RESEARCH NOTE

CREEP LIFE ASSESSMENT OF PRIMARY REFORMER HP40-NB MODIFIED STEEL TUBE OF AN AMMONIA PLANT

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Abstract   Assessment of creep damage and residual creep life of a cast HP 40 Nb Mod. reformer tube was performed, wherein the experimental Larson–Miller diagram and area fraction of creep voids were adopted. The state of damage of the tube in service was metallographically analyzed by using light and electron microscopy. Samples from the serviced reformer furnace tube were cut and prepared for void examination and creep test at 940°C-1000°C under 20-30 MPa stress. Microstructural examination was carried out with an Scanning electron microscope with secondary and backscattered electron detectors. Inter-granular voids in the microstructure of the worked tube as a result of a creep phenomenon are ranked relating to the remaining life.

Key Words   Creep Life Assessment, Ammonia Plant, HP40 Nb Modified Steel Tube

چکیده   در این مقاله میزان تخریب و عمر باقیمانده لوله ای از جنس HP 40 تعدیل شده با نیوبیوم مربوط به کوره پرایمری ریفرمر واحد آمونیاک با استفاده از پارامتر لارسن –میلر و کسر سطحی حفره های خزشی موجود در ریز ساختار مورد بررسی قرار گرفته است. ارزیابی حفره های خزشی با روش متالوگرافی و با استفاده از میکروسکوپ نوری و الکترونی انجام شده است. برای این منظور از لوله کار کرده نمونه های تست خزش و متالوگرافی تهیه گردید. نمونه های خزشی در دمای ۹۴۰ الی ۱۰۰۰ درجه سانتیگراد و تحت تنش ۲۰–۳۰ مگا پاسکال آزمایش شدند. با استفاده از نتایج آزمایش خزش و رابطه لارسن –میلر عمر باقیمانده پیش بینی گردید. بـرای تعیین ریز ساختار لوله نیز از میکروسکوپ روبشی و از الکترون های ثانویه و برگشتی استفاده گردید. میزان حفره های خزشی ریز ساختار با چارت تجربی مقایسه و میزان تخریب با این روش نیز سنجیده شد.

1. INTRODUCTION

A major aspect of plant life management is estimating the remaining life of high–temperature components, which have a finite life due to creep. Methods based on post-service evaluations of the actual component material and direct estimation of the remaining creep life has gained popularity in the last decades. This is mainly because the results of such methods are expected to be more accurate in view of the fact that no assumption needs to be assumed regarding the materials properties or the past history of the component [1]. In this research the post – service evaluation of an HP-40 Nb modified reformer tube was done based on the accelerated, uniaxial stress rupture testing of samples excised from the tube.

In tubes, which are filled with supported nickel catalyst, methane reacts with steam, carbon dioxide and oxygen into the synthesis gas. Reformers are the heart of the fertilizer industry and any failure in this section of the plant results in premature shutdown leading to huge losses in terms of damage to the equipment, production losses and safety hazard [2].

2. ALLOY DEVELOPMENT

Since the catalyst tube assembly can amount to 25% of total cost of the furnace, there is a great incentive to optimize its design from chemical, thermal, and mechanical points of views. In the 80s, HP (25Cr/35Ni) modified alloys were developed by using certain metals, such as,

TABLE 1. Designation and Composition of HP Alloy [3].

ACI designation	UNS number	ASTM specification	Composition wt%				
			%C	%Cr	%Ni	%Si	%Mn
HP	NO8705	A297	0.35-0.75	24-28	33-37	2-2.5	2

TABLE 2. Characteristic of As Cast HP Alloy [4].

Melting point	Density kg/dm^3	Coefficient of expansion mm/mm/°C	Thermal conductivity W/m°C	El%	0.2% proof stress (MNm^{-2})	UTS MNm^{-2}
1350°C	8.02	$10^{-6} \times 18.5$	At 1050°C 30	8, 6*	250	450

