Simultaneous sulfidation/oxidation of a ferritic steel under a simulated mixture of flue gas from an oil refinery

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Abstract. Ferritic steels are exposed to simultaneous oxidizing/sulfidation environments during their service in industrial furnaces, which intensify their degradation and reduce their expected lifetime. This research supplies different corrosion details from those highly reported for the studied alloy under single oxidation or sulfidization atmospheres, as well as from those works developed on oxyfuel gas mixtures. The experimental data obtained by us were compared with an oxidation paper previously published by the same authors but without the additional effect of sulfur oxides. The simulated conditions used included temperatures from 450 to 750 °C, exposure times up to 200 h, and a flue gas molar composition without the carbon dioxide influence. As a result, the oxidation mechanism was markedly affected by bulk and surface sulfur compounds, due to their strong adsorption, pathways blocking, and induced layer spallation. This study aimed to identify sulfur compounds onto the oxide layers by means of X-ray photoelectron spectroscopy, which were later validated through a ferritic-steel sample extracted from a refinery furnace. Finally, the present work contributes to the field of physics—physical chemistry—by providing the thermodynamic equilibrium of sulfur oxides at tested conditions and the kinetic behavior of the scale.

1. Introduction
The current oil refining process employs recovery gases as the energy source for boilers and furnaces [1], despite this strategy introduces chemical agents such as H₂S or SOₓ to the equipment, intensifying the damage over the metal structure. In this regard, sulfidation is one of the main corrosion problems presented in the petrochemical industry [2,3] causing up to 20 % of reported failures [4]. 9Cr-1Mo (P91) pipes are often implemented in high temperatures processes—even above many stainless steels—thanks to its outstanding thermo-mechanical properties [5,6]. Though, this alloy has been found susceptible to high degradation rates under wet and sulfidation environments [7-10]. Several researchers have addressed said limitations over comparable ferritic steels, developing controlled lab test into SO₂ [11], H₂-H₂O-H₂S [12-14], H₂-H₂S [10,15], and oxyfuel atmospheres at high temperatures [16-19]. They have supplied valuable information about the clash of both mechanism (oxidation/sulfidation); while oxide layers tend to be protective, the addition of H₂S/SOₓ induce their embrittlement and increase their corrosion rates. The oxide layer morphology reported is duplex: the outer layer composed by iron oxides while the inner by Fe₃O₄ + (Fe, Cr)₂O₄, both with internal sulfides but mostly localized at the oxide/metal interface [11].
Likewise, SO\textsubscript{2} sulfidation has also proved to slowdown the corrosion rate of alloys by blocking the inward of oxidizing molecules through the adsorption of surface sulfates [19].

Up to this point, different authors have provided data related to the sulfidation of diverse ferritic steels under oxyfuel or isolated sulfidation atmospheres. However, the aim of this work is to provide special detail about the simultaneous oxidation-sulfidation of P91 at oil refining conditions. Then, we recreated the N\textsubscript{2}-H\textsubscript{2}O-O\textsubscript{2}-SO\textsubscript{2} refinery flue gas to perform lab trials at equidistant temperatures from 450 to 750 °C and exposure times up to 200 h.

2. Experimental

To determinate the sulfidation role over oxide layers, we previously studied the P91 behavior in the oxidizing mixture of 90.53H\textsubscript{2}O/9.47O\textsubscript{2} %mol [20] to elucidate how the SO\textsubscript{2} contribution modify the duplex structure of the scale. Besides, we compared our results with an extracted P91 pipe from a refinery’s furnace.

2.1. Experimental conditions

Based on the aforementioned research work [20] in which the flue gas molar composition 72.15N\textsubscript{2}/9.10CO\textsubscript{2}/1.74O\textsubscript{2}/16.67H\textsubscript{2}O/0.34H\textsubscript{2}S was reported- we excluded the carbon dioxide specie to obtain the desire mixture of gases of 79.37N\textsubscript{2}/1.92O\textsubscript{2}/18.34H\textsubscript{2}O/0.37H\textsubscript{2}S. SO\textsubscript{2} compounds resulted from the interaction between H\textsubscript{2}S and free oxygen to change its chemical identity from SO\textsubscript{3} to SO\textsubscript{2} at high temperatures. The complete experimental conditions were: 1, 20, 50, 100, and 200 h of exposure times, 1 atm of pressure, four equidistant temperatures from 450 to 750 °C, 0.40 g/h of oxygen mass flow, 14.58 g/h of H\textsubscript{2}S-N\textsubscript{2} mass flow, and 2.15 g/h for the steam mass flow. According to this, 20 tests were carried out -a standard factorial design- since duplicates were implemented in each run.

2.2. Materials

The P91 samples used were obtained by cylindrical machining and wire cutting from a 15 cm long and 2.5 cm thick tube, whose composition was determined by atomic emission spectroscopy (Table 1). The coupons dimensions were 15 mm high, 10 mm long and 2 mm wide, with an exposed area of approximately 4.11 cm\textsuperscript{2}. These samples were sanded with silicon carbide paper until reaching the mirror finish and then immersed into an ultrasonic bath with acetone to remove possible impurities.

| Table 1. P91 elemental weight fractions. |
| --- |
| %Mo | %C | %Si | %Mn | %P | %S | %Ni | %Cr | %V | %Nb | %Al | %N | %Fe |
| 0.989 | 0.106 | 0.768 | 0.316 | 0.013 | 0.003 | 0.271 | 8.439 | 0.024 | 0.008 | 0.006 | 0.015 | 89.042 |

