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Effect of coking in massive failure of tubes in an ethylene cracking furnace

Jose Luis Otegui [a,*], Jeremías De Bona [b], Pablo G. Fazzini [b]

[a] YPFTecnologia S.A., Conicet, Argentina
[b] GIE S.A. Integrity of Assets, Argentina

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ABSTRACT

The causes and characteristics of the massive failure of the radiant coil tubes in an ethylene cracking furnace, which failed during an emergency non-programmed stop, are investigated. The failed tubes had been in service for about three and a half years, while lifetime had been estimated in five years. Tensile testing showed severe in-service degradation of material mechanical properties. Longitudinal cracks on failed tubes are brittle and originate in the inner side of the tubes wall. All failed tubes display a thick layer of coke adhered to the inner wall. This coke comes easily broken by bending or tension stresses, but sustains compression.

The origins of loads which lead to the fracture were replicated; cracks were lab-induced by longitudinal cutting and resulting openings measured. Mechanical modeling allowed concluding that loads that led to failures were due to differences between thermal expansion coefficients of tube alloy and the coke growth within them. When the furnace was cooled down, thermal contraction of tube metal was restricted by the thick coke layer. This layer grew in service in the pressure expanded tubes.

The failures were due to a combination of circumferential loads induced by coke during fast cooling and low strength of tube material. Recommendations include monitoring coke thickness and comparing with critical thickness for tube rupture in case of an emergency stop. This way, operators will have a parameter useful to schedule decoke processes.

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1. Introduction

The causes and characteristics of the massive failure of the radiant coil tubes in an ethylene cracking furnace, which failed during an emergency non-programmed stop, are investigated (see Fig. 1) [1]. This analysis leads to establish material, manufacturing and assembly quality on one hand, and to determine operative conditions that contributed to the failure, on the other. As there are similar components operating in the same plant as well as in other plants, this study aims to identify failure mechanism/s, to determine the causes that created the conditions for this mechanism to cause premature failure of the material, to establish the likeliness for this failure to happen again on similar components and to establish possible mitigation measures.

The furnace has twenty similar coil assemblies. The tubes have an inner diameter of 102 mm, and 10 mm thickness. Tube length varies depending on its position in the assembly. Tube specification agrees with a Cr–Ni centrifugal casting with additions of Nb, Ti, Si [2]. Operating temperature is 850 °C, outlet pressure of the cracked gas is 0.5 barg.

* Corresponding author.
E-mail addresses: jose.l.otegui@ypftecnologia.com (J.L. Otegui), fazzini@giemdp.com.ar (P.G. Fazzini).

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The failed tubes had been in service for about 3.5 years, while the estimated lifetime for these tubes is about five years. Since the start up, a periodical decoke process is planned every 90 days, depending on the "Nozzle Factor", among other influence factors [3]. This guarantees the cracking process not to be altered by the presence of the coke inside the tubes. The coke gets deposited on the inner surface of the tubes, raising flow rate and decreasing thermal transfer as thickness grows.

During an emergency stop the furnace was taken out of service, letting it cool down from service to room temperatures. The day after, plant personnel realized that all the radiant coils in the furnace suffered cracking, leaving the furnace completely useless (Fig. 1).

This is not the first failure in this kind of equipment occurring within this petrochemical company. Cracking in three convection tubes [4] were analyzed some years ago; in that case the leaks were located in the surroundings of the pressure measurement nozzle. The results suggested that cracks initiate at the inner surface and propagate in an intergranular way. Microstructures were compared in the inner surface and in mid-section of the thickness. The results indicated that material suffered carburization. A failure of apparently similar characteristics occurred in another plant of the same type, during a non-programmed stop of the furnace. In that case, the failed tubes were brand new.

Heat resistant alloys have widespread uses in the petrochemical industry. These alloys have replaced the traditional nickel based superalloys and have equivalent properties under creep conditions, with excellent resistances to high temperature oxidation [5]. In most cases, these complex alloys are used in their as-cast condition but, during service, ageing and phase transformations occur. The typical microstructure of as-cast alloys is an austenite matrix with intergranular eutectic-like primary chromium-rich carbides (M7C3 and/or M23C6 types) and niobium carbides (MC type). During service at temperatures of 850–1050 °C, all the primary chromium carbides eventually transform into M23C6; intragranular secondary M23C6 carbides also precipitate within the austenite grains, contributing to strength and creep resistance [6,7].