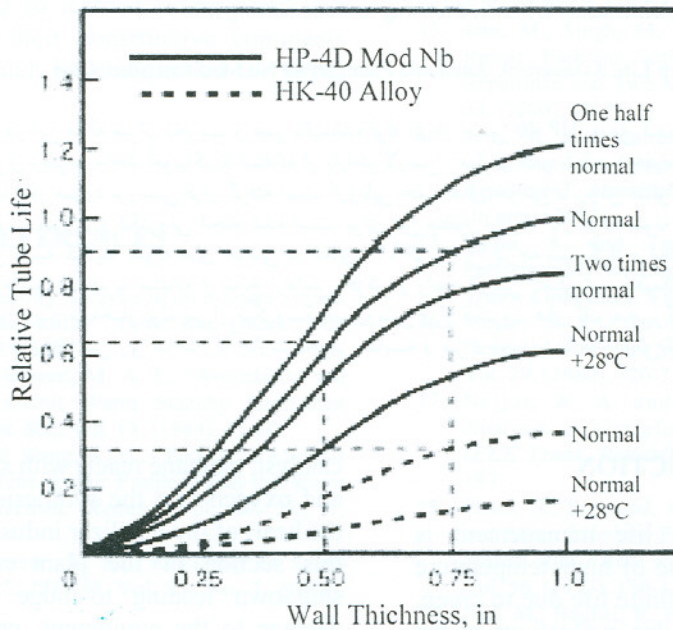* For centrifugally cast pipes 8 and for static castings 6

Figure 1. Shows the relation between w thickness and amount cycli that is an important consideration tube life [5].

molybdenum, niobium, tungsten and titanium. Designation and composition of the HP alloy are shown in Tables 1 and 2 [1,2,3].

The requirements of a cost effective reformer design are maximum reliability, operating stability and high thermal efficiency. The materials used must have a high creep strength confirmed with good strain relation, good weld ability, and excellent oxidation resistance and, after aging, good ductility and good weld ability [5].
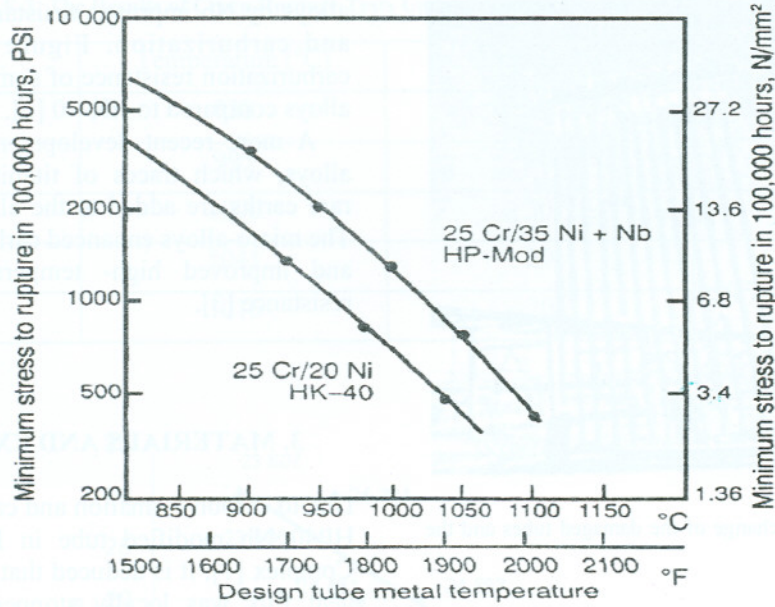
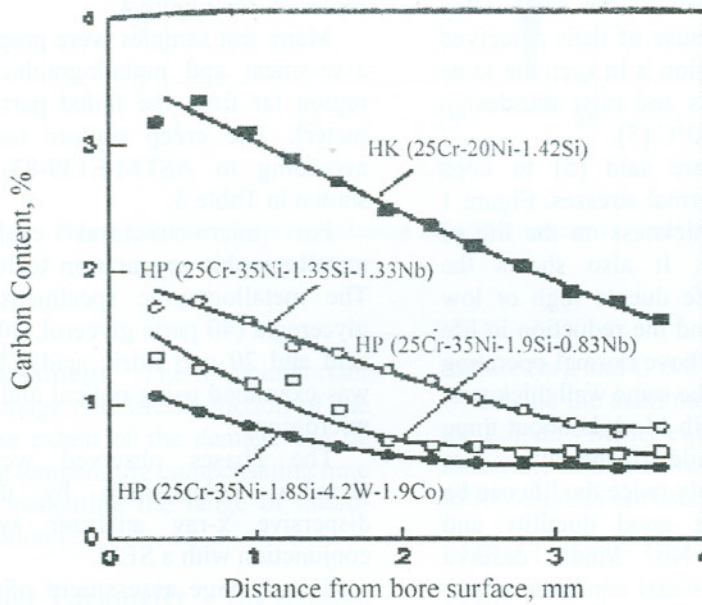**Figure 2.** Minimum creep rupture stress versus temperature for a period of 100,000 h [5].