2.3. Experimental setup

To recreate the calculated mixture of gases and avoid unwanted aqueous reactions, we implemented two streams: one to drag water vapor into the experimental system by humidifying O\textsubscript{2} in a bubbler at 96 °C, and another of 0.5H\textsubscript{2}S/99.5N\textsubscript{2} just before the entrance of the electric furnace. The assembly line was assisted by electric heating cords to avoid the water vapor condensation before and after the tubular reactor, which in turn was made up of 316L stainless steel for better corrosion resistance. Finally, an argon network line was employed to prevent the progression of chemical reactions outside the control times. Figure 1 shows the experimental setup composed by: (1) argon cylinder, (2) O\textsubscript{2} cylinder, (3) flow valve, (4) relief valve, (5) pressure regulator, (6) digital flow meter, (7) bubbler, (8) humidifier temperature control, (9) heating cord, (10) nitrogen cylinder, (11) H\textsubscript{2}S cylinder, (12) pressure gauge, (13) horizontal tubular electric furnace, (14) furnace’s control temperature, (15) samples, (16) sample holder and (17) residual gases outlet.
2.4. Characterization techniques
We rely on the following techniques to describe the surface and bulk corrosion products: scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and x-ray photoelectron spectroscopy (XPS). Table 2 listed explicit information about the equipment and their work parameters.

Through SEM-EDS analysis we determine the morphology of the layers at the cross-section and their kinetics law of growth, but it also provided data linked to the scale’s elemental composition. Otherwise, XRD deliver the bulk crystalline phases while XPS evidence of adsorption phenomena.

Table 2. Characterization equipment and their parameters.

| Technique | Equipment | Parameters |
|-----------|-----------|------------|
| SEM-EDS   | Quanta FEG 250, BSED-SSD, EDAX APOLLO X | Voltage 25 kV, high vacuum, and detector resolution of 126.1 eV (Mn Kα) |
| XPS       | SPECS: FOCUS 500, PHOIBOS150 2D-DLD | Monochromatic Al-Kα x-ray source, vacuum pressure of 10⁻¹² atm, instrumental broadening of 0.75 eV, and adventitious carbon peak settled at 284.8 eV |

3. Results and discussion

3.1. Thermodynamic approaches to the oxidation of sulfur hydroxide
We carried out a thermodynamic equilibrium analysis to determine the most favorable conditions for the SO₂ and SO₃ molecules. Figure 2 indicates a greater presence of SO₃ below 600 °C while more prominent SO₂ concentrations above said temperature. The influence of each sulfur oxide at tested temperatures resulted particularly useful to attach their role over the P91 sulfidation -as argued in section 3.2.

3.2. Logarithmic growth law
As discussed above, we reported that the growth of the P91 oxide layer responded to parabolic kinetic within the H₂O/O₂ environment [20], but this time under the SO₃ stimulus that curve-fit changed to a logarithmic one (Figure 3). It means that P91 samples respond to fast corrosion rates -at the early stages-followed by a quick stabilization phase. According to this and as suggested by the thermodynamic analysis (Figure 2), at low temperatures SO₃ encourages O₂/H₂O molecules to increase the mass transfer processes. Meanwhile, at high temperatures SO₂ proved its capacity to reduce the mass interchange regarding oxidation results. Although, another explanation could be intuitively associated with the spallation induced by the sulfur enrichment at the outer layer.
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Figure 2. SO$_x$ thermodynamic behavior between 450 and 750 ºC.

Figure 3. Corrosion kinetics under simultaneous oxidation/sulfidation conditions compared with isolated oxidation at (a) 450 ºC, (b) 550 ºC, (c) 650 ºC, and (d) 750 ºC.

3.3. Scale composition
As anticipated the kinetics analysis, we found an oxide structure vastly covered by sulfur compounds (Figure 4). Most of the sulfur species were equally deposited at the inner layer and at the layer’s surface. It implies that the inward of oxidizing molecules as much as the outward of metal cations were affected by the SOx accumulation. Otherwise, we validated these results with the qualitative data supplied by
one sample of P91 extracted from a refinery furnace (Figure 4), despite an organic film embedded onto the provided sample as coating disturbed more precise conclusions.

SOx are assumed to be superficially adsorbed to release sulfates and sulfides (Figure 5). Thus, the reaction between SOx and metal cations conduces to the degradation of the scale since iron sulfates have proved to be chemically unstable above 550 ºC [21], leading to the spallation of the outer layer. However, even if adsorption processes were discarded, the direct reaction of sulfur oxides with the steel cations would be still feasible, troubling the growing mechanism of the outer layer as well. Notwithstanding these disadvantageous effects, the degradation velocity obtained under the SOx atmosphere was lower than within the pure oxidizing environment (Figure 3), that is: surface blocking effects may be beneficial for some ferritic alloys.

![Figure 4. BSE images of P91 cross-section from (a) One sample tested at 450 ºC up to 200 h and (b) The sample extracted from a refinery’s furnace.](image)
4. Conclusions
In this research work, we focused on describing the early corrosion of P91 under a simulated oxidizing/sulfiding environment from an industrial furnace. The experimental conditions settled were 1 atm of pressure, exposure times up to 200 h, and temperatures from 450 to 750 °C. As a result, we proved that SO\textsubscript{x} gases change the P91 oxidation mechanism. At low temperatures SO\textsubscript{3} while at high temperatures SO\textsubscript{2}, both adsorbed superficially to release sulfates and sulfides. These compounds also cover the entire oxide layer obstructing the inward of oxidizing species as much as the outward of metal cations. Likewise, the sulfur enrichment of the outer layer contributes to its embrittlement and final detachment. We encourage researchers to focus on adsorption phenomena, internal corrosion, and long-term trials for future studies related.

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