The operation range of these alloys is 533–1150 °C. High heat transfer coefficient, mechanical strength at elevated temperatures, creep resistance, microstructural stability, carburization resistance, oxidation resistance, and economics are considered for the selection of these materials for equipment structures [8]. The demand for higher creep strengths at higher temperatures, with ever diminishing wall or section thickness, has been the major driving force behind these material developments [9].

Both microstructure and operational conditions are the main parameters which affect the fracture of these alloys [10]. Failure mechanisms generally encountered are fatigue, stress corrosion cracking and ductile fracture [11,12].

Creep resistant alloys also contain a significant quantity of carbon, required for solid solution strengthening as well as carbide formation. Of further importance is the secondary carbide formation, where carbides precipitate during operation at high temperatures. Precipitation takes place at operating temperature. In general, they have an austenitic (γ-phase) matrix and contain a wide variety of secondary phases. The most common second phases are metal carbides (MC, M23C6, M6C, and M7C3) and γ', the ordered face-centered cubic strengthening phase [Ni3(Al, Ti)] found in age-hardenable Fe–Ni–Cr and nickel-base superalloys.

Exposure to an excessively high temperature could have three detrimental effects [13]. First, creep can lead to the accelerated formation of grain boundary voids; creep deformation can also lead to cracking of the protective oxide scale causing an accelerated carburization attack. Secondly, high temperature accelerates the rate of carburization attack. The effect of creep is compounded by the presence of a continuous network of grain boundary carbides [14]. Thirdly, the changes in mechanical properties are connected with the evolution of intermetallic phases and other intermetallic compounds arising in service [15].

The carburization behavior of the tubes used under the conditions of petrochemical cracking processes depends in a first line on the temperature. Up to 1000 °C carbon pickup is low, but above 1050 °C heavy carbon pickup and increasing carburization depth must be counted with. This temperature dependence is due to the fact that at 1050 °C equilibrium is attained between chromium oxide and carbide, so that the oxide is no longer stable and the original protective effect of the oxide

Fig. 1. Failed tubes within the furnace after emergency stop.

layer is lost. Carburization of a surface layer may set in at temperatures as low as 800 °C. Carburization is delayed by high Cr and Ni contents.

2. Experimental failure analysis

Analyzed samples show cracks that are mostly longitudinal and quite open, with about a 2 mm wide maximum surface opening, see for example Fig. 2. After findings, in-situ arresters were flame cut to avoid the cracks to propagate further into the U-shaped pieces which connect the tubes. As seen in Fig. 3, some cracks eventually deviated from their axial paths, leading to complete separation of the tubes. This is frequent in fast running axial cracks in pressurized pipes, especially when crossing a discontinuity such as a weld. Cracks tend to branch and form two hellical cracks that quickly coalesce into a circumferential crack. The crack detailed in Fig. 4 developed as a wholly circumferential fracture surface; brittle behavior is evident.

All tubes display a thick layer of coke adhered to the inner wall. The coke layer is thicker than the tube, Fig. 4; average layer thicknesses in failed tubes were 8–12 mm. Coke characteristics and properties depend on the raw material used in the furnace. In this case the coke layer displays a multilayered structure, with at least 3 distinct layers (Fig. 4). This coke layer is harder than that found in other failures, with a very low porosity and a shiny aspect. Simple tests showed that this coke layer does not thresh or brake when touched. It displays a ceramic-like behavior, which means that it comes easily broken in presence of bending or tensile stresses, but sustains large compression loads.

Metallographic samples were prepared, etched and analyzed according to ASTM standards. The photographic composition of Fig. 5 shows a metallographic specimen from a circumferential cross section of the pipe wall, the inner side of pipe wall is shown at the right side of the picture. The crack path in the circumferential cross section indicates propagation from the inside, all through the thickness until reaching the outer surface. This was the case in all examined cracks.

Microstructure of tube material, Fig. 6 (X200), consists in an austenitic dendritic matrix, which contains a complex network of carbides and fine precipitated particles within the dendrite branches, some of them coarsened. The interdendritic nature of the crack path is evident in Fig. 7 (X50), secondary cracks can also be observed.

