Studies on Behaviour of in Service Tubular Material Used at Refinery Process Furnaces

IBRAHIM NAIM RAMADAN, EUGEN VICTOR LAUDACESCU, MARIA POPA, LOREDANA IRENA NEGOTA*
Petroleum-Gas University of Ploiesti, 39 Bucharest Blvd, 100680, Ploiesti, Romania

The purpose of the heat transfer analysis at the level of the technological furnace in radiation section was to determine the medium temperature on the outside wall of the pipeline through which the effluent is processed. It is important to keep an outside temperature of the wall of the duct below the maximum allowable temperature at which this carburizing process takes place. Thus, the temperature calculated on the outside pipe wall is 523.5 °C and the maximum allowable temperature of the outside pipe wall is 595.5 °C. The carburizing process leads to the modification of the thermal conductivity of the tubing material. Therefore, if steel is enriched with carbon, thermal conductivity decreases.

Keywords: refinery furnaces, heat transfer, steel carburization, tubular material, thermal conductivity

The most important degradation phenomenon is creep, it having the highest rate in tubular material failure. According to API 579, creep intensity increases with temperature over the creep exclusion temperature, below which creep effects are negligible. Also, the loads to which tubular material is exposed during operation, can gain varying loads character, when temperature and pressure fluctuations are large and over degradation effects due to creep its combine with destructive effects of fatigue.

Carburization and oxidation phenomena, also specific to tubular coils, due to circulated technological fluids through coils and the atmosphere inside the furnace, have secondary role in degradation of pipes, as there is thermal controlling possibility, materials with good characteristics regarding creep and fatigue resistance selection and the use of inhibitors [1, 2].

In the technological processes inside furnaces, due to high temperatures and technological fluids circulated through coils, the carbon clogs on the internal surface, forming coke, which must be constantly removed, because it may not produce changes of the mechanical properties. On the internal surfaces, an oxide scale (Cr2O3, Al2O3) is formed, that inhibits the passage of carbon in the metallic material. The carbon is not soluble in chromium, and can penetrate the metallic wall just by diffusion of molecules passing through cracks or pores in the protective layer formed on the surface of tubular material. In normal operating conditions, the formed oxide scale presents defects, due to degradation by creep and to pipe decoking procedures, which makes the carbon atoms to diffuse into the pipe surface through discontinuous zones formed on the surface of tubes [1, 2, 4].

The increase of steel pipe carbon percentage, determined by inside carburization, due to carbon diffusion from technological fluid in pipe wall, will determine thermal conductivity decrease [1]. In the following, the variation of thermal conductivity, \( \lambda \), with temperature change will be demonstrates.

### Technical Conditions of the Tubes

The tube parameters in the furnace radiation section at the catalytic reforming plant in refinery are outside diameter, \( D_o = 91 \) mm and wall thickness, \( \delta = 8 \) mm and the pipes are made of P91 (9Cr1MoV) stainless steel. The operated furnace was functional for a period of 344 days and has not been use 55 days due to regular technical revisions. Data representing operating conditions found in the figures 1 and 2, excluding temperatures whose values are below the minimum needed to produce the phenomenon of creep. Thus, in figures 1 and 2, the sequence of a) were taken for the abscissa the intervals shown in the table 1, and the sequence b), were cumulatively these ranges [5].

#### Table 1

| Hours | 24 | 48 | 72 | 96 | 120 | 168 | 192 | 288 | 336 | 384 | 408 | 648 | 744 | 864 | 1200 | 1344 |
|-------|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|
| Number of hourly intervals | 15 | 1  | 3  | 1  |

![Fig. 1a. Histogram: temperature - operating unequal time intervals](http://www.revistadechimie.ro)
In figure 3 the inside and outside surfaces of furnace tubes can be seen. The analysis of some metallic samples of the tubes was performed on a Scanning Electronic Microscope (SEM). It can be seen that the cementite layer disintegrates, resulting in particles catalyzing the coke deposit on the surface of the steel tubes. Initially, on the surface, small scattered pitting sites were present, which united due to continuous exposure to the working environment, finally causing generalized degradation of steel.