Figure 3. Carbon concentration profiles of HK and HP alloys exposed at for 1200h in $3CH_4 - 40H_2O - 37N_2$[5].

In retrofit or revamp design, the HP-40 Nb Mod. allows two possibilities. First, with the outside diameter fixed because of existing inlet and outlet manifolds, make the tubes thinner. This improves the rate of heat transfer and increases 30% to 40% production capacity. With the thinner
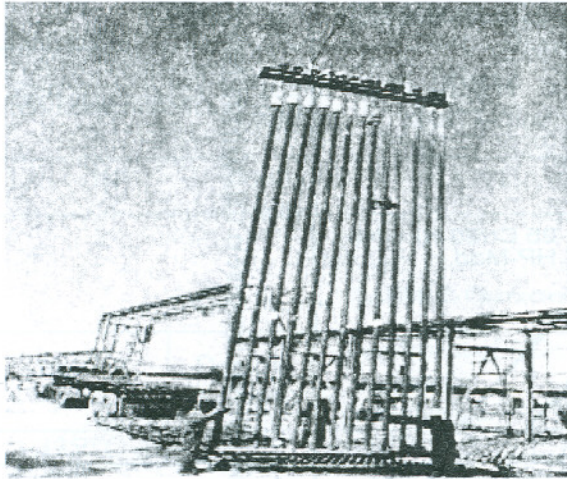
Figure 4. A view of exchange of the damaged tubes and the catalyst.

wall, the cost per foot of catalyst tubing is comparable, and in some cases less than HK-40, even though the cost of HP-40 Nb Mod. alloy tubes seem to be more because of their perceived expense [5]. The second option is to keep the same tube diameter and thickness and raise the design tube metal temperature by 60°C [5].

The HP-Mod. alloys are said [5] to cope substantially better with thermal stresses. Figure 1 shows the effect of wall thickness on the life of HP-40 Mod. and HK-40. It also shows the reduction or increase in life due to high or low number of thermal cycles and the reduction in life caused by operating 28°C above normal operating temperature. Note, that for the same wall thickness, the relative life of HP-40 Nb Mod. is about three times that of HK-40, while if the alloys are designed for the strength, only twice the life can be expected. In addition, the good ductility and weldability of HP-40 Nb Mod. deserve mentioning. It has, in the as-cast condition, about 8% elongation that after prolonged service drops to about 4%.

f field repairs are required on HP-40 Nb Mod. a solution anneal for about two hours is recommended, which will restore much of the elongation [5].

Figure 2 shows minimum creep rupture stress versus temperature for a period of 100,000 h [5].

It has been found that modification of HK-40

alloys by Nb improves resistance to creep rupture and carburization. Figure 3 illustrates the carburization resistance of some of these modified alloys compared to HK-40 [6].

A more recent development is the HP micro-alloys, which traces of titanium, zirconium and rare earths are added to the alloys during casting. The micro-alloys enhanced carburization resistance and improved high- temperature creep-rupture resistance [3].

3. MATERIALS AND EXPERIMENTS

Due to carbon formation and catalyst break up in a HP40 Nb modified tube in Razi Petrochemical Complex [7], it is deduced that the consume of the heat flux was locally stopped. Therefore, local overheating occurs which caused the failure of the tube after 12350 hr of its operation. Due to this overheating the tube and all of the catalyst were replaced, see Figure 4.

Many test samples were prepared for creep life assessment and metallographic analysis from a region far from the failed part of the tube (four meter). The creep rupture test was preformed according to ASTM-E139-83. The results are shown in Table 3.

For micro-structural evaluation, standard metallographic preparation techniques were used. The metallographic specimens were etched in glyceregia (40 parts glycerol, 40 part hydrochloric acid and 20 part nitric acid). The microstructure was examined using optical and scanning electron microscopy.

