defects that may exist [17-21]. MR 0175-2000 for carbon steel establishes requirements for selection of materials in the presence of H<sub>2</sub>S.

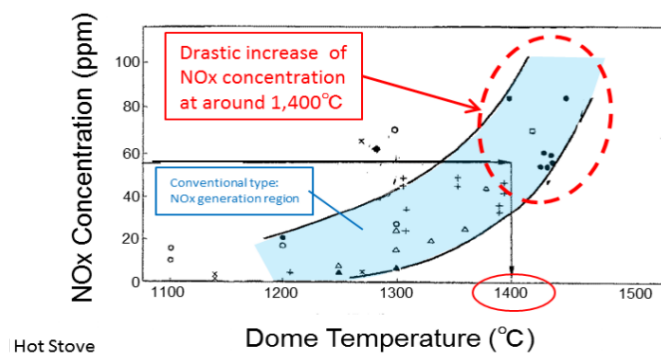


Figure 9 – NO<sub>x</sub> concentrations from combustion in metal burners, adapted from [4]

There are still gaps to be further investigated for better proof of the corrosion mechanisms of the regenerator casing, such as the use of advanced X-ray photoelectron spectroscopy (XPS) and glow discharge optical emission spectroscopy (GDOES) techniques for characterization of the oxides, nitrides and sulfides formed in the corrosion reactions and elemental analysis of composition profile. The study of the electrical properties of the regenerator casings, measurement of resistance/impedance, potentials, and evaluation of the influence of grounding on the electrical properties of this equipment are also relevant and the investigation of the particulate content of the gases used, the SO<sub>x</sub> content of the flue gases and its influence on the corrosion kinetics of different structural or low alloy steels also deserves investigation.

#### IV. Corrosion mitigation in regenerators

According to Schaub et al [2] most of the catastrophic failures of metal casings caused by SCC could have been prevented by regular

inspection. Their study also reinforces different approaches from a design point of view to address this relevant issue, exemplifying various actions for new regenerators, with all these approaches considering eliminating one of the following influencing factors: stress forces, chemical attack, and material sensitivity to SCC.

However, no references were found in the literature indicating ways to mitigate these mechanisms in the regenerators of blast furnaces already built. In this sense, the following suggestions of measures to protect the regenerators against the above-mentioned mechanisms are presented. They were divided, didactically, between internal and external aspects of the regenerators.

##### 4.1 Internal aspects

In the blast furnace operation routine, depending on the state of conservation of the regenerators and their useful life, the following objectives, and actions to be implemented for mitigation of corrosion in regenerators can be considered (Table 3).

**Table 3**–Objectives and actions to be implemented for mitigation of the corrosion of regenerators

Objectives	Actions	Corrosion mechanism
Fuel Gas Quality - reduction of particulate and water entrainment by blast furnace and coke oven gas	Maintain the quality of the combustible gases used and check and maintain the operating conditions of the coke oven gas washing/desulfurization systems within the design parameters Insert in the shutdown schedule the maintenance of the main items of inspections, cleaning, calibration, and corrections of the gas washing system;	Internal Pitting Uniform corrosion (reduce attack by sulfur and ammonia)  Uniform corrosion (reduce flue gas condensate and likelihood of damage to refractory lining) CST (reduce speed of micro crack propagation)
Minimize metal casing corrosion	Periodic monitoring of the metallic casing thickness, according to a frequency consistent with the time of use of the regenerator since its start-up Strengthen the maintenance plan for all the peripherals of the blast furnaces, aiming at reducing stoppages and their duration; On longer shutdowns (e.g., over 5 days) hire controlled heating to minimize temperature losses and temperature equalization of the checker’s chamber; Evaluate the implementation of cathodic protection  Periodically analyze the combustion gases used and check the efficiency of the burners;	Only identification of the regions most affected by advancing corrosion  Uniform corrosion (reduce flue gas condensate and likelihood of damage to refractory lining) CST (reduce speed of micro crack propagation)  Uniform corrosion (reduced electrolytic reactions with flue gas condensate) Uniform corrosion (correct burning of fuel gases) CST (ensure burner efficiency)
Dome temperature control	Keep the dome within the established operating ranges and correlate it with the previous action.	Uniform corrosion (correct burning of fuel gases) CST (ensure burner efficiency)

#### 4.2 External aspects

From an external point of view, the most logical action is to reduce the entry of raw materials with higher contaminant content, especially sulfur, phosphorus, chlorides, and others, from the metallic load and reductors. This action does not coincide in being the most profitable from the economic point of view. With the control of the raw material one can predict and mitigate the corrosion mechanisms that can occur by the action of contaminants.

#### V. Conclusions

This paper proposed to present and discuss the main corrosion mechanisms associated with the metallic casing of regenerators.

Uniform or generalized corrosion was observed in the regenerators. The greatest thickness loss observed over a 26-year period in a studied regenerator was a 63% reduction of the original plate thickness, i.e., a corrosion rate of 0.48 mm/year. The lowest thickness loss recorded

corresponded to a corrosion rate of only 0.06 mm/year.

In the upper parts of the regenerators, internally, the corrosion mechanisms of the metal casing are present with the formation of siderite ( $\text{FeCO}_3$ ), sulfides and that both favor stress corrosion.

Different mechanisms of metallic casing corrosion can be associated in the lower parts of the regenerators, being favored by the presence of electrolyte formed by the flue gas condensate.

Main mitigation actions for corrosion in regenerators were proposed such as reducing contaminant ingress through the materials and performing periodic flue gas analysis, controlling burner efficiency.

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