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REPORT OF REFORMER TUBE INSPECTION BY LONG RANGE GUIDED WAVE ULTRASONIC METHOD (GW), METAL MAGNETIC MEMORY (MMM), EDDY CURRENTS (ET), TIME-OF-FLIGHT DIFFRACTION (TOFD), MAGNETOSCOPY, HARDNESS TEST AND METALLOGRAPHY

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ABSTRACT

In this article, report of reformer tube inspection by long range guided wave ultrasonic method (GW), metal magnetic memory (MMM), Eddy currents (ET), Time-Of-Flight Diffraction (TOFD), magnetoscopy, hardness test and metallography is assessed. tubes' catalysts are of microalloy under trade name of Centrally G 4852 Micro (G-X40 NiCrSiNb 35-25) and reducers of this reformer is made of Centralloy G 4859 (G-X10 NiCrNb 32-20). Results show that tubes classifications includes 35.1% trouble free, 15.4% in minor risk class, 38.5% in medium risk class and 11.1% are located in high risk class. Enlargement of austenite grain boundary carbides and also those carbides between dendrites, tangible decrease in tensile strength, hardness and strength against creep rupture may be evidence of exceeding temperature rise in tubes. Furthermore, temperature increase also will have significant impact on remaining life of tubes within a reformer system and increase of creep rate.

Keywords: *Reformer Tubes, Long Range Ultrasonic, Metal Magnetic Memory, Eddy Currents, Ultrasonic Diffraction*

INTRODUCTION

Reformer a are used to produce hydrogen in petrochemical industries. Reformer tubes are most critical elements of reformers where due to imposed work conditions on them; those are made of special austenite which has very high resistance against creep and corrossions. These tubes are usually designed to have age of 100000 hours at normal operational conditions. However, early ruptures frequently are seen in these tubes because of some mechanisms such as creep, carburization, oxidation, thermal shock and overheating (Alvino *et al.*, 2010).

At high temperatures, metal parts are yielded under lower than tension loads and are continually deformed. This under tension and related to time deformation in equipments is called creep where is one of the main leading mechanism to rupture in reformer tubes. Therefore, in recent several decades those alloys with high resistance to creep are used in order to make reformers' tubes (da Silveira TL and May, 2006).

Deformation rate of creep impact is a function of material type, applied load and temperature. Rupture rate (or Strain Rate) is sensible to both temperature and applied load or tension. Overall, each 12°C increase in temperature or 15% tension depends on alloy leads to a decrease of half or more performance life (API RP 571, 2011).

One of the mechanism of probable rupture is overheating where leads to localized heating. Overheating may be caused by deficiency in fluid flow within tube and related problems to burners. When burners are not set, there might be turbulence in flame and flame collides directly into tubes and leads to a flame impingement situation. This situation causes increase temperature of hot spot on tube's surface and high rates of oxidation, carburization and rapidness in creep process and also end to brittle fracture (Eschbach,

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no date). Thus, burners should be monitored regularly to avoid any impact of unsuitable heat distribution which leads to overheating in some tubes relative to others. Unsuitable heating will affect primary calculations of heat transfer in tubes. For example, by advance in reaction, rate of gas flow process and temperature in lower part of tube would be changed (Eschbach, no date). High level of temperature results in tube heating expansion and since this expansion is confined by reducer and collector, tube will be bended. Tube bend is also causes increase in tension and finally creep process is become more rapid and at last tube rupture will occur (Eschbach, no date).

It seems that overheating is a main factor in reformers tube ability to provide service. Wall temperature of tubes is related to several factors. Regulating burner is one of the factors that may offset during times. Catalysts activity also becomes decreased by time, where to compensate this deficit temperature may be increased. By increase in catalyst age and gradually, there would develop a preferred path for gas flow through catalysis ground. Therefore, cooling is not occurred uniformly at tube section (due to gas flow) and hotter (and brighter) zones in outer surface of tube develop giraffe neck patterns where this phenomenon is observable through furnace's window. Even when there is more severe increases in temperature, hot spots become oval shapes. Testing heat distribution along tubes indicates that temperature of lower half is more and in some instances it is estimated to be more than 1000 °C (Chaudhuri, 2008). Thus, these furnaces should be designed and used to minimize developing hot spots and localized overheating (API RP 571, 2011).

Enlargement of austenite grain boundary carbides and also those carbides between dendrites, tangible decrease in tensile strength, hardness and strength against creep are evidence for tubes overheating (Chaudhuri, 2008).

Start downs and start ups or thermal cycles are appropriate to decrease or increase temperature slopes and also effective in tubes age. Implications of thermal cycles, particularly in second half of tubes age might be lead to brittle fracture in tubes (Jakobi and Gommans, 2003).