The phases observed were analyzed for chemical composition by using an energy dispersive x-ray analyzer system (EDX) in conjunction with a SEM.

The damage assessment of reformer furnace tube is based on Larson Miller parameter (LMP) and on the metallographic analysis of a serviced individual tube. Although this tube is not the real representative of the complete furnace tubes but it is important note that destroying a large number of the tubes is not practical, in addition this tube is the most damaged one. Therefore the extent of damage is the highest and its remaining life is the lowest.

TABLE 3. The Results of Creep Rupture Tests Under Different Stresses and Temperatures.

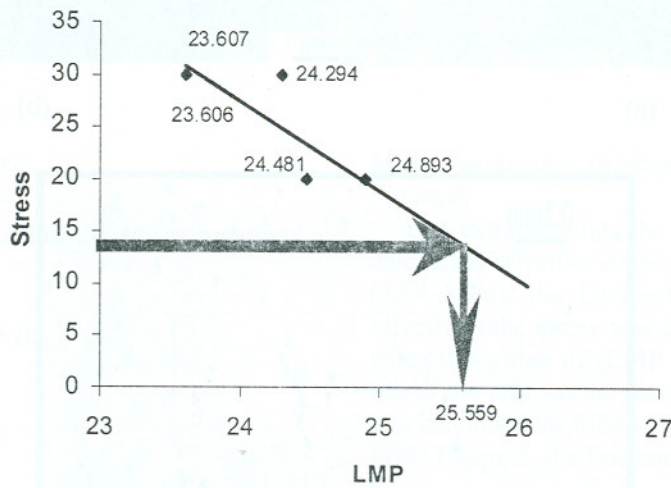| Specimen No.	Temperature (°C)	Stress (MPa)	Rupture time (hr)
1	938	30	108.3
2	995	30	14.4
3	1000	30	42.1
4	1041	20	25.2
5	1016	20	71.3

Figure 5. Rupture stress versus Larson and Miller parameter (master curve).

3.1 Damage Assessment   The most important mechanism for damage and life extinction of the tubes is creep. The extent of the damage can be calculated by using temperature compensating time parameters or by evaluating the range of micro-structural deterioration [2].

3.2 Larson- Miller Parameter   The standard method used to interpret creep stress -to- rupture data is the parametric expressions such as the one which developed by Larson and Miller [8-10] that is defined by the following equation:

$$LMP = \frac{T}{1000}(\log t + C)$$

where; T, is the service temperature (K), t, time to

rupture (hr), and C is a constant.

To find the maximum value of the constant C in the Larson - Miller equation, or in other words, to assess the minimum remaining life of the tubes the following data are used:

$$LMP = T (\log t + C)\ 10^{-3}$$ at a constant stress

$$LMP = constant$$

$$LMP(1) = (938 + 273)(\log 108.3 + C)$$

$$LMP(2) = (995 + 273)(\log 14.4 + C)$$

At stress 30Mpa LMP(1) = LMP(2)