Fig. 2. Open longitudinal crack, arrester to stop crack propagation.

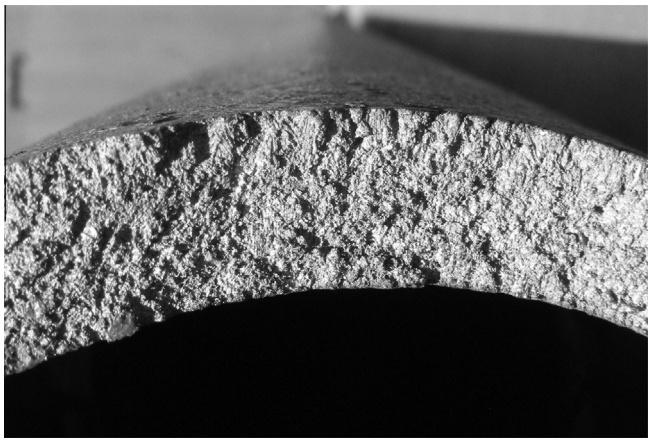

Fig. 3. Surface of a circumferential brittle fracture.

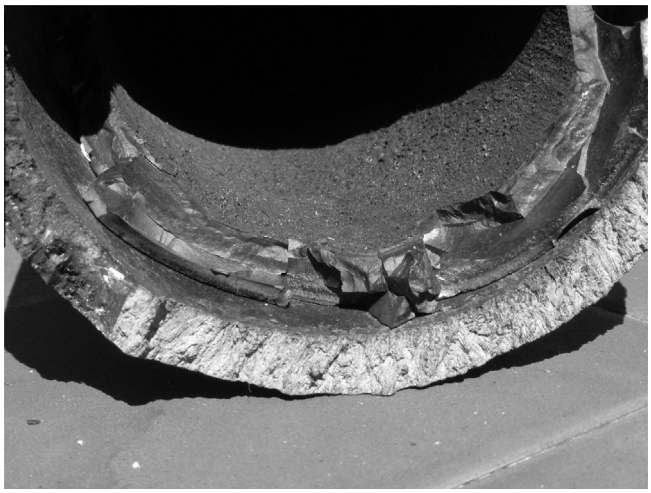

Fig. 4. Detail of coke layer within failed tubes.

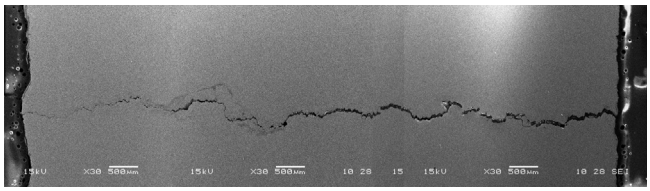

Fig. 5. Metallographic specimen of circumferential cross section of pipe wall, inner side at right.

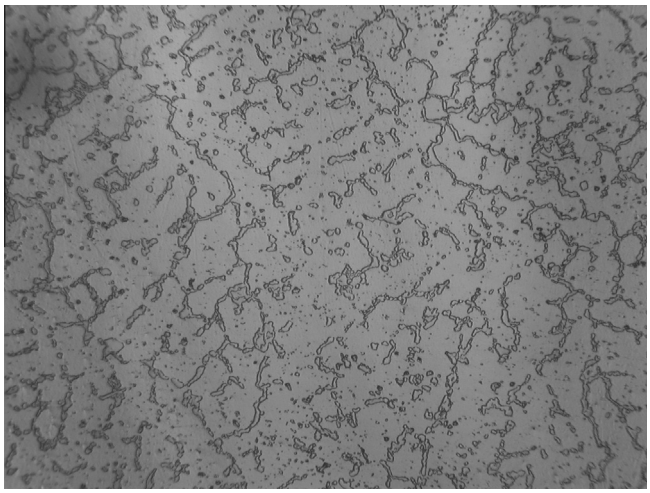

Fig. 6. Tube material microstructure (X200).

Tensile properties for base material of failed tubes are summarized in Table 1, where are compared with nominal material properties. Note the reduced strength and ductility. Fracture surface of test samples is brittle, as shown in Fig. 8.

