



# Effect of severe operation conditions on the degradation state of radiant coils in pyrolysis furnaces



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## ABSTRACT

This work arose from the need to understand the degradation phenomena taking place in the radiant coils of pyrolysis furnaces of the petrochemical plant of REPSOL POLÍMEROS in Sines, Portugal, in order to extend their service lifetime.

The radiation coils were studied through the finite element method, rendering stress and displacement analysis and calculation of the Larson–Miller parameter in severe operation conditions. The studied operation parameters were temperature increase, pressure increase, net coil weight increase through coking. Additionally, microstructural analysis of samples of H39WM and H46M alloys in as-supplied and used conditions was carried out.

Attained results suggest that the operating lifetime of similar coils can be extended by tuning their temperature profile and especially the amount of coke weight loaded, both during current operation and on decoking. Frequent and standardized temperature readings are mandatory to assure a temperature profile below project temperature, determining the coke weight loaded at a given time would also allow a more accurate knowledge of the remaining furnace creep life.

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## 1. Introduction

In ethylene production the hydrocarbon feeds are thermally cracked in the presence of steam at low pressure and process temperatures of 788–843 °C. While the shield section, the lower convection section, the outlet transfer line and the quench unit of the ethylene cracking furnace operate at relatively low temperatures, the radiant section of some of the furnaces operate at end-of-run tube metal temperatures up to 1150 °C. This is in practice the upper temperature limit for available heat resistant alloys [1]. Steam cracking furnaces thus provide one of the most aggressive settings to which alloys can be exposed, combining high temperatures with a very aggressive chemical environment, which includes oxidizing and nitriding flue gases at the outside, carburizing atmosphere at the tube inner surface, and severe start/stop and decoking cycles [2,3]. As a result of oxidation and nitriding the material outer surface becomes glazy and spalls from the tube wall, decreasing tube wall thickness [4]. Carburization results in a carbon layer build up inside the hotter sections of the coils during operation,

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increasing tube net weight and promoting carbon diffusion into the alloy matrix with increasing time and temperature [3,5,6].

Carburization is a primary cause of ethylene furnace tube replacement [7], wherein most cases there is a combination of factors leading to coils failure, e.g. carburization and creep ductility exhaustion [2,8–10]. This results in bulging, bending and ovalization of the tubes. Also, brittle fracture during furnace trips can result in large, longitudinal cracks on many tubes in the furnace. Creep ductility exhaustion is determined by the number of cycles (start/stop and decoking cycles) and the nature and severity of those cycles.

Radiant coils of pyrolysis furnaces are usually designed for a normal life of 100,000 h (11.4 years) of service at an operating temperature of 900 °C [7,11–15]. Their actual service life, however, varies from 30,000 to 180,000 h, depending on service conditions and on the quality of materials [16]. After 10,000 h in service, the tubes crack length increases and their weldability decreases. Also, creep resistance and ductility are reduced and the material becomes more prone to fracture, particularly during thermal cycle.

Pyrolysis tubes failure can be prevented by a combination of proper furnace operation, materials selection, regular inspections and appropriate design [2,8–10,17–19]. Each pyrolysis plant performs with different and specific operating conditions and philosophies; hence each plant has characteristic causes for radiant coil failure [2]. The analysis and understanding of those typical mechanisms is thus of great significance, allowing the operators to carry out the most adequate selection of tube materials and furnace operation parameters.

In this context, radiation coils from the petrochemical plant of REPSOL POLÍMEROS in Sines (Portugal) was studied through the finite element method. Stress and displacement analysis and Larson–Miller parameter calculation were accomplished in severe operation conditions: increase of temperature, coke weight and gaps in the guides. Individual and comparative characterization study of samples of H39WM and H46M alloys in as-supplied and used tubes was carried out. Attained results allowed to establish a relationship between the operating conditions and the degradation state of the samples.

## 2. Materials and methods

Two different locations in a radiant section of a coil tube from the REPSOL POLÍMEROS plant were studied. Coil behavior was analyzed with Finite Element Analysis (FEA) (Section 3). Also, the metallurgy of the corresponding alloys was studied. For that purpose tube samples were collected and analyzed in as-supplied and used (after failure) condition. Fig. 1 shows the correspondent coil configuration and the location of sample collection.

Samples were cut in the radial direction, both in as-supplied and in used condition tubes. The collected samples, labeled S1 and S2 for convenience, correspond to different service conditions and lifetime, which are slightly more severe for S2 (Table 1). The samples were first grinded and polished to a 1 µm finish, and etched with glyceric acid solution [20]. Microstructural features of the alloys were then assessed using field emission gun scanning electron microscopy (FEG-SEM) (JSM-7001F, JEOL), coupled with energy dispersive spectroscopy microanalysis (EDS) (Inca pentaFETx3, OXFORD INSTRUMENTS).

The tube portion where S1 was collected was manufactured in high temperature alloy H39WM, while the S2 portion was manufactured in high temperature alloy H46M. These alloys correspond to the main materials used nowadays in centrifugally cast tubes for steam cracker furnaces, especially for the hot outlet tubes [21]. Mechanical properties of both high temperature alloys are rendered in Table 2. The H39WM alloy presents high creep strength and high carburization resistance [21]. It is a fully austenitic alloy, with high Cr contents, which is essential for the formation of a protective Cr<sub>2</sub>O<sub>3</sub> layer that enhances oxidation and carburization resistance at high temperature [22]. Alloying elements such as Cr, Nb, Mo, Ti and W act as carbide formers and retard the rate of softening at high temperature [1]. Ni, Si, Al and Mg strengthen ferrous alloys through solid solution strengthening and grain-boundary control [1,23]. Higher nickel grades such as H46M were developed in the 1980s aiming to improve chemical resistance up to higher temperatures, with sufficient creep strength for ethylene tubes [21], while further increasing resistance to carburizing atmospheres and carbon diffusion [6,21]. Additionally the high percentage of nickel improves resistance to thermal fatigue and maintains an austenitic structure so the alloy remains ductile [22,23]. In both alloys increased creep performance results from the introduction of Nb additions: Nb precipitates eutectic niobium-carbides, predominantly at grain-boundaries and also among the chromium carbides [21]. The high melting point niobium carbides are insoluble up to 1250 °C and remain in their positions without volume change during alloy exposure to high temperatures [24]. Grain growth is inhibited and the formation of creep voids during coalescence of chromium carbides is transported to longer times or higher stresses and/or higher temperatures [21,25].

## 3. Finite element analysis

FEA was carried out using the ABAQUS® program, in order to simulate radiant coil behavior and response during various stages of the furnace service and run length.

The radiant coils of pyrolysis furnaces are suspended vertically. Depending on their arrangement, coils are combined into a transfer line, TL, whose output is at the top of the combustion chamber. Each coil has tabs on the top and bottom. The upper guides, which extend through the roof of the combustion chamber, are fixed outside the furnace, using a spring suspension system. The left part of the coil (due to this being approximately symmetrical) was drawn and modeled (Fig. 1a) to determine the stress and displacement distributions arising from the loading conditions (Fig. 1b).

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