When tubes due to heating cycling are repeatedly become hot and cold, tensions are increased temporary and results in rapid creep rupture. Once heating and cooling is very fast, rupture would be caused by thermal shock (Huber and Jakobi, 2011).

During implementation and before catalyst becomes active by reduction; reaction provided heat is not adjusted. Therefore, operating reformer should be accomplished in accurate testing and control to avoid overheating of tubes. As Schmidt + Clemens company report, rate of thermal changes must be at most 50°C/hr (Eschbach, no date).

Wall thickness and level of thermal cycling during tube life is important. Most of ruptures or fractures in HK-40 alloy of risers, manifolds, transferring headers and other components are caused by thermal cycling. HP-Mod alloys bear thermal tensions more efficiently (Schillmoller, 1992; Kasaeipoor *et al.*, 2015).

Formation of secondary carbides due to carbonization leads to chrome level in proximal layers to tubes surfaces and this layer gradually will be remained without primary carbides of chrome and become thicker. Carbide sediments which reinforce alloy and increase creep resistance reduce and finally lead to decrease in sound wall thickness feature of tube. This causes increase in tension and consequently rapidness in creep process within substance (Jakobi and Gommans, 2003).

As a result, most related problems to reformer tubes is relevant to operational conditions of furnace. Therefore, by proper application of furnace, some cases such as overheating, flame collision, oxidation, decrease of gas liquidity and particularly brittle fracture.

In this study, testing of reformer tubes No. H-2101 is assessed by long range guided wave ultrasonic method (GW), metal magnetic memory (MMM), Eddy currents (ET), Time-Of-Flight Diffraction (TOFD), magnetoscopy, hardness test and metallography.

Job Description

In this project; testing of reformer tubes No. H-2101 is assessed by long range guided wave ultrasonic method (GW), metal magnetic memory (MMM), Eddy currents (ET), Time-Of-Flight Diffraction (TOFD), magnetoscopy, hardness test and metallography.

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Reformer of this project is Top Fire type where its tubes catalysts are located in 4 rows of 52 pieces and in a different case, its burners also are assembled on ceiling of this case. Tubes catalysts are of microalloy type under trade name of Centralloy G 4852 Micro (G-X40 NiCrSiNb 35-25) and its reducers are made of Centralloy G 4859 (G-X10 NiCrNb 32-20).

These kind of alloys are the newest types of alloys that are used in reformers and their utilization allows increase of tubes diameters and better implementation and bearing higher degrees of heat than previous generations of HK40 and modified HP.

Reformer has 208 tubal branches where are made of Centralloy G 4852 Micro (G-X40 NiCrSiNb 35-25) with outer diameter 135.8 mm., inner diameter 110mm., thickness 12.1 mm and length of 12.077 m. This testing aims to assess situations and level of deficiencies in tubes and providing report and qualitative categorizing by using advanced non-destructive testing methods.

Testing through long range guided wave ultrasonic method (GW) was conducted under ASTM, E2775 version 2011 standard. The assessment device was Wave maker G4 and also received graph was fine tuned and filtered to make evaluation better.

Testing through metal magnetic memory (MMM) was conducted under ISO 24497 ver. 2007 standard and test was accomplished by using SD-1-8M probe with four vertical channels and four horizontal channels.

Assessment device was TSC-5M-32 and received signal was filtered to acquire better evaluation and device's level of contrast is also increased.

Testing through Time-Of-Flight Diffraction (TOFD) was conducted under protocol of ASME, Section V, Article 5 version 2010 and test device was under brand name of Silver wing NDT UT 400. Selected frequency was 1 MHz and data evaluation was accomplished based on received wave.

Testing through magnetoscopy approach was conducted under ASTM, A342 standard Ver. 2010 and test device was Foerster 1.069.

Testing through hardness test method was conducted under ASTM, E-110 Ver. 2010 and test device was from Proceq Testing Instruments inc.

Testing through metallography method was conducted under ASTM, E-1351 Ver. 2002 and test device was a Portable Set.

Testing operations was applied on four rows of fifty two tubes where total tubes numbers reached to two hundred eight pieces.

Testing Operations

Guided Wave Ultrasonic Testing

In this testing method, after mounting an long range ultrasonic testing ring at upper location of reducers, waves are sent and received completely along the tube by accessing a point on same tube and based on this procedure testing graph is prepared. Considering obtained data from this graph, deficiencies are identified and would be enlisted in testing schema to be tested by other testing methods.

Metal Magnetic Memory Testing Operations

In this testing method, by metal magnetic memory testing sensor movement on surfaces of tubes deficit regions and residual tension are identified.

Furthermore, testing is repeated more accurately and sensitively in deficit regions where were known through long range ultrasonic testing method.

According to obtained data from this method, all deficits are categorized and Eddy Current Testing enlisted in testing scheme to find crack and creep in tubes.