Spectroscopy chemical composition is summarized in Table 2, and compared with manufacturer specifications and composition of the tubes used to replace the failed ones.

Spectroscopy Analysis was complemented with SEM and EDX analyses. All SEM samples show the same microstructure, a fine particle distribution in the matrix (less than 1 micron size), see Fig. 9 (X2500). Thickening of the interdendritic interfaces is evident. EDX in these interdendritic surfaces (Fig. 10) reveals two precipitated carbides: high chromium carbides (darker in Fig. 9), and high niobium-low chromium carbides (lighter in Fig. 9). Niobium is added to high temperature alloys to

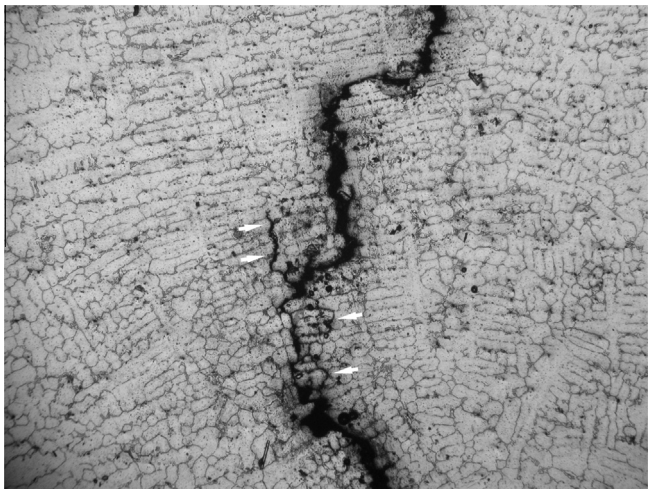

Fig. 7. Interdendritic crack paths (X50).

Table 1
Tensile test properties of failed tubes.

	Specimen N° 1	Specification
Elongation (%)	1.6	8
Area reduction (%)	<1	–
Yield strength 0.2% (MPa)	355	230
Ultimate strength (MPa)	392	470

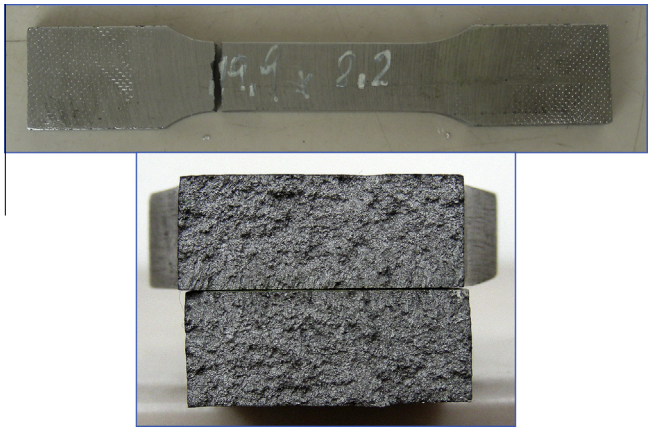

Fig. 8. Tensile test specimen (longitudinal) and fracture surface.

Table 2
Chemical compositions.

Source	Elements %							
	C	Si	Mn	P	S	Cr	Ni	Nb
Chem. An. (failed tubes)	0.3–0.4	1–2	0.9–1	0.026	0.034	20–25	30–40	0.66
CENTRALLOY 4852	0.45	1.5	1.00	–	–	25	35	1.5
Chem. An. (new tubes)	0.06	0.5–1	0.9	0.02	0.03	35–40	30–35	0.7

decrease the migration of chrome from the matrix during carbide precipitation, thus avoiding the detriment of mechanical properties due to the lack of chromium.

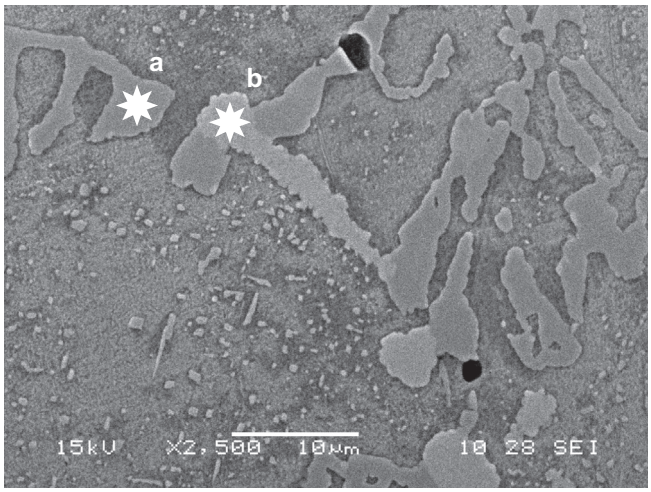

Fig. 9. Material microstructure. Two kinds of precipitated carbides (SEM X2500).