In order to determine the hardness of metallic materials, a pyramid diamond indenter is pressed, a certain time $\tau_d$ ($\tau_d = 10...35$ s), with a force $F$, on a sample of tested material and after passage of time $\tau_d$, the penetrator is removed and both diagonals, $d_1, d_2$, are measured, in order to determine their arithmetic average [7]:

$$d = \frac{d_1 + d_2}{2}$$  \hspace{1cm} (1)

For hardness determination, the arithmetic average of three values obtained on samples tested on a hardness testing machine was made for each of the distances along the thickness, from inside to outside of the tubes. The assessing hardness values accuracy was performed using Youden diagram [8, 11]. As it can be seen in table 2, the hardness values of the samples from the three technological furnaces, H1, H2, H3, in the catalytic reforming plant have significantly higher values than the unused (new) tube.

The effluent (hydrofined gasoline and a recirculated gaseous mixture), at high temperatures, favors the passage of carbon by diffusion from the working environment in the tube surface. Because of the carburizing process from inside of tubes, hardness values are slightly higher at the inside of the tubes.

### Tubular material hardness test

The Vickers hardness test is regulated by [6], and uses a square-based pyramid diamond indenter with the faces set at a 136 ° degree angle from one another. Schematic representation of Vickers hardness test is shown in figure 4 [7].

### Tubular material chemical composition test

The determination of chemical composition was made on the same samples as for hardness testing using Optical Emission Spectroscopy principle; the arithmetic average of three obtained values was made, both on the inside and on the outside of the tubes.

Optical Emission Spectroscopy works by exciting atoms with energy produced by a spark formed between an electrode and the sample. This energy makes electrons from the sample to emit light that is processed into a spectral pattern. By measuring the intensity of the spectrum, the analyzer indicates the chemical compositions of the samples.

As can be seen from tables 3 and 4, the chemical compositions, determined on the samples taken from the steel tubes are in accordance with the stipulations of standard [9].
Analyzing the percent concentration of tube steels (Table 3) an increasing carbon concentration inside the tubular material was observed, which reflects the carburizing phenomena.

The calculation of the outside temperature of the pipe wall from the radiation section in catalytic reforming furnace

The case study aims to determine the outside temperature of the wall pipes in the radiation section at a technological furnace in the catalytic reforming plant. Temperature changes will modify the thermal conductivity of the tubing material. Study of heat transfer through cylindrical simple walls or/and cylindrical compound walls, involves calculations for determining the temperatures of the wall, taking into account the working fluid temperatures [12, 13]. To highlight the effect of carburization on the tubular material, a study was carried out on heat transfer to U-shaped tubes in the furnace of the radiation section of the catalytic reforming plant in a petroleum refinery.

Their main geometric features are shown in figure 5. The raw material, effluent, consists of a mixture of hydrofined gasoline and recirculated gases (this gaseous mixture contain about 87 % vol. H2, 6% vol. CH4, 4 % vol. C2H6 and 3 % vol. other gaseous hydrocarbons). The main design features of the tubes and the effluent properties are shown in table 5.
Velocity of fluid inside the pipes is calculated with the relation [10]:

$$w = \frac{m}{\rho \pi D_i^2 \cdot n_i}, \text{ m/s}$$  \hspace{1cm} (2)

For the calculation of partial heat transfer coefficients (a), the relation 3 [10] is used

$$Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{0.4}$$  \hspace{1cm} (3)

where:

$$Re = \frac{D_i \cdot w \cdot \rho}{\mu}$$  \hspace{1cm} (4)

$$Pr = \frac{c_p \cdot \mu}{\lambda}$$  \hspace{1cm} (5)

$$Nu = \frac{\alpha_i \cdot D_i}{\lambda}$$  \hspace{1cm} (6)

The inner wall temperature, $t_w$, was determined with the following formula [10]:

$$Q = \alpha_i \cdot A_i \cdot (t_{tw} - t_{ew})$$  \hspace{1cm} (7)

where $Q$ is heat transfer flow and this was calculated with the formula listed below,

$$Q = m \cdot c \cdot \Delta t$$  \hspace{1cm} (8)