Eddy Current Testing Operations

In this testing method, eddy current testing sensitive probe moves along surfaces of tubes to identify locations of crack, creep and structural change (Conductivity).

Moreover, on all surfaces of reducers and all resulted deficit regions where were identified by long range ultrasonic and metal magnetic memory testing methods; eddy current testing also was performed. According to obtained data through this method, all deficits are categorized and enlisted in testing scheme to endorse ultrasonic and metallography testing methods.

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Ultrasonic Testing Operations

In this testing method, by moving transducer of ultrasonic testing method on surfaces of tubes; the locations with crack and drop ultrasonic waves are identified. This method is used to endorse results of other methods.

Magnetoscope Testing Operations

In this testing method, by moving magnetoscopic testing sensor on surfaces of tubes; level of magnetic permittivity is measured. This method is used to analysis results of other methods.

Hardness Testing Operations

In this testing method, by using hardness testing probe on surfaces of tubes; level of surface hardness is measured. This method is used to analysis results of other methods.

Metallography Testing Operations

Microstructure testing was conducted on different regions of reducers and tubes of primary reformer furnace.

Tubes Specifications

Received information regarding material, design and performance aspects of tubes are as following:

Material: Centralloy 4852 Micro

OD: 135.8 mm

ID: 110 mm

Minimum Sound Tube Wall Thickness (MSW): 12.1 mm

Corrosion allowance: 0

Design pressure: 36.8 barg

Design temperature: 924°C

Operating pressure: 34 barg

Operating temperature: 750-945 °C

Mettalography Testing

Considering acquired structure from new sample of reformer pipe and comparison of modified still HP structure as shown in Figure 1, it may be concluded that existing pipes are same type. Chemical analysis of this alloy is demonstrated in Table 1.

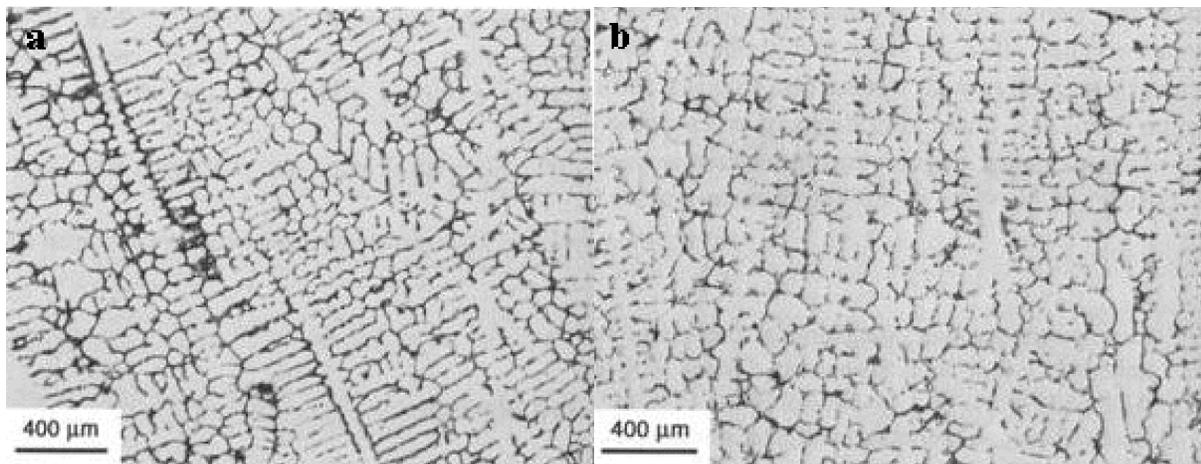


Figure 1: Microscopic Structure of Foundry Sample under HP still Centrifuge Technique, Dendrite Carbides are in Austenite Background (de Almeida *et al.*, 2002)

Table 1: Chemical Compound of Modified HP still (Alvino *et al.*, 2010)

| | C | Si | Mg | Cr | Ni | Nb | Ti | Fe |
|----------------|------|-----|------|-------|-------|------|------|------|
| HP-Nb Modified | 0.45 | 1.5 | 1.00 | 25.00 | 35.00 | 1.50 | Var. | Bal. |

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As shown in Figure 1, this still has an completely austenite background along with abundant amount of rich in titanium and niobium carbides where are formed at dendrites border lines, availability of niobium and titanium in this type of still prevents chrome carbides formation.

Referring to mentioned issues, gradually by increase in temperature both M_7C_3 and $M(C, N)$ carbides in this still transform into chrome rich carbides of $M_{23}C_6$ and M_6C where by considering process temperature of mentioned alloy (About 900 – 1000 °C) this result is inevitable. In Table 2, formation and expansion of these carbides respected to temperature are demonstrated.

