

Methodology for Evaluation of Corrosion Damage During Combustion Process in Refinery and Petrochemical Industry. Case Study: AISI 304 and ASTM A335 P5 Steels

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Prevention of the corrosion damage is key point to assure process safety in the refinery and petrochemical industry. Controlling and stopping corrosion is only possible through the detailed evaluation of all processes related with the corrosion damage.

In this work was proposed a methodology to evaluate the corrosion damage during combustion process in the refinery and petrochemical industry. As a study case the evaluation of AISI 304 and ASTM A335 P5 steels was realized in an atmosphere generated during the combustion process. The corrosion products formed on each material were simulated at 750 °C in the software HSC Chemistry. As a model mixture for the simulation it was used the historical chromatographic records from the gas mixture used in a typical furnace from Barrancabermeja (Colombia) refinery. These results were compared with experimental results, in which corrosion coupons of AISI 304 and ASTM A335 P5 steels were installed inside a furnace from Barrancabermeja refinery at 750 °C. The corrosion rate was calculated by gravimetric analysis, and the morphology and composition of the corrosion products were obtained by Scanning Electron Microscopy with X-Ray Microanalysis (SEM-EDS) and X-Ray Diffraction (XRD) analysis respectively; showing similarity between the corrosion products thrown in the simulation. The gravimetric analysis showed that the corrosion rate of ASTM P5 steel was higher than in AISI 304 steel; it was explained because the no formation of an internal protective chromium oxide layer in ASTM P5 steel. On the other hand, the SEM-EDS analysis showed that the corrosion products formed on AISI 304 steel corresponded mainly to iron oxides and spinels. Unlike to the corrosion products obtained for ASTM P5 steel, for which only iron rich layers were formed. Additionally, the EDS analysis revealed carburization and sulfidation in both steels, although these effect were more representative on AISI 304 steel. Finally, the kinetic study suggested the formation of non-protective oxide layers, which was confirmed through SEM analysis; where were revealed cracks and gaps in the morphology of the oxide layers formed in both steels. Finally, it is important to mention that the methodology applied in this work is applicable to other steels in typical corrosive environments from the refinery's equipment.

1. Introduction

Having in consideration the increasing needing in to reduce the spent of energy in the petrochemical industry, have been planted some strategies: the use of alternatives energies, the strengthening of energy management and the reusing and recovering of energy in the processes (Lunghi & Burzacca, 2004). This last strategy is actually used in the combustion process from Barrancabermeja refinery, where a refinery gas (RG) is used as energy source (Saavedra et al., 2013).

The RG consists in a mixture of natural gas and other currents obtained during the refining process, which are highly variable in composition and calorific power. The use of these mixtures can increase the high cost of avoidable corrosion in the industry, which can affect the national economy of countries as USA, UK and Japan, up to 5% of Gross Domestic Product (GDP) (Biezma & San Cristóbal, 2005).

For all these reasons, it is important to connect aspect of energy efficiency with aspects of processes security; thus in this work was established a methodology to study the effect of corrosion at high temperatures in a petrochemical industry, as a contribution of the problem.

This research follows the lines of the studies realized by (Kafarov et al., 2015) and (Saavedra et al., 2013), where the eco-efficiency of the combustion process in a refinery was evaluated, having in consideration CO₂ emission and adiabatic temperature of the furnace. In this work was evaluated the security aspect through the corrosion study of typical steels from the furnaces of Barrancabermeja-refinery; as is the case of AISI 304 and ASTM A335 P5 steels.

Corrosion at high temperatures (CHT) has been usually studied on austenitic stainless steel 304 (S304), especially in oxidizing environments. In dry environments it shows a good oxidation resistance due to its ability to thermally grow a protective Cr-rich α -(Cr_xFe_{1-x})₂O₃ scale. However, in wet atmospheres the water vapor reacts with the chrome in the scales to produce volatile species (Kim et al., 2013). In these cases, the scale converts into a non-protective Fe-rich α -(Cr_xFe_{1-x})₂O₃ scale. This leads irreversibly to “breakaway” oxidation, that is a catastrophic increase in oxidation rate (Peng et al., 2005).