$$(938 + 273)(\log 108.3 + C) =$$

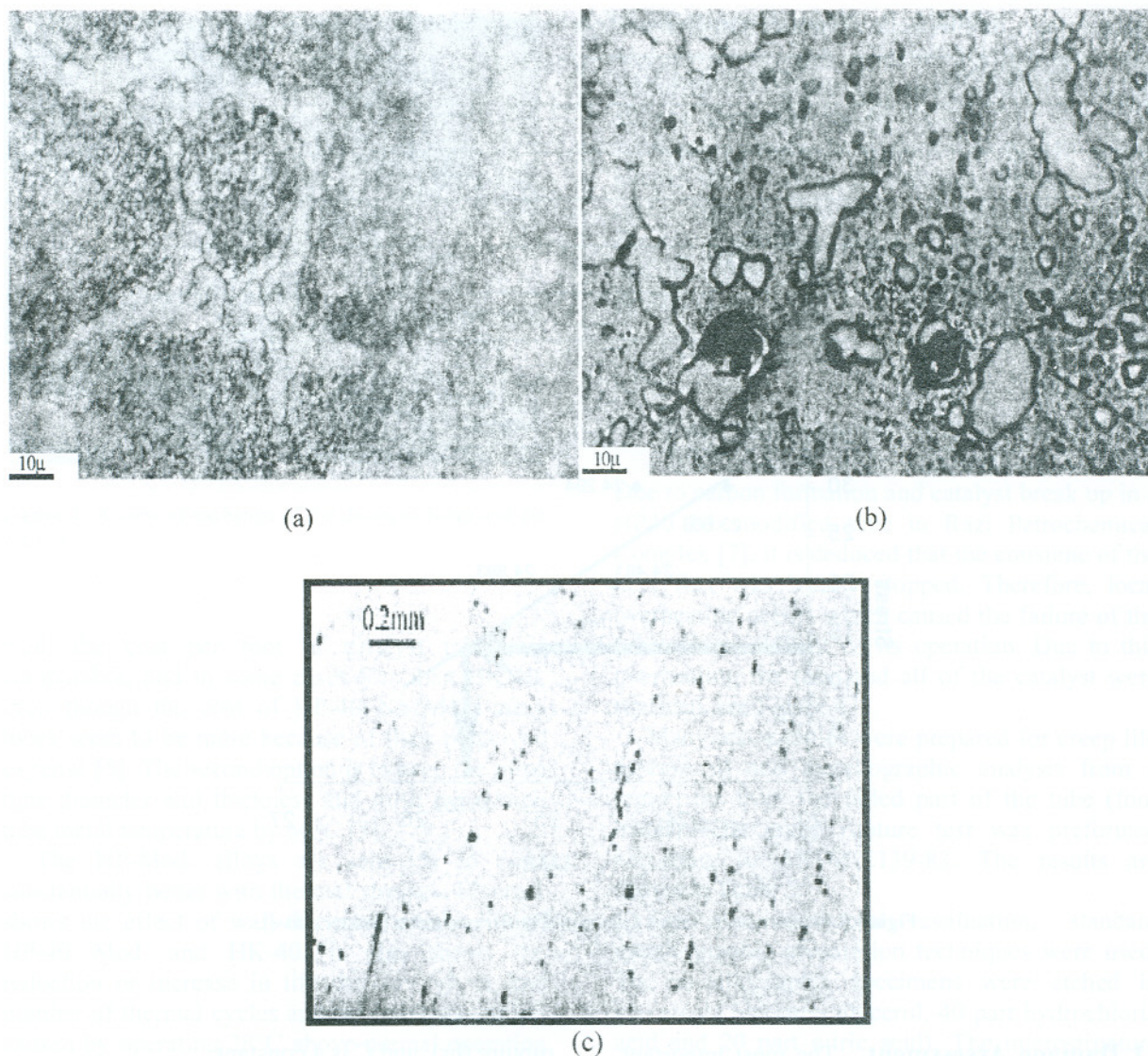$$(995 + 273)(\log 14.4 + C) \rightarrow C = 17.459$$

(a)

(b)

(c)

Figure 6. (a) SEM micrograph shows massive primary carbides in an austenitic matrix and fine secondary carbides within the austenite grain upon exposure to elevated temperature, (b) SEM micrograph shows the damage part of the tube which due to high temperature, secondary carbides were reduced and the inter-dendritic carbides had undergone significant agglomeration and coarsening and (c) light micrograph shows random creep voids.

The stress state in the material is complex, but it is clear that stress due to internal pressure plays a leading role in damage accumulation. As the internal pressure varies little along the tubes, damage concentrates in the hotter section [11,12]. Therefore, in the present work the average stress in the tubes or the effective stress was used for calculation.

The following data and equations were used for finding the effective stress in the tubes, [13].

$r_i = 41$ mm, $r_o = 54$ mm,

$P_i = 33.35$ bar $= 3.34$ MPa
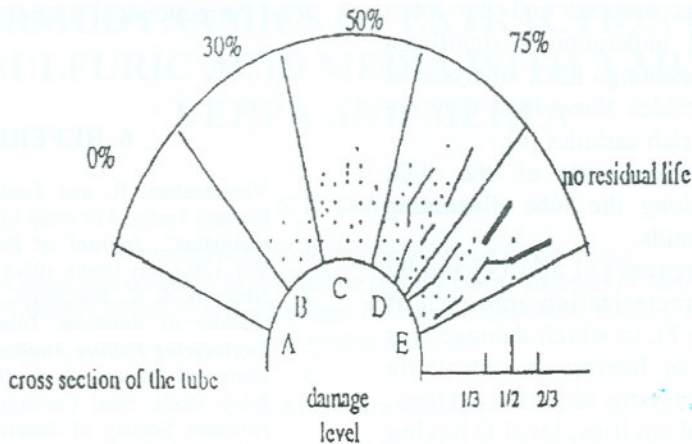
$\sigma_r = -3.34$,   MPa $= \sigma_3$

Figure 7. Classification of the damage in a reformer furnace tube, as indicated after metallographic preparation [15].