Table 2: Image Analysis Results of some Examples of Modified HP still Creep Testing (Berghof-Hasselbacher, 2007)

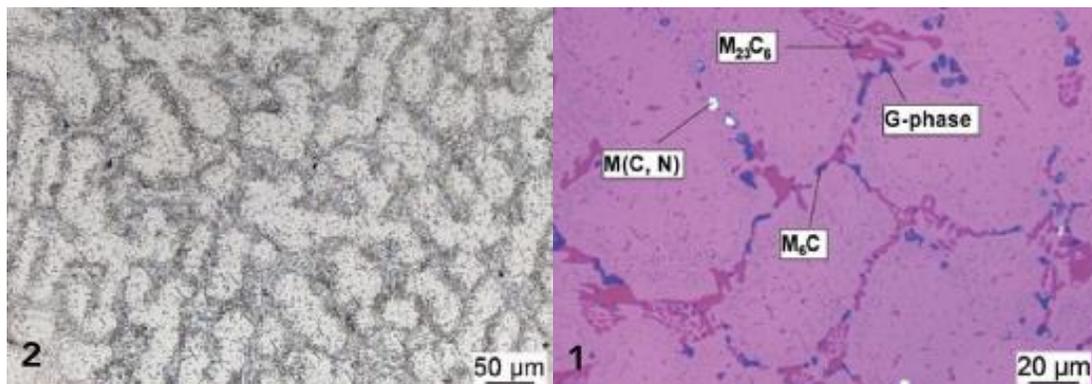
| Sample_ID | Sample | Temp. °C | Temp °F | Stress MPa | Stress Ksi | Expo. Time hrs | area fraction in % | | | | | | | | | | | | |
|-----------|------------|----------|---------|------------|------------|----------------|--------------------|----------|-------------|--------|------------|-------------------|--------|----------|-------------|--------|------------|---------|---|
| | | | | | | | core | | | | | outer zone / edge | | | | | | | |
| | | | | | | | M(C,N) | M_7C_3 | $M_{23}C_6$ | M_6C | $M_1(C,N)$ | G-Phase | M(C,N) | M_7C_3 | $M_{23}C_6$ | M_6C | $M_1(C,N)$ | G-Phase | |
| A234_036 | HPNb-1 (b) | as cast | as cast | | | | 0.9 | 3.9 | | | | | + | ++ | | | | | |
| A234_038 | HPNb-2 | 913 | 1675 | 44.6 | 6.5 | 659 | 0.3 | | 8.0 | 0.5 | | 1.8 | (+) | | +++ | + | | | + |
| A234_039 | HPNb-3 | 927 | 1700 | 58.8 | 8.5 | 59 | 1.0 | | 8.0 | 0.7 | | | + | | +++ | + | | | |
| A234_040 | HPNb-4 | 955 | 1750 | 35.2 | 5.1 | 794 | 0.4 | | 7.5 | 2.4 | | (+) | (+) | | +++ | ++ | | | |
| A234_041 | HPNb-5 | 970 | 1778 | 35.5 | 5.2 | 286 | 0.5 | | 6.7 | 1.1 | | | + | | +++ | ++ | | | |
| A234_042 | HPNb-6 | 970 | 1778 | 26.0 | 3.8 | 1,185 | 0.4 | | 7.1 | 0.7 | | | (+) | | +++ | + | | | |
| A234_043 | HPNb-7 | 982 | 1800 | 37.4 | 5.42 | 191 | 3.0 | | 7.6 | | | | ++ | | +++ | (+) | (+) | | |
| A234_044 | HPNb-8 | 982 | 1800 | 37.4 | 5.42 | 4,467 | 2.2 | | 6.4 | | | | ++ | | +++ | (+) | | | |
| A234_045 | HPNb-9 | 982 | 1800 | 37.4 | 5.42 | 7,833 | 1.7 | | 7.1 | | | | ++ | | +++ | (+) | (+) | | |
| A234_046 | HPNb-10 | 982 | 1800 | 19.3 | 2.8 | 10,637 | 0.4 | | 11.1 | 3.9 | | | (+) | | ++++ | ++ | + | | |
| A234_047 | HPNb-11 | 1010 | 1850 | 24.8 | 3.6 | 707 | 0.7 | | 7.8 | 0.9 | | | + | | +++ | ++ | + | | |
| A234_048 | HPNb-12 | 1038 | 1900 | 15.8 | 2.3 | 2,555 | 0.6 | | 8.4 | 2.5 | | | + | | +++ | ++ | + | | |
| A234_049 | HPNb-13 | 1038 | 1900 | 13.1 | 1.9 | 5,373 | 0.6 | | 9.5 | 1.0 | | | + | | ++++ | ++ | + | | |

Annotations: (+) very few, + few, ++ many, +++ very many, ++++ abundant

In case that metallographic operation to identify type of carbide being conducted in specified experimental conditions, type of carbide might be identified by optical microscope where examples may be observed in Figure 2.