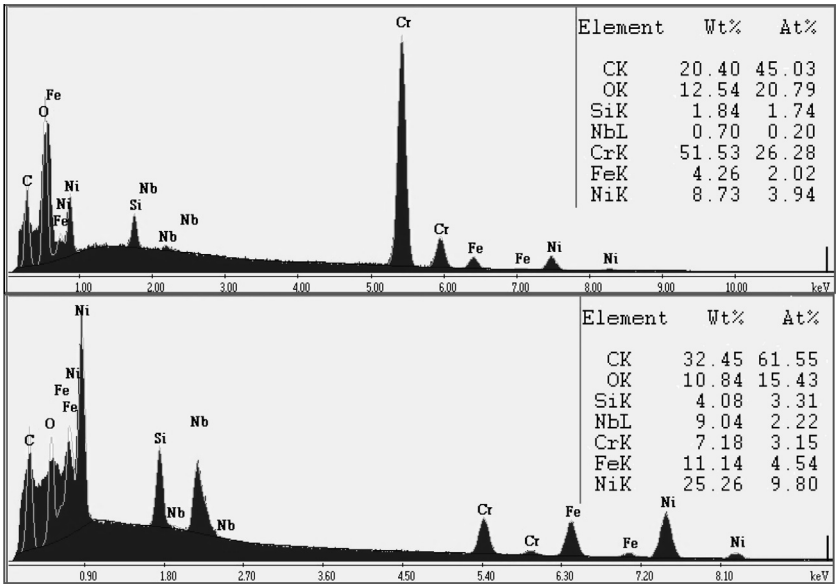

Fig. 10. EDX Analyses of precipitated carbides.

Indication "a" in Fig. 9 pinpoints chromium content of about 50%, twice the global content. Nickel content in this spot is very low, 8% (compared to 35% global Ni content). Indication "b" reveals a niobium content of 10%, almost 7 times the global content (1.5% Nb). This verifies that different kinds of carbides precipitated in grain boundaries during operation.

3. Mechanical model of failures

When the tubes are put in service, they sustain a raise in temperature from room to about 850 °C, which leads to a thermal dilatation of the tubes. Tubes increase in length as well as in diameter. The thermal expansion coefficient in these alloys for the process temperature is [16]:

$$\alpha = 17.25 \times 10^{-6} \frac{1}{^{\circ}\mathrm{C}} \tag{1}$$

The strain that these tubes sustain is, therefore:

$$\varepsilon = \alpha \times \Delta T = 17.25 \times 10^{-6} \frac{1}{^{\circ}\mathrm{C}} \times 850\ ^{\circ}\mathrm{C} = 0.0146625 = 14700\mu\varepsilon$$

This strain makes the tubes to increase 1.5 mm in diameter, from 102 mm to 103.5 mm.

The coke layer grows within the tubes, in the inner walls, as a result of the gas-cracking process at the operating temperature, that is, when tubes are dilated. When the furnace is stopped and temperature decreases, the tubes tend to recover their original dimensions. In this cooling process, the tubes find a restriction due to the thick coke layer developed in service. Coke thermal expansion coefficient, even though it varies with composition, is in the order of 4×10^{-7} 1/°C [17], this is an order of magnitude lower than that for the tube material.

The result can vary depending on the strength and thickness of the coke deposit:

1. If the coke deposit is thin or has low strength, during size recovery the tube generates compressive loads that break the coke apart.
2. If the coke deposit is thick or has high strength, it sustains the compressive loads that the tube imposes, thus impeding the tube from recovering its original diameter.