On the other hand is the ferritic ASTM A335 P5 (P5) steel, which is commonly used in furnaces, heat exchangers and boilers at 500 °C. However, between the few studies reported around this steel, (Otero et al., 1996) demonstrated that P5 steel can have a better behavior at 700 °C than at 500 °C in an atmosphere of SO₂/O₂ after 120 hours of exposure. Nevertheless, it is suggested to pre-oxidation treatment for this steel before its installation in plant; to produce species such as SiO₂ and Cr₂O₃ that improve corrosion resistance.

After above argue it is clear the importance of this work, highlighting the fact that not exist a methodology to evaluate corrosion at high temperature in the petrochemical industry for S304 and P5 steels.

2. Methodology

The methodology selected to evaluate the CHT on S304 and P5 steels was divided in simulation and experimental part, as follows in next sections.

2.1 Simulation methodology

The simulation required the selection of a mixture model of RG from a furnace of Barrancabermeja-refinery; it was done through the statistical study of the most representatives compounds found in the historical chromatography's records. With the RG mixture were obtained the theoretical combustion products (TCP) in *Aspen HYSYS*, which were used in *HSC chemistry* to throw the theoretical corrosion products (TCOP) for both steels. The procedure is shown in the following figure.



Figure 1: Methodology for the simulation of theoretical corrosion products

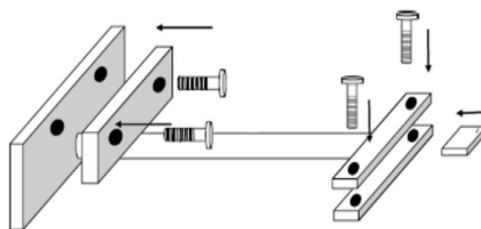


Figure 2: Coupons holder: It was fixed in the entrance of the furnace and had the capacity to support several coupons

2.2 Experimental methodology

For the experimental development, it was realized the installation of corrosion coupons of S304 and P5 steels in the aromatics unit furnace from Barrancabermeja-refinery. The coupon holder was designed of stainless steel and it had no direct contact with the coupons, due to the use of graphite in the coupling area (Figure 2). The dimensions of coupons were 3 x 2 x 0.9 cm for each one, with enough area to get appreciable mass gain.

Regarding to the preparation of coupons, they were sanded with silicon carbide paper until reach the sandpaper 600 on all the sides and corners before testing. Each coupon was cleaned with acetone and dried, subsequently they were marked following the recommendations of the standard ASTM G1 (ASTM, 2011).

Seven different times of exposure were established for the exposition of coupons to the combustion environment in the furnace, from 50 to 1500 hours (50, 100, 150, 400, 600, 800 and 1500 h). At last, the coupons extracted from the furnace were cleaning through an ultrasonic washing with acetone for 5 minutes, and prepared to the

chemicals and physics analysis, according to standard ASTM E407 (ASTM, Standard Practice for Microetching Metals and Alloys, 2007).

Finally, the coupons were subjected to SEM-EDS, XRD, hardness, micro hardness and metallography analysis. In addition, the kinetic study was carried out taking into account the dimensions of the coupons and the mass gained or lost for each exposure time. The complete experimental methodology is shown in the following figure.

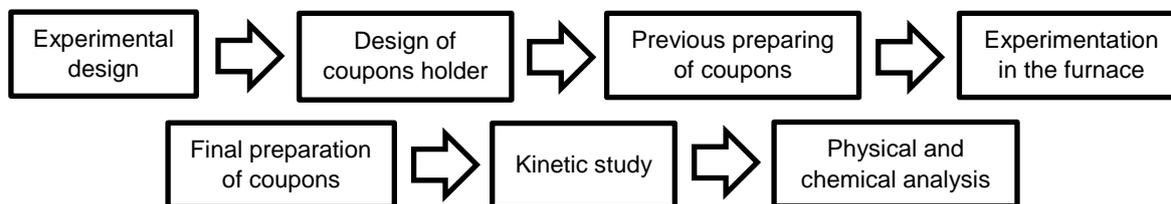


Figure 3: Methodology for the experimental development

Finally, it was realized the discussion of the results obtained through each methodology.

3. Results and discussion

It is important to mention that the temperature was selected according to a thermography taken from the radiation zone of the furnace. So that, it was determined the temperature where the coupons were exposed as 750 °C.