But through testing microstructures of inner tubes of furnace and taking operating conditions out of laboratory, identification of carbide type with optical microscope is not possible. However, what is completely explicit is observable change in structure due to service at high temperatures almost in all cases. This issue is expressed comparing to referral images in Figure 3.

These phase related changes and formation of secondary carbides, however is not meant the end of tubes lifetime and what is known as damage and risk factor for tubes being discarded is micro-cracks which are developed by connections between resulted micro-cracks of creep process. In Figure 4, examples of these micro-cracks are demonstrated.



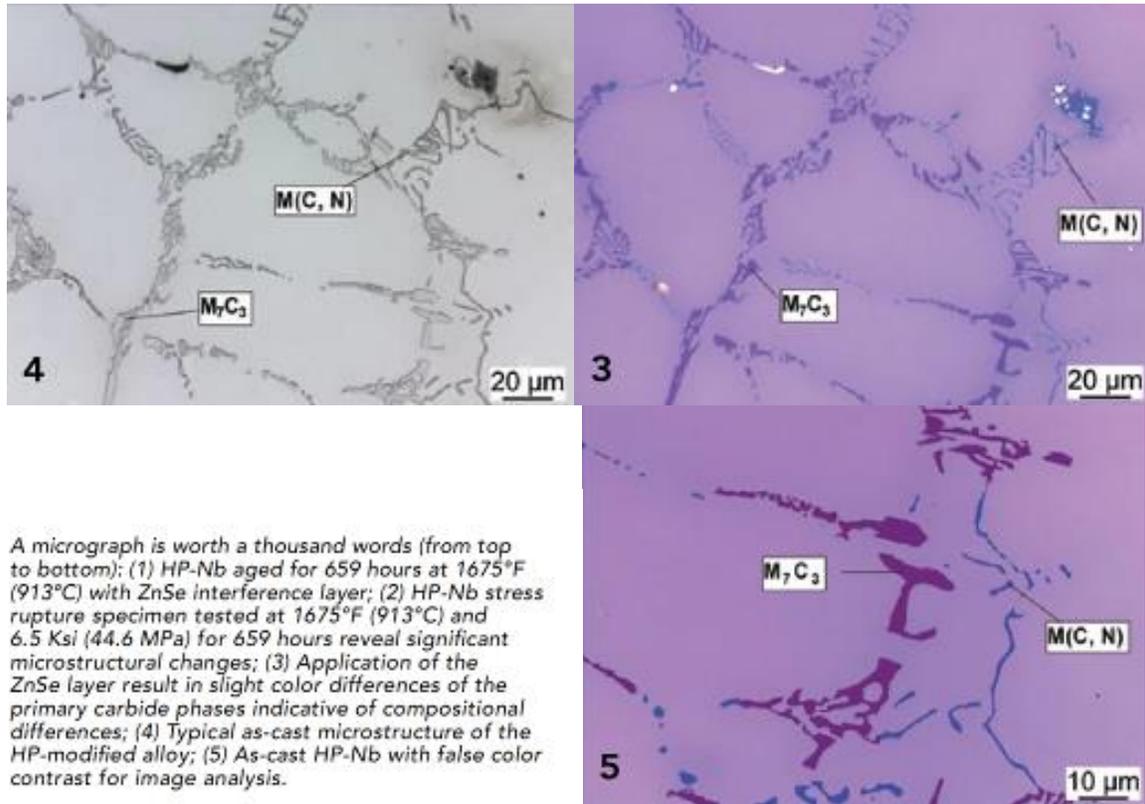


Figure 2: Different Types of Carbides and Method of their Identification by Optical Microscope (Berghof-Hasselbacher *et al.*, 2007)