### Table 5

**Main Geometrical Parameters of the Tubes and the Effluent Physical Properties**

| Parameters                          | Symbol | Value | Unit |
|-------------------------------------|--------|-------|------|
| Tube outside diameter               | $D_t$  | 91    | mm   |
| Tube inside diameter                | $D_i$  | 75    | mm   |
| Tube wall thickness                 | $\delta_t$ | 8 | -    |
| Tube length                         | $L_t$  | 12.755| m    |
| Total length (coil and prop)        | $L_t$  | 13.12 | -    |
| Initial temperature of the effluent | $t_i$  | 450   | °C   |
| Outlet temperature of the effluent  | $t_o$  | 529   | °C   |
| Medium temperature of the effluent  | $t_{me}$ | 494.5 | °C   |
| Temperature difference between inlet and outlet temperatures of the effluent | $\Delta t$ | 69 | °C   |
| Inside surface area of the coil     | $A_i$  | 144.3 | m²   |
| Outside surface area of the coil    | $A_o$  | 175   | m²   |
| Necessary heat flow of the effluent | $Q$    | 4.278 | kW   |
| Flow rate of the effluent           | $m$    | 14.12 | kg/s |
| Fluid density                       | $\rho$ | 3.27  | kg/m³|
| Effluent specific heat              | $c_p$  | 3.7485| J/(kg °C) |
| Effluent dynamic viscosity          | $\mu$  | 0.027×10⁻⁴| kg/(m·s) |
| Effluent thermal conductivity       | $\lambda$ | 0.1986| W/(m·°C) |

### Table 6

**Values of the Calculated Parameters**

| Parameters                          | Symbol | Value | Unit |
|-------------------------------------|--------|-------|------|
| Temperature of the fluid gas        | $t_{gas}$ | 730 | °C   |
| Outside convective heat transfer coefficient | $\alpha_o$ | 108 | W/(m²·°C) |
| Global heat transfer coefficient    | $\alpha_i$ | 96  | W/(m²·°C) |
| Thermal tension                     | $T_t$  | 34.441| W/m² |
| Maximum thermal tension             | $t_{max}$ | 36.911| W/m² |
| Global heat transfer coefficient between the feedstock and external surface | $K_{sw}$ | 84.2| W/(m²·°C) |
| Maximum temperature on the outside pipe wall | $t_{max}$ | 595.5| °C   |
| The new thermal conductivity for steel | $\lambda_{steel}$ | 32.6| W/(m²·°C) |

Velocity of fluid inside the pipes is calculated with the relation [10]:

$$w = \frac{m}{\rho \pi D_i^2 \cdot n_i}, \text{ m/s}$$  \hspace{1cm} (2)

For the calculation of partial heat transfer coefficients (a), the relation 3 [10] is used

$$Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{0.4}$$  \hspace{1cm} (3)

where:

$$Re = \frac{D_i \cdot w \cdot \rho}{\mu}$$  \hspace{1cm} (4)

$$Pr = \frac{c_p \cdot \mu}{\lambda}$$  \hspace{1cm} (5)

$$Nu = \frac{\alpha_i \cdot D_i}{\lambda}$$  \hspace{1cm} (6)

The inner wall temperature, $t_w$, was determined with the following formula [10]:

$$Q = \alpha_i \cdot A_i \cdot (t_{tw} - t_{ew})$$  \hspace{1cm} (7)

Where $Q$ is heat transfer flow and this was calculated with the formula listed below,

$$Q = m \cdot c \cdot \Delta t$$  \hspace{1cm} (8)
The Fourier law applied for the cylindrical wall (figure 6) is given by the following expression (9):

\[
Q = \frac{2\pi \cdot n_2 \cdot L_1 (t_{w2} - t_{ow})}{\ln \frac{D_2}{D_1}}
\]

(9)

If the medium temperature in the heating chamber is known, it is possible to calculate \( \alpha_0 \) (on the combustion gas side) using the following relation [10]:

\[
Q = \alpha_0 \cdot A_0 \left( t_{gas} - t_{ow} \right)
\]

(10)

The thermal conductivity was calculated after a variation of shape [10]:

\[
\lambda_{steel} = 37.4 - 0.008 \cdot t
\]

(12)

The global heat transfer coefficient was calculated using the expression [10]:

\[
k_g = \frac{1}{\frac{D_2}{\alpha_1} + \frac{D_2}{\alpha_2} \ln \frac{D_2}{D_1} + \frac{1}{\alpha_2}}
\]

(13)

Thermal tension in the radiation section will be determined [10]:

\[
T_{th} = \frac{Q}{A_0}
\]

(14)

Maximal allowable thermal tension will be determined with [10]:

\[
T_{maxallowable} = C_1 \cdot C_2 \cdot C_3 \cdot T_t
\]