$\sigma_H = 12.43 \quad MPa = \sigma_2$

$\sigma_{ax} = 4.5$ MPa $= \sigma_1$, by using VonMises equation;

$$\bar{\sigma} = \frac{1}{\sqrt{2}} \sum \left[\begin{matrix} (\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + \\ (\sigma_2 - \sigma_3)^2 \end{matrix} \right]^{\frac{1}{2}},$$

$\bar{\sigma} = 13.4 MPa$

By using data in Table 3 and the highest value of the constant C according to the creep data, the (LMP)s values were determined for various stresses and temperatures as below;

LMP(1) = $(930 + 273)(\log 108.3 + 17.459)10^{-3}$ = 23.607

LMP(2) = $(995 + 273)(\log 14.4 + 17.459) 10^{-3}$ = 23.606

LMP(3) = $(1000 + 273)(\log 42.1 + 17.459) 10^{-3}$ = 24.294

LMP(4) = $(1041 + 273)(\log 25.2 + 17.459) 10^{-3}$ = 24.481

LMP(5) = $(1016 + 273)(\log 71.3 + 17.459) 10^{-3}$ = 24.893

Using the results of the creep rupture tests (Table 3), the plot of the stress versus Larson

Miller parameter (master curve) was drawn in Figure 5.

By extrapolating the master curve to the calculated effective stress experienced in the tubes (13.4 MPa), the Larson-Miller parameter at the effective tube stress was deduced to be 25.56. By using this value of (LMP = 25.56), the remaining life of the tubes at the service temperature (870 °C) was calculated as follow.

From Figure 5, the line equation is:

Stress = -8. 505 $\quad$ LMP + 230.88

At stress 13.4 MPa $\quad$ LMP = 25.559

LMP = T $(\log t + C) 10^{-3}$

25.559 = $(870 + 273)(\log t + 17.459)10^{-3}$

t = 79860 $\quad$ hr = 9.2 year

3.3 Micro-Structural Deterioration Creep damage starts in the wall as round voids randomly distributed on dendritic boundaries figure 6 Their preferred formation is on boundaries perpendicular to the tensile stress.

The structure consists of massive primary carbides in an austenitic matrix (Figure 6a) in addition; fine secondary carbides were precipitated within the austenite grain upon exposure to elevated temperatures. In serviced material removed from the damaged part of the tube (Figure 6b), temperature was high and the number of

secondary carbides was reduced and the inter-dendritic carbides had undergone a significant agglomeration and coarsening. EDX analysis of these inter-granular carbides shows that they are chromium and niobium rich carbides [6].

Figure 6c shows the result of the light metallurgical survey along the tube illustrating random distribution of voids.

With regard to references [11 and 14] and by five level damage characterization approach of I. Le May [15] (Figure 7), in which damage was classified as level A or having no detectable voids, level B as displaying isolated cavities, level C having oriented cavities, level D having micro-cracks and level E having macro-cracks, the damage was revealed to be in the end range of level B. This means the approximate remained life is something around seventy percent of the designed life (which is generally 100,000 hr).

4. CONCLUSIONS

1. The remaining life of primary reformer tubes was predicted to be about 9 years. This was done by utilization stress and temperature assisted acceleration that involves the use of Larson – Miller parameter.

2. Calculations based on the stress-rupture test results showed that the Larson-Miller Constant (C) for 12350 hr serviced HP-Nb modified reformer steel tube was about 25.56.

3. On the basis of the metallographic, damage that have been observed in the microstructure of the serviced tube and its comparison with the classification of the damage in the reformer tubes it was indicated that around seventy percent of the designed life (~70,000 hr = 8.1 years)) was remained.

5. ACKNOWLEDGEMENTS

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