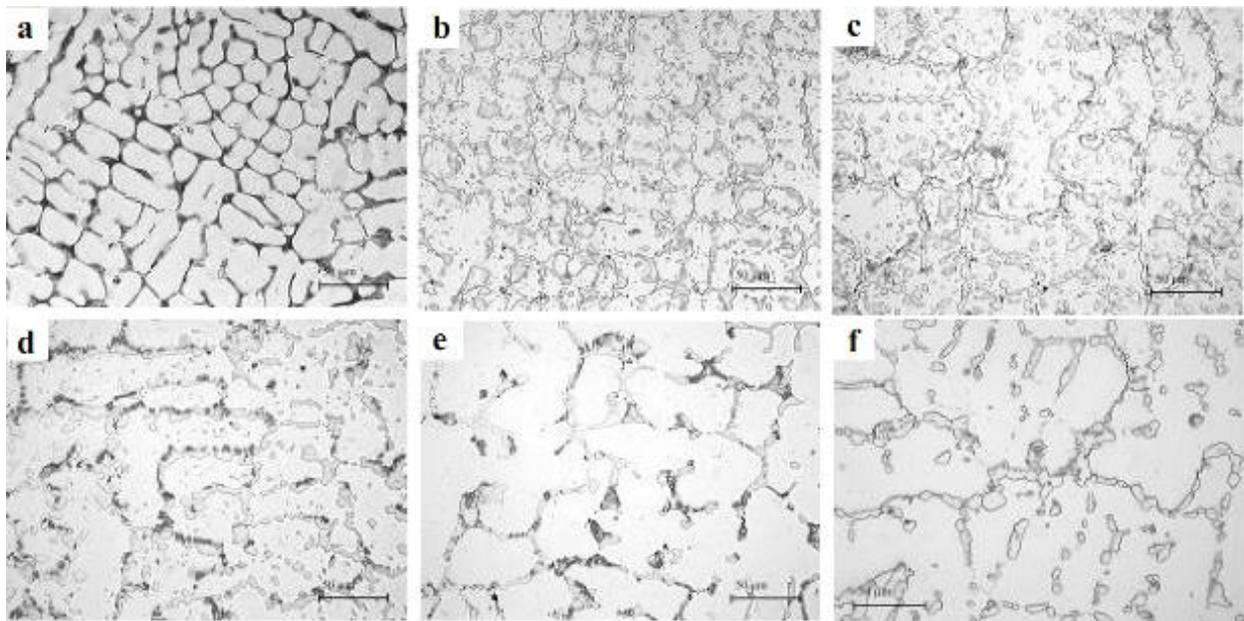


Figure 3: Metallographic image of HP still : a) Original sample, b) aged and c-f) liquidation for one hour at c) 1000 °C, d) 1100 °C, e) 1200 °C, f) 1250°C (Hasegawa, 2001)

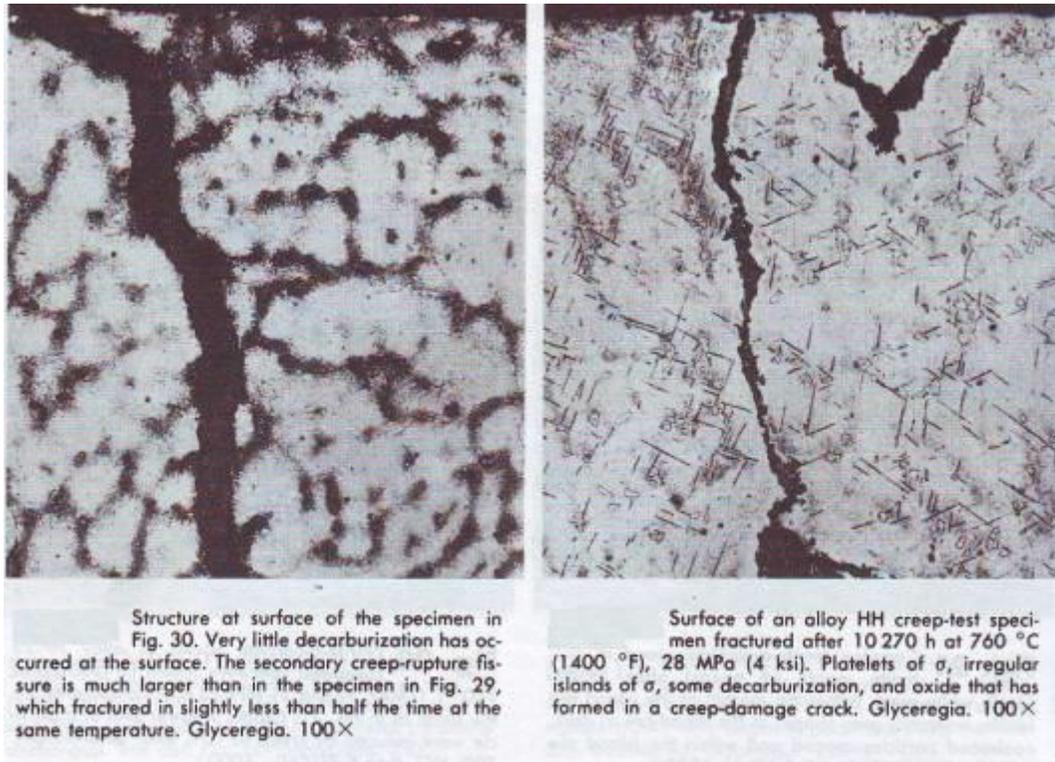


Figure 4: Developed Micro-Cracks by Creep Mechanism in HP still (Vander Voort, 2004)

Overall, it may be stated that, apart from structural change in metallurgical materials and taking above issues, all locations are free from micro-cracks (At least at metallurgized regions). But in some scarce cases (particularly in tube No. 48), abnormal structures and unusual arrangements in carbides are observed where those might be results of increase in temperature up to more than permitted applicable levels.