(15)

where, \( C_1 = 1.93 \), \( C_2 = 1.25 \), \( C_3 = 0.95 \) [10]

The maximum value of temperature on the outside pipe wall is [10]:

\[
t_{max}^{ow} = t_{eff} + \frac{T_{maxallowable}}{k_f_{ow}}
\]

(16)

where \( k_f_{ow} \) is the global heat transfer coefficient between the feedstock and outside surface of pipe walls and is calculated with [10]:

\[
k_f_{ow} = \frac{1}{\frac{D_0}{\alpha_1} + \frac{D_2}{\alpha_2} \ln \frac{D_2}{D_1} + \frac{1}{\alpha_2}}
\]

(17)

As will be seen, increasing the wall temperature will reduce the thermal conductivity.

Based on relationships (2)-(17), the results for the calculated sizes are shown in table 6.

Conclusions

Structural changes during exploitation refer to alloying elements, that are distributed at grain boundaries or inside the ferritic or austenitic matrix: carbides, nitrides or carbonitrides (of alloying elements) and intermetallic compounds, due to diffusion of carbon excess on the inside walls of pipes.

Assessment of technical condition of coils by mechanical and technological tests carried out with periodic revisions involves specific procedures in order to be able to determine any changes resulting from exploitation, for different periods of time.

The paper only refers to tubular material components without defects, but in many cases, they may have indentations due to manipulation or accidental mechanical contacts.

It is important to keep an outside temperature of the wall of the duct below the maximum allowable temperature at which this carburizing process takes place. Thus, the temperature calculated on the outside pipe wall is 523.5 °C and the maximum allowable temperature of the outside pipe wall is 595.5 °C. The carburizing process leads to the modification of the thermal conductivity of the tubing material. Therefore, if steel is enriched with carbon, thermal conductivity decreases.

The increase of outside wall temperature of the pipe near or above the permissible maximum temperature shows that the carburizing process takes place at the level of the pipes in the furnace radiation section.

References

1. GRABKE, H.J., Materiali in Tehnologije, 36 Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, 2002, p. 297
2. RAMADAN, I. N., Studies about Increasing the Service Life of Tubular Material from Furnaces in Refineries and Petrochemical Plants, PhD Thesis, Petroleum-Gas University of Ploiesti, September 2016
3. A. J. M. H. HABEEB, N. N. ANTONESCU, M. G. PETRESCU, Journal of the Balkan Tribological Association, 21, no. 4, 2015, p. 842
4. NATESAN, K., ZENG, Z., MARONI, VA., SOPPET, W.K., RINK, D.L., Metal Dusting Research at Argonne National Laboratory, International Workshop on Metal Dusting, Argonne National Laboratory, S.U.A., 2001, 25 pages
5. NEACSA, A., ANTONESCU, N.N., STOICA, D.B., Journal of the Balkan Tribological Association, 15 (4), 2009, p. 474
6. *** ISO 6507-1:2018, Metallic materials - Vickers hardness test - Part 1: Test method
7. ZECHERU, Gh., DRAGHICI, Gh., Elemente de stiinta si ingineria materialelor, vol. I, ILEX and Petroleum - Gas University of Ploiesti Publishing Houses, 2001
8. DINITA, A., 13TH International Conference on Tribology (ROTrib'16), IOP Conference Series-Materials Science and Engineering, Volume: 174, 2017, p. 537
9. *** EN 10216-2, Seamless Steel Tubes for Pressure Purposes. Technical Delivery Conditions. Non-alloy and Alloy Steel Tubes with Specified Elevated Temperature Properties, 2014
10. DOBRINESCU, D., Procese de transfer de caldura si utilaje specifice, Didactic and Pedagogical Publishing House, Bucharest, 1983
11. NEACSA, A., DINITA A., BARANOWSKI, P., SYBILSKI, K., RAMADAN I. N., MALACHOWSKI, J., LUKYUKHER, B., Journal of Pressure Vessel Technology - Transactions of the ASME, 138, Issue: 3, 2016, p. 17 (digital collection).
12. POPA, M., ONUTU, I., Rev. Chim. (Bucharest), 60 no.11, 2009, p.1185
13. PATRASCIOIU, C., NEGOITA, L. (2014). The Convection Heater Numerical Simulation, XII International Conference on Thermal and Fluids Engineering, Venice, International Science Index 8, No.4, 2014, p. 333

Manuscript received: 7.03.2018