3.1 Determination of the gas mixture and its combustion products

From the average data obtained for each compound registered in 190 chromatographs taken between 2008 and 2015 from the refinery furnace, was selected the following mixture of RG.

Table 1: Composition of the mixture of RG

Compounds	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	H ₂ S	H ₂	C ₅ H ₁₂
%Molar	81.946	6.407	1.612	0.578	0.496	0.134	0.002	8.267	0.558

The TCP were determined for a 10 % of air in excess in an adiabatic combustion furnace simulated in Aspen HYSYS.

Table 2: Composition of the combustion gases

Compounds	CO ₂	O ₂	N ₂	H ₂ S	H ₂ O
%Molar	8.86	1.74	72.21	0.02	17.17

3.2 Theoretical corrosion products

By using the *HSC Chemistry* program and the phase stability diagram, theoretical potential corrosion products were established at 750 °C for one atmosphere of pressure. The molar ratio used between steel and gas was 1/1000, as is recommended by (John, 2010). The Table 3 shows the composition of the different steels.

Table 3: Steels composition

Steel	%C	%Mn	%Ni	%Si	%Cr	%Mo	%Fe
P5	0.15	0.45	0	0.50	5	0.55	93.35
S304	0.08	2	9.05	1	19	0	68.87

Among the corrosion products found on S304 steel, mainly sulfides and oxides were obtained; sulfides followed the molecular formula XS₂, with X as Fe, Ni and Mn. As oxides were obtained: hematite (Fe₂O₃), magnetite (Fe₃O₄), wustite (FeO), wplustita (Fe_{1-x}O), chromium oxide (Cr₂O₃), silicon oxide (SiO₂), CrO₂, FeOOH and spinels of Cr and Mn (FeCr₂O₄ and Fe₂MnO₄).

For P5 steel similar behavior was obtained in the formation of corrosion products. Among the sulfides obtained for S304 steel only NiS₂ was not shown for P5 steel, but instead MoS₃ was reported. With regard to the oxides, the only change respect to S304 steel, was the presence of molybdenum oxide (MoO₃).

On the other hand, using the phase stability diagram at 750 °C was showed that is thermodynamically feasible the stabilization of iron oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) in both steels (as shows the black star of the Figure 4).

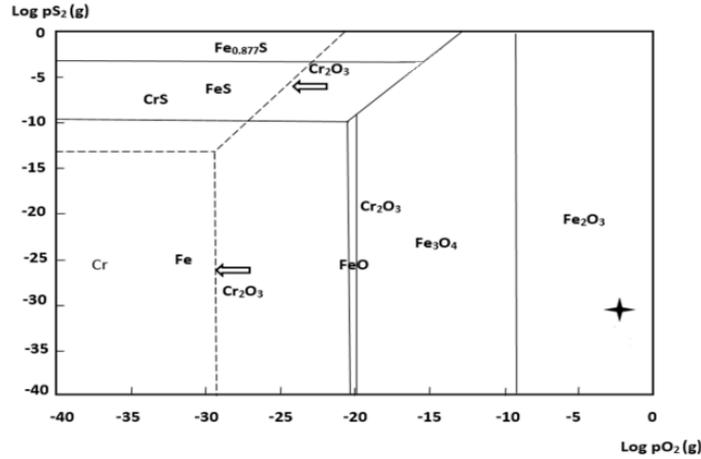


Figure 4: phase stability diagram at 750 °C

3.3 Experimental Results

3.3.1 Metallographic analysis

A metallographic characterization for coupons of both steels, before and after the exposition time of 1500 hours, was performed to determine microstructural changes.

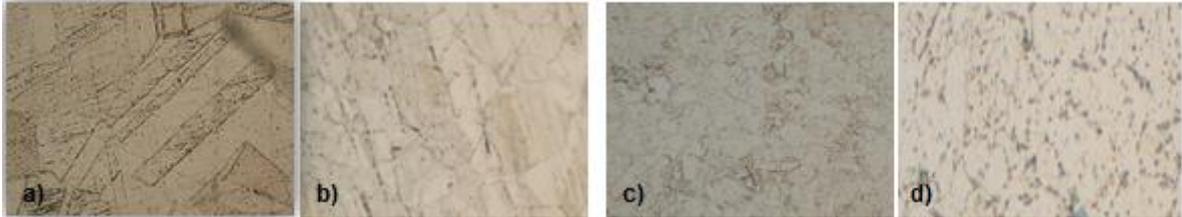


Figure 5: Optical microscopy (500x) for both steels: a) before and b) after an exposure time of 1500 h for S304 steel, and c) before and d) after an exposure time of 1500 h for P5 steel

At 750 °C and 1500 hours of exposure for S304 steel the grain growth phenomenon appears, due to the reduction of the area between the grain boundaries. Carbide precipitation in the grain boundaries was also observed, implying intergranular corrosion. Additionally, it was observed that the *maclas*, initially found in the structure, disappeared after the thermal treatment.