However, considering operation conditions of furnaces and existing processes; formation of carbon particles on inner wall of tubes and consequent permeabilization of carbon into structure and elimination of elements such as niobium and titanium may be significant factor in formation and expansion of chrome carbides (Alvino *et al.*, 2010), while in order to test this factor; level of exit catalyst from inner side of tubes may be analyzed and in case of finding carbon some operations such as cleaning inner side of tubes within stops and overhaul periods might be conducted. This issue is addressed orally with employer and is written in this report so as to be more assessed.

RESULTS AND DISCUSSION

Results

Reformer Tubes:

In Table 3, calculated life span of tubes respected to design conditions at different temperatures are observable. Furthermore, in Figure 5; graph of tube life span against temperature for different design conditions is indicated.

Calculations of Tube Life Span:

In this section, taking design conditions and related information to temperature and time where are provided by employer, tube life span is calculated. It should be noted that as we pointed to in API 530 standard, due to approximation in temperatures and ignoring other factors such as probable pressure changes, thermal tensions, start ups and shut downs and etc., these calculations are approximations. If temperature is designed for 924°C and pressure 36.8 bar. In compliance to API 530; we have [3,7]:

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$$MSW = \frac{OD \times P}{2Sa + P} \quad (\text{with fixed OD})$$

$$MSW = \frac{ID \times P}{2Sa - P} \quad (\text{with fixed ID})$$

By inserting related values to tube design conditions into above equations, level of tension is obtained:

$$12.1 = \frac{135.8 \times 3.68}{2Sa - 3.68}$$

Sa=18.81 MPa

Larson – Miller parameter for design is equal to low scatter band 28.23 and average 28.55.

By using derived Larson-Miller formula for this alloy, tube life spans values may be calculated given constant pressure for design and operation conditions of low scatter band and average.

$$LMP = \frac{T(18.6 + \log[tr])}{1000}$$

Where LMP is Larson-Miller parameter, T temperature in Kelvin and t_r is time interval up to rupture in hours.

Given time efficiencies for tube operation and calculated values for passed life span of each period of time are shown in Table 4.

Table 3: Tube Life Spans for Different Design Conditions at Different Temperature

| T(°C) | LMP | tr(hr) | |
|-------|-------|--------|------------------|
| 924 | 28.23 | 95720 | |
| 936 | 28.23 | 55844 | |
| 945 | 28.23 | 37539 | |
| 960 | 28.23 | 19615 | Low Scatter Band |
| 972 | 28.23 | 11802 | |
| 984 | 28.23 | 7171 | |
| 996 | 28.23 | 4398 | |
| 1008 | 28.23 | 2722 | |
| 1020 | 28.23 | 1700 | |
| <hr/> | | | |
| 924 | 28.55 | 177136 | |
| 936 | 28.55 | 102714 | |
| 945 | 28.55 | 68735 | |
| 960 | 28.55 | 35653 | |
| 972 | 28.55 | 21329 | Average |
| 984 | 28.55 | 12885 | |
| 996 | 28.55 | 7859 | |
| 1008 | 28.55 | 4838 | |
| 1020 | 28.55 | 3005 | |

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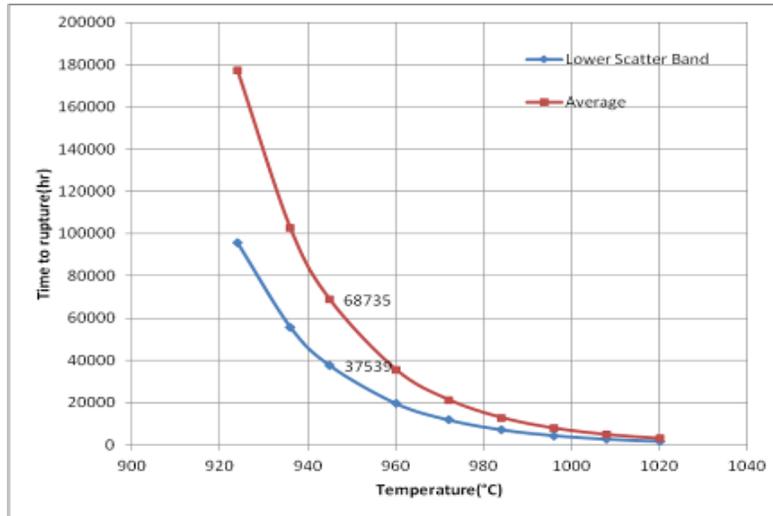


Figure 5: Tube Life Span Graph against Temperature for Different Design Conditions