In this latter case, the stresses generated in the tube are important. These stresses can be estimated at least in three different ways:

1. Using a model of tube opening after rupture.
2. Measuring the remaining ligament at rupture, and using the tensile test results to estimate the load.
3. Instrumentation of a tube section using Strain Gauges, and measuring the relaxation after sectioning.

For the first calculation, the average gap between the two fracture surfaces of the failed tubes was measured. The gap is about 2.45 mm, when the coke is still within the tube. Once the coke is mechanically removed, the tube experiments an elastic recovery, and the gap is reduced to about 0.75 mm. Contraction of the pipe wall against the coke layer creates a bending-type distribution of hoop stress, which varies linearly in the pipe thickness only as long as the material remains elastic. The through-thickness distribution of hoop strain, however, remains linear even after the material yields. Taking this into account, the total strain (elastic plus plastic) can be directly determined from the total gap Δ [18]:

$$\varepsilon = \frac{\Delta t}{\pi D^2} \tag{2}$$

$$\varepsilon = 780\mu\varepsilon$$

where D and t are pipe diameter and thickness. Strain at the elastic limit was taken from the stress–strain curve after the tensile test. This strain is:

$$\varepsilon_{el} = 1700\mu\varepsilon$$

Note that total strain relaxed after cracking is less than half the elastic limit of the pipe material, and is only a small fraction of the total thermal contraction calculated in Eq. (1). It is concluded that the failure process involved very little plastic deformation of the tubes, if any. The small remaining gap after the coke layer was taken should therefore be related to fabrication residual stresses in the tube.

This result leaves the second method useless, since the failure occurred due to brittle fracture before massive yielding of the remaining ligament; which is what happened during the plastic collapse of the specimen in the tensile test (Table 1).

For the third calculation, a strain gage was placed in an un-cracked 30 cm long tube section with a uniform and continuous coke deposit within. A longitudinal cut was carried out carefully, getting uniform cut depth in stages. The tube broke up when the remaining ligament was 44% of the tube thickness, due to stresses generated by the coke layer (Fig. 11). Measured strain relaxation was

$$\varepsilon = -6.084 \times 10^{-4} = 608\mu\varepsilon$$

This is the total elastic relaxation and can be directly compared with the result of Eq. (2). Note that this test was made in a tube that did not crack; it is reasonable then that most of the failed tubes experienced a larger stress than this one. The difference between which tubes failed and which did not is partly due to the different location of the tubes in the furnace, involving also differences in service temperature, which lead to differences in the growth of the coke layer inside the tubes. In the instrumented piece, the coke layer was about 6 mm, about half that found in the failed samples (Fig. 4).

4. Results and discussion

Analyzed cracks in the failed tubes have their origin in the inner side of the tube walls, and propagating across their thickness. These cracks, mostly longitudinal at their origins, were generated due to circumferential stresses overcoming material strength and toughness. The cracks are brittle, involving low energy dissipation during propagation. The defined cracking mechanism is a process controlled by displacement, and not load controlled, like most cracking mechanisms in pressurized tubes are.

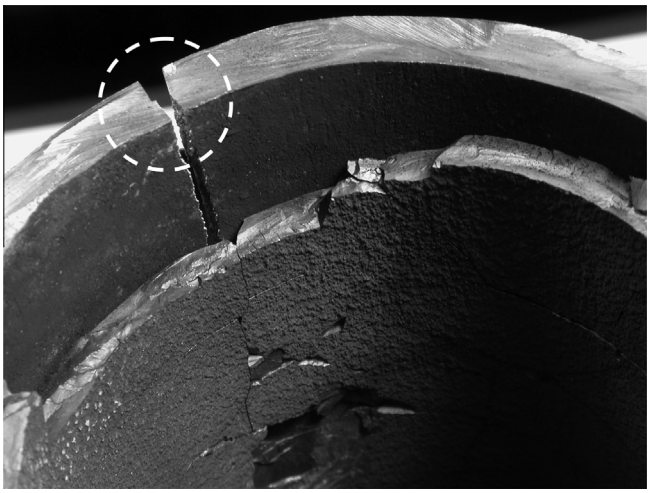

Fig. 11. Detail (inner view) of lab-induced fracture by longitudinal cutting.

The mechanical models allow confirming that circumferential stresses produced by the coke layer during the fast cooling of the tubes during the emergency stop are high enough to justify the observed tube cracking, even if tube properties were close to the nominal values.