With respect to P5 steel at the same experimental conditions, the grain growth was not clearly identified; which was related to the rapid extraction of the coupons from the furnace, avoiding the proper recrystallization of the grains. Furthermore, a higher precipitation of carbides at the grain boundaries was evidenced; it was explained because the absence of a protective oxide layer.

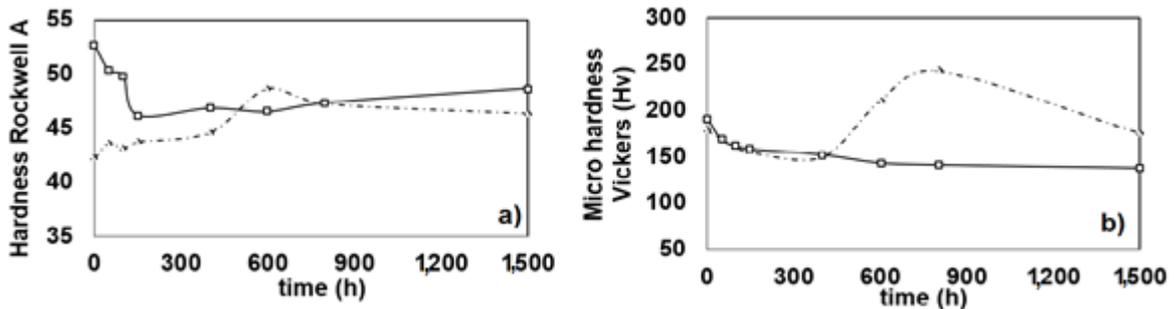


Figure 6: a) Hardness vs time and b) micro hardness vs time. The solid line refers to P5 steel and the dotted line to S304 steel

3.3.2 Analysis of hardness and micro hardness

For all coupons used during the experiment, hardness (Rockwell A) and micro hardness (Vickers) analysis were performed.

The decrease in hardness and micro hardness for P5 steel was explained by the formation of internal oxides, while the increases obtained for S304 steel could be related to the formation of carbides or by the rapid cooling suffered for the coupons when they were extracted from the furnace.

3.3.3 Kinetic study

The Figure 7 shows the polynomial behavior described for both steels in the mass gain graphs. This behavior does not correspond precisely to protective oxides layers (Parabolic behavior). In addition, a much greater and continuous mass gain was observed for P5 steel, which was able to form a layer with a thickness of 950 μm , compared to the 10 μm obtained for S304 after 400 h of experimentation.

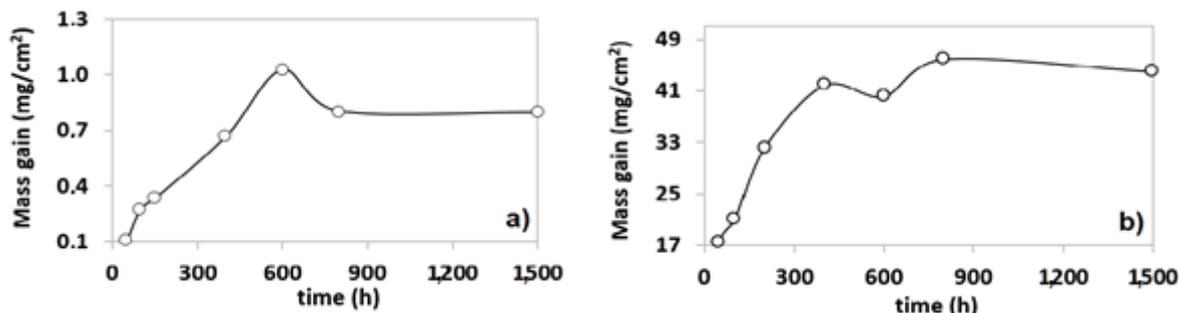


Figure 7: Mass gain for a) S304 steel and b) P5 steel

3.3.4 Results of chemical analysis

3.3.4.1 Scanning Electron Microscopy SEM-EDS

Through this study, it was possible to observe the morphology of the oxide layers deposited on each steels. In addition, from the EDS analysis it was possible to identify the presence of sulfides and carbides in alloys.