Table 4: Calculated Values for Tubes Passed Life Span

| Operation Period | Duration a (year) | Pressure (MPa) | Stress (MPa) | Temperature (°C) | Rupture based on Minimum Strength | Time on Average Strength | Rupture based on Average Strength | Time on |
|---|-------------------|----------------|--------------|------------------|-----------------------------------|--------------------------|-----------------------------------|---------------|
| | | | | | a | Life Fraction | a | Life Fraction |
| 1 | 6 | 3.68 | 18.81 | 924 | 10.9 | 0.55 | 20.2 | 0.30 |
| 2 | 0.2 | 3.68 | 18.81 | 957 | 2.5 | 0.08 | 4.6 | 0.04 |
| 3 | 0.7 | 3.68 | 18.81 | 924 | 10.9 | 0.06 | 20.2 | 0.03 |
| “a” is the international unit symbol for “year” | | | | | Accumulated damage= | | 0.69 | 0.37 |

Now, by considering obtained passed life span, remaining fraction of life span might be calculated:

Minimum rupture strength: $1 - 0.69 = 0.31$

Average rupture strength: $1 - 0.37 = 0.63$

Referring to tubes passed fraction of life span at minimum rupture strength (Value 0.69), passed life span is equal to 7.5 years while is more than real passed life span (6.9). Therefore, this difference may be mentioned as evidence for implications of abnormal conditions on tubes.

If we assume that tubes pass their remaining life span under design conditions, then remaining life span can be calculated. These values are shown in Table 5.

Table 5: Calculated Remaining Life Span for Tubes

| Operation Period | Pressure (MPa) | Stress (MPa) | Temperature (°C) | Rupture Time (Minimum) | Rupture Time (Average) | Remaining Time based on Minimum Strength | Remaining Time based on Average Strength |
|------------------|----------------|--------------|------------------|------------------------|------------------------|--|--|
| | | | | a | a | Life Fraction a | Life Fraction a |
| 4 | 3.68 | 18.81 | 924 | 10.9 | 20.2 | 3.4 | 12.7 |

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As shown in Table 5, obtained values for remaining life span at low scatter band case is equal to 3.4 years and at average strength is equal to 12.7 years. Given that in real conditions, these tubes usually are designed for about 100000 hours (11 years), it is better that level of remaining life span at minimum strength condition or 3.4 years to be selected for measure of decision makings.

Regarding results of advanced non-destructive tests, all tubes were assessed qualitatively and categorized by registered indications under NDT methods as 35.1% trouble free, 15.4% in minor risk class, 38.5% in medium risk class and 11.1% in high risk class.

Considering results of mettalography testing on new and used samples at doubted regions, it was identified by other NDT methods that main background of tubes is austenite type and conducted studies on infrastructures indicate availability of primary and secondary carbides at boundary grains. It may be concluded from developing secondary carbides at boundary grains that deformation of structure is serving at excess temperatures than normal attitude and this is not related to termination of tubes life span and risk factor in these tubes is availability of micro-cracks and their connection together to develop creep phenomenon but in experimental sample; micro-cracks are not observed at all but in some cases abnormal structures and unusual arrangements of carbides were observable.

Regarding advanced NDT tests and conducted studies on obtained results of testing methods and mettalography on doubtful regions, temperatures at higher levels than permitted ones are main factors in confining service efficiency of reformer tubes.

Enlargement of austenite boundary grains carbides and also located carbides between dendrites, tangible loss in tensile strength, hardness and strength against creep rupture are evidence for increase in tube temperature above permitted levels.

Therefore, by proper application of furnaces and observing highest operational temperatures levels, some situations such as excess heating, flame collision, oxidation, gas flow decrease and developing brittle fractures might be avoided and suspend occurrence of creep phenomenon and its rupture consequence. Overheating has significant impact on shortening tubes life span and its remaining working time in reformer system and creep rates as well.

Conclusion

In this paper, report of reformer tube inspection by long range guided wave ultrasonic method (GW), metal magnetic memory (MMM), Eddy currents (ET), Time-Of-Flight Diffraction (TOFD), magnetoscopy, hardness test and metallography is assessed. tubes' catalysts are of microalloy under trade name of Centralloy G 4852 Micro (G-X40 NiCrSiNb 35-25) and reducers of this reformer is made of Centralloy G 4859 (G-X10 NiCrNb 32-20). Following results were obtained:

- 1- classifications includes 35.1% trouble free, 15.4% in minor risk class, 38.5% in medium risk class and 11.1% are located in high risk class.
- 2- Enlargement of austenite boundary grains carbides and also located carbides between dendrites, tangible loss in tensile strength, hardness and strength against creep rupture are evidence for increase in tube temperature above permitted levels.
- 3- Overheating has significant impact on shortening tubes life span and its remaining working time in reformer system and creep rates as well.

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