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Performance and Life Assessment of Reformer Tubes in Petrochemical Industries

Abstract: High temperature mechanical properties of service exposed reformer tubes are compared and revalidated with those of virgin material for the sake of health assessment studies. Technical interpretations of creep and stress rupture (accelerated creep) data usually are in close proximity in absence of defects. Results of extrapolation of accelerated creep data were optimized. This review article is aimed at studying life prediction methodology of reformer tubes operating at high temperature and aggressive chemical environment, in response to the designed time frame for preventing failures and accidents, even before stipulated design time schedules in some cases.

Keywords: ammonia, pressure stress, hoop stress, microstructure, stress rupture, creep, remaining life, revalidation, life assessment, damage analysis, carbon deposition, coke formation, hot spots, decoking

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1 Introduction

Accelerated creep or stress rupture data is used for remaining life assessment for life management studies of elevated temperature components, e.g. for reformer tubes where packed nickel catalysts are used for synthesis of hydrogen, ammonia etc. This research has become a regular task because of large range of time for failure (3 to 15 years) compared to designed life (11.4 years or 100,000 hours) and huge loss associated to damage, production and safety hazards. Utilization of appropriate inspection during plant shut down has been strategic short term life assessment. Tests have been typically done by high temperature mechanical properties, microstructure analysis and accelerated creep. Inspection of micro-cracks, hot spot formation, carburization/metal dusting for inner wall and oxidation, tube diameter increment for outer wall inspection have been traditional symptoms of end of life of tubes.

Incidences of number of shut downs within one year [1–5] have been interpreted as failure consequences from following reasons when catalyst poisoning has been criterion: (i) flow of occasional heavier hydrocarbons in natural gas, which has developed Giraffe necking signs inside tubes, (ii) related incidental pressure drops, (iii) anomalous thermal expansion between catalyst and tube material during shut down and warm up schedule to result catalyst shuttering (during warming) and crushing (during cooling/shut down) because of low coefficient of expansion for catalyst material, (iv) chocking of tube-catalyst zones of preference where heavier hydrocarbons have deposited carbon, (v) inefficient heat absorption tendency at carbon deposited zones to produce hot spots and inducing material to be creep prone, (vi) undesirable drop in pressure of synthesis gas mixture. Exercise of systematic life assessment at regular intervals during plant shutdown has been a means to ensure absence of strategic failure.

Aim of this review has been to study the life prediction methodology of reformer tubes operating at high temperature and aggressive chemical environment, in response to the designed time frame for preventing failures and accidents, even before stipulated design time schedules in some cases.

2 Performance of HK40 reformer tubes

ACI HK40 (0.4wt.%C-25wt.%Cr-20wt.%) and HP40 (0.4wt.%-25wt.%Cr-35wt.%Ni) have been centrifugally cast for preparation of tubes in manufacture of ammonia, methanol, etc. in petrochemical industries. Reaction of naphtha and steam in these tubes has been conducted at temperatures within 800–1000 °C and at a pressure of 5–40 kgf/cm^2. Even if life time is calculated and standardized, consequences of high pressure and temperature appear to cause premature failure within the creep life time stipulated for the alloy in aggressive chemical environment. Therefore periodic inspection of mechanical properties has been treated as mandatory step in application of these tubes. This practice of periodic investigation has increased prior estimation about remaining life time, increase productivity of the plant, proper schedule of maintenance and operation and plant safety. Lee et al. [1] have investigated reformer tubes exposed for 60,000–90,000 hours in hydrogen manufacture plant. Traditional inspection has been done by creep tests, stress rupture tests, microstructural and mechanical tests and prediction of remaining life times from usage of Larson-Miller curves. In addition to these inspections authors have described possibilities of remaining life time from variation in microstructure after solutionizing heat treatment within 1373 and 1473 K. Sigma phases have appeared to dissolve at these temperatures after four hours. Interpretations have included following arguments: Remnant life time has been strongly dependent on presence of brittle sigma phases in matrix. Figure 1 shows appearance of precipitates. Marked zones as 1 (matrix), 2 (carbide phase) and 3 (sigma phase) have shown different phases. Chemical compositions of these phases have been reported from electron probe microanalysis (EPMA). Results (in wt.%) of EPMA have been shown in Table 1.