In this case, the controlled displacement is given by the differential thermal contraction between the tubes and the thick, stiff coke layers within them. When comparing results from Eqs. (1) and (2), it is noted than the coke layer restrained a very small portion of the thermal contraction of the pipe material (about 5%), and yet, it was enough to provoke massive longitudinal cracking in the tubes. In some sections the propagation rate, combined with any in-homogeneities in the pipe material and the effect of longitudinal stresses due to dead weight, made the cracks split in two. When the cracks joined back, they cut sections of the tubes, as can be seen in Fig. 1.

In conclusion, tube ruptures were due to a combination of (1) fast cooling of the furnace do to an emergency stop, (2) circumferential stresses induced by a thick coke deposit, and (3) material degradation due to time in service (which was about 70% of the estimated life). Note however that both last effects are related to a coke layer that was thicker than desirable. A thicker coke layer means a poorer heat transfer through the pipe wall. The metal between the heating fumes and the coke layer is therefore heated to higher temperatures than designed, in order to maintain the necessary heat to the process fluid inside the tubes. Material degradation was therefore accelerated by long time exposure to larger than expected tube wall temperatures.

Tube material is a Cr–Ni centrifugal casting. The austenitic matrix in this kind of high-temperature alloy provides a great mechanical resistance at high temperatures, as long as it is correctly reinforced with finely precipitated and disperse carbide particles. As mentioned in the introduction, extended exposure at the normal operating temperature of 850 °C have three detrimental effects in these microstructures: grain boundary voids and cracking of the protective oxide scale due to creep, carburization attack and the evolution of intermetallic compounds [14–16]. All these reduce both mechanical strength and ductility during service life.

The failed tubes had been in service for about three and a half years, while lifetime had been estimated in five years. Tensile testing shows that in-service degradation had a remarkable influence in material mechanical properties. Both the elongation and UTS are underneath nominal values. Elongation is just 20% of nominal and strength is just 83%. The material shows no signs of strain hardening; yield strength and UTS are very close (Table 2). Macroscopically, fractures are brittle and intergranular (Fig. 5); microstructurally, crack paths are interdendritic (Fig. 7). Along with the observed thickening of the interdendritic surfaces and precipitated carbides (Fig. 10), all these features confirm temperature-induced service damage.

According to data given by the operators, a parameter called ‘‘nozzle’’ is controlled during furnace operation. This parameter is related directly to an increased fluid velocity, necessary to maintain the specified flow rate as the effective inner diameter of the tubes is reduced due to the growth of the coke layer.

A computer based model could be carried out, for determining the limit of the coke layer. The model should be able to predict the thickness of the coke layer for which, in case of putting the furnace out of service, the result will be broken coke layers instead of broken tubes. For this model to be realistic, coke properties will need to be estimated or measured.

Model results should allow defining safe limits for coke layer thickness, in order to avoiding compromising the integrity of the equipment in case of an emergency stop. This safe thickness should then be related with the above mentioned nozzle factor, so the operators could program decoke processes and deal with the assumed risk. Note however that allowable coke thickness will be a function of material degradation, so most probably decoking intervals will have to be reduced as the tubes reach the end of their designed service lives. This in turn could result in a reassessment of the allowable service life of the tubes, in terms of both reliability and economics.

5. Conclusions

High temperature microstructural changes and larger than expected hoop stresses during an emergency shut-down lead to the brittle fracture of many tubes in an ethylene cracking furnace. Large stresses developed due to differences between thermal expansion coefficients of the tube alloy and the thick, stiff coke layer formed inside the tubes.

The excessive thickness of the coke layer was responsible for conditions, high stresses and brittle tubes, since tube metal degradation was accelerated by higher than designed in-service temperatures in the tube walls.

Therefore, mitigation recommendations include maintaining coke thickness under control. Monitoring coke thickness can be done by measuring fluid velocity and relating its variation to the reduction of the inner cross section of the tubes. The allowable thickness of the coke layer can be defined with thermal mechanical models of the furnace in conditions of fast cooling for different coke thicknesses. Decoking intervals can therefore be defined, which are expected to be reduced as the tubes reach the end of their designed service lives.

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