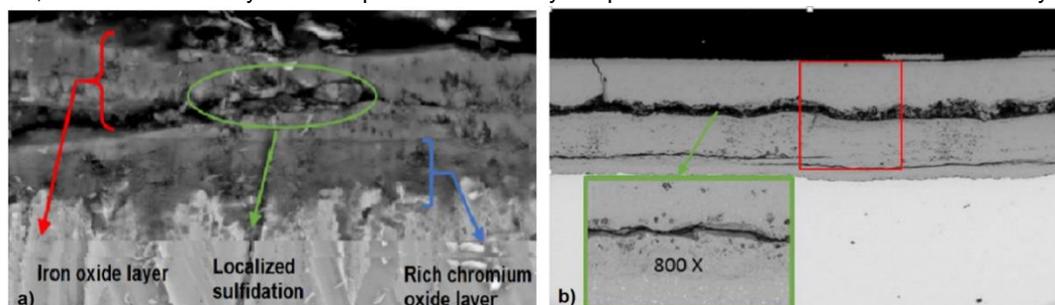


Figure 8: SEM-EDS for a) coupon of S304 exposed to 1500 hours (10000X) and b) coupon of P5 exposed to 1500 hours (100X)

The S304 steel revealed the presence of two layers of oxides; one external rich in iron and one internal rich in chromium. In addition, carbides and sulfides were identified as well as cracks between the oxide layers. For P5 steel a similar behavior was found in the oxide layers, with the difference that the layers were richer in iron and that the crack between layers was more severe. Furthermore, carbides were reported but sulfides were not found.

The confirmation of carbides helped to support the increments in the hardness of the alloys. On the other hand, in contrast to the results of the simulation there was congruence in the chromium and iron oxides. Also, it was possible to identify the presence of elements as Mn, Mo, Ni and Si in the layers.

3.3.4.2 X-ray diffraction (XDR)

The x-ray analysis allowed to identify the compounds formed on the surface of each alloy. For P5 steel the presence of wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3) were confirmed, whereas for steel S304 only the last two were reported.

However, considering the results of EDS, is not ruled out the formation of chromium-rich spinels in the inner oxide layers of each alloy, nor the presence of other oxides. The formation of carbides and sulfides is not ruled out either, as were suggested by simulations.

4. Conclusions

The novel methodology for corrosion evaluation in the petrochemical industry was developed and applied on S304 and P5 steels. Coupons of both steels were exposed to a combustion environment at 750 °C, which was generated in an aromatics furnace from Barrancabermeja-refinery (Colombia). In addition, it was realized the design of a coupons holder that allowed the loading of several coupons of both steels inside the furnace.

It was found congruence between the experimental and simulations results; where, the compounds supported by EDS and XDR analysis shown the presence of external oxide layers rich in iron and inner layers rich in chromium. These results are similar to those reported by (Kim et al., 2013) for S304 steel; where a non-protective Fe-rich α -(Cr_xFe_{1-x})₂O₃ scale was reported in a wet environment. However, the results obtained for P5 steel were opposite to those reported by (Otero et al., 1996), because in this occasion it was not a dry atmosphere and the inner oxide layer was non-protective. These conclusions were supported by the results of the kinetic analysis, where parabolic behavior was not evidenced but rather polynomial for both steels. Another indicator of the non-protective behavior of the oxide layers formed on S304 and P5 steels was the presence of intergranular carburization and located sulfidation; where mainly carburization affected the hardness and micro hardness of the steels. Nevertheless, it is important to mention that S304 steel had a better performance than P5 steel; it was reflected in the formation of more compact and thinner oxide layers, and because the appearance of breakaway oxidation in P5 steel.

Finally, this methodology could be applied to carry out studies of corrosion on wide class of alloys under typical refinery conditions.

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