Extensive degradations of mechanical properties have been described in alloys even at room temperature because of these precipitates. These consequences have raised risk of operation in response to extra temperature variation during startup and shut down operations. Figure 2 shows variation in sigma phase formation during creep rupture tests on used reformer tubes for 90,000 hours. This has shown a gradual decreasing rate of percent sigma phase volume fraction with increasing creep-rupture time.

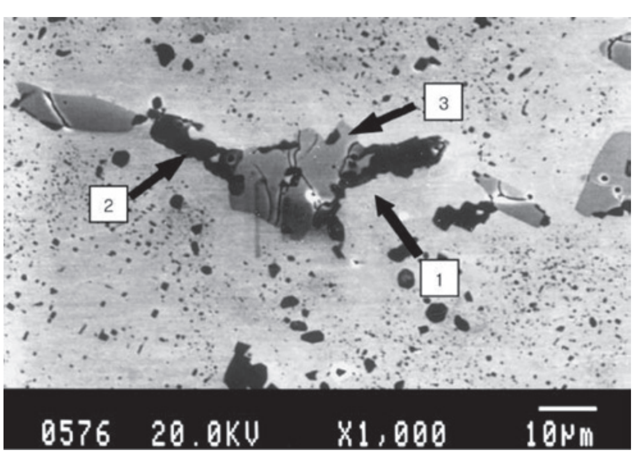

Fig. 1: SEM micrograph showing brittle sigma phase [1].

Table 1: Electron probe microanalysis (EPMA) results of three phases in wt.% [1].

Feature	Fe	Cr	Si	Ni
1. Matrix	54.24	22.58	1.26	21.91
2. Carbide	9.30	86.91	0.27	3.62
3. Sigma phase	42.43	47.26	2.33	7.98

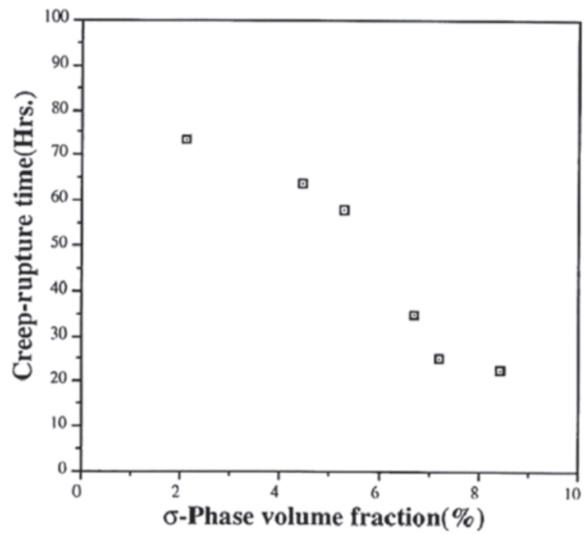

Fig. 2: Relationship between volume fraction of sigma phase and creep-rupture time in the HK40 tubes used for 90,000 hours [1].

Heat treatments of these used tubes at solutionising temperature have improved room temperature mechanical properties, however they do not seem to have any influence in improving creep-rupture properties. Elongation percentage in solutionised specimens has been reported to increase four times compared to that before heat treatment or used specimens. Dissolution of sigma phases on other hand has improved resistance to thermal fluctuation during start-up and shut-down schedules under high pressure and temperature required for synthesis reactions. After stress rupture tests on used and solutionised specimens; creep cavities have appeared at zones, from where sigma phases have been dissolved out into the matrix during solutionising treatment [1].

HK40 steel tubes [2] exposed for 80,000 hours has reported actual results as required, from evaluation of (i) surface flaw detection, (ii) metallographic examination, (iii) Charpy V impact test, (iv) creep rupture strength and (v) creep crack growth rate [2] tests. Hong et al. [3] have analyzed furnace tubes after long-term elevated temperature services. Observations have described increase in brittleness assisted from minicracks from inner and outer walls of reformer furnace tubes. Residual lifetimes have been reported on basis of creep-rupture tests at 1223 K [3].

Wen et al. [4] have analyzed HP40 boiler steam heating tubes after servicing for 46,000 hours. Experiments have included (i) visual inspection, (ii) X-ray diffraction (XRD) analysis of oxides, (iii) measurement of wall thickness and diameters, (iv) hardness measurements, (v) optical metallographic analysis and (vi) danger point analysis. Experience has shown deterioration from (a) oxidation and carbonization of surface material, (b) decrease in wall thickness and hardness compared to virgin cases, (c) disappearance of framework eutectic carbides and coarsening of first and second carbide precipitation in austenite where as precipitation of sigma phases take place. Residual life has been predicted on basis of these results [4].

de Almeida et al. [5] have used cast steel of 25%Cr-20%Ni type (HK type steel) since 1960, in reformer and pyrolysis furnaces. This steel has replaced traditional superalloys with reduction in cost and has similar properties under conditions of creep, which has principal degradation mechanism at elevated temperature. Stability of phases increased the life of tubes operating at elevated temperature. This basis has produced HP variety by addition of more nickel (around 35%) in HK type compositions. Addition of Nb and Ti has increased fragmentation of as cast microstructure with partial replacement of chromium carbide by more stable carbides. Stable precipitate selection has been to reduce creep deformation by high temperature glides and dislocation motion, e.g. better performance of nickel-niobium silicides than niobium carbides within temperature range of 973–1273 K. This has established application of Nb-modified HK and HP steels in reformer tubes. Present context describes modification and related advantages of Nb-Ti-addition to HK or HP variety of steels in cast welded and aged conditions. Concentration of Nb has promoted primary “Chinese script” morphology precipitation while Ti has promoted finer and equidistributed secondary precipitation. Transformation of (NbTi)C to G-phase has been inhibited by presence of Ti. This transformation has occurred from outside to center of precipitates without dissolving Ti. Therefore G-phase has been observed to contain less in Ti-modified HP steels. Compared to HP steels containing only Nb, Ti modification in addition has shown improvement in creep properties because of (i) fine and even distribution of precipitates, (ii) less-continuous dendritic carbide network and smaller volume fraction of G-phase. Description regarding welding of HP-NbTi tubes by weld metal of same composition has been shown in Table 2. The welding process was

Table 2: Chemical composition of the HP-Nb and HP-NbTi alloys and weld metal (wt.%) [5].

Alloy	C	Cr	Ni	Si	Mn	Nb	Ti
HP-Nb	0.43	24.8	34.1	1.67	1.0	1.34	–
HP-NbTi	0.41	25.5	34.9	1.19	1.0	0.78	0.04
Weld metal	0.39	26.6	35.8	1.21	0.9	0.79	0.04
Balance: Fe							

Table 3: Welding parameters used for the HP-Nb and HP-NbTi tube joints (GTAW) [5].

Bead	Voltage (V)	Current (A)	Work speed (mm s^{-1})	Heat input (kJ mm^{-1})
1	15	85	0.80	1.10
2	15	95	0.65	1.50
3	15	85	1.00	0.80
4	15	90	1.00	0.90

gas tungsten arc welding process (GTAW). Welding parameters have been shown in Table 3.

Figure 3 shows as-cast microstructure for both HP-Nb and HP-NbTi alloys. The microstructures were prepared by using electrolytic etching in an electrolyte solution of 64% H_3PO_4, 15% H_2SO_4 and 12% H_2O and stainless steel cathode with 5 V direct current at 298 K for 4 seconds. Figure 3(a) reveals typical dendritic network of carbides in austenite matrix for HP-Nb steels whereas Figure 3(b) shows comparatively less continuous dendritic network for HP-NbTi steels. Figure 4 has shown etched microstructure after aging. At high magnification austenite matrix appears to be decorated by carbide precipitates. Figure 5 has shown weld metal after aging for both types of HP steels. Difference between base and weld metal is that weld has more refined grain structures compared to that in the base metal. Figure 6 has revealed details of secondary Cr-carbides ($M_{23}C_6$) precipitations. This has shown orientation relations with the matrix defined as $[110]_{carbide}/[110]_{\gamma}$ orientation [5].

Kenik et al. [6] have described effects of long term aging in Nb modified HP tube steels used in chemical and petrochemical industries. Heat resistant (H-series) cast alloys have typical development with high level of chromium and nickel to provide corrosion resistance, strength and austenite phase stability. Addition of silicon was to restrict carburization of alloys. Analysis of microstructure and nature of distribution of phases in centrifugally cast HP tubes in styrene production furnace has been described, which were operated at temperature within 1200

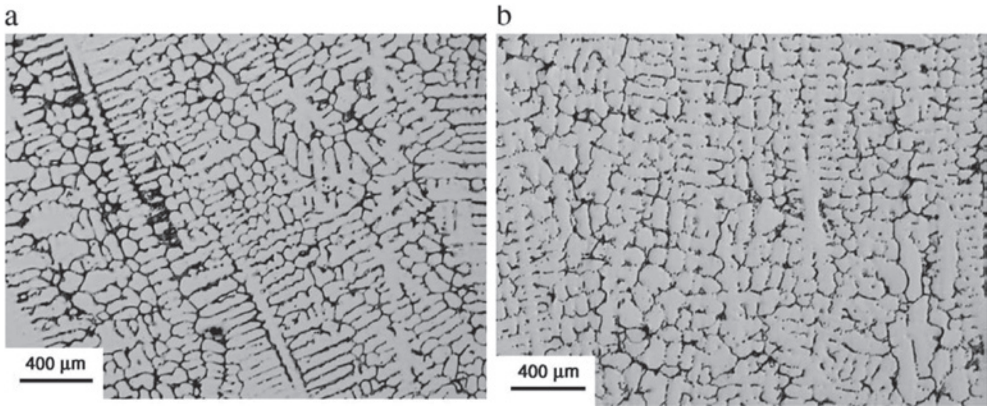

Fig. 3: Light optical micrographs of both alloys in the as-cast condition, (a) alloy HP-Nb; (b) alloy HP-NbTi [5].

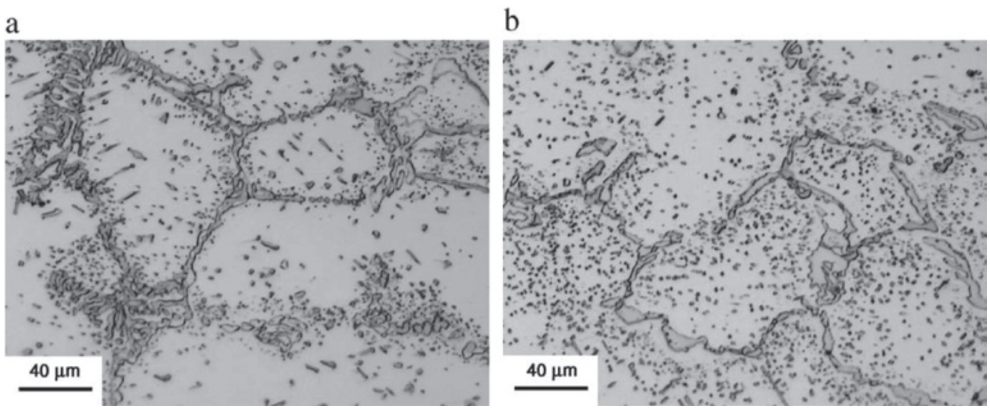

Fig. 4: Light optical micrographs of both alloys in the aged condition, (a) alloy HP-Nb; (b) alloy HP-NbTi [5].

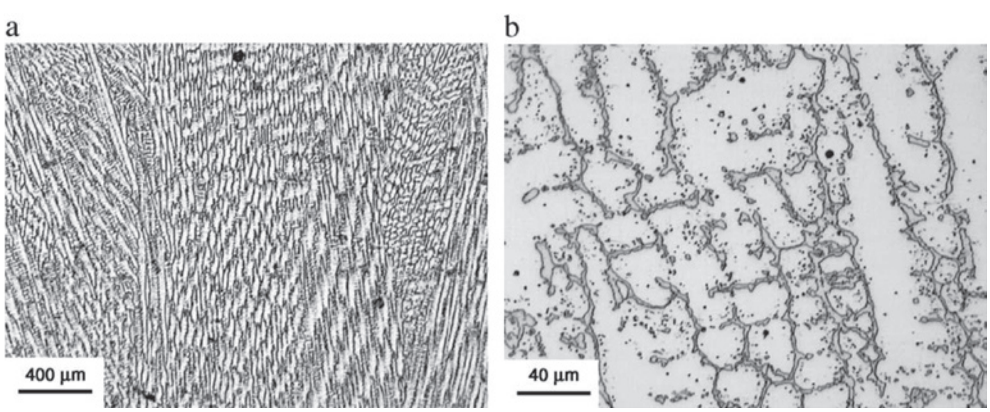

Fig. 5: Light optical micrographs at two different magnifications of weld metal in aged condition [5].

to 1339 K for 105,000 hours (12 years). E.A. Kenik et al. have reported interplays of precipitates. These precipitates include eta phase, G-phase of MC, $M_{23}C_6$, M_6C, $M_3M_3'C$, $M_6M_6'C$, $M_2M_3'SiC$, etc [6]. Remaining life assessment of primary reformer tube material has been investigated by Krishna Guguloth et al. [7]. These catalyst primary micro-paralloy grade tubes have been service exposed for 13.5 years in fertilizer plants. Investigators have described that due to coarsening of primary carbides of chromium and niobium along grain boundary materials have failed

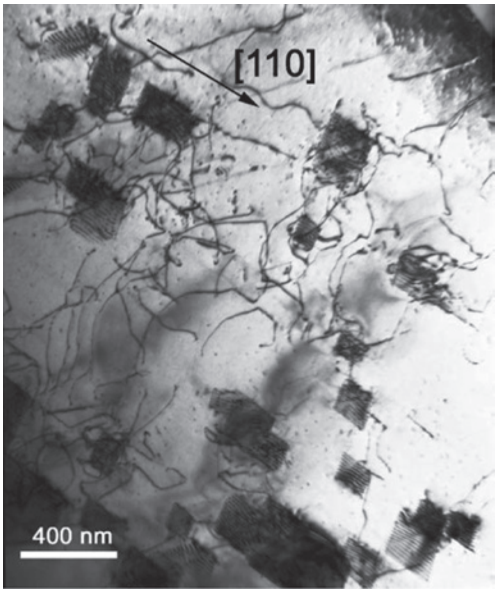

Fig. 6: TEM bright field image, HP-NbTi alloy, showing details of the secondary chromium carbide precipitation. The $[110]_{carbide}/[110]_{\gamma}$ orientation relationship is illustrated [5].

earlier in creep rupture tests. NbC has been degraded by transformation to Ni-Nb-Si phase and reconversion partially to NbC-phases. Degradation in hot (1123–1223 K) tensile properties have been within specified limits. Common failure of reformer tube in premature life (e.g. after 3–5 years of exposure) has been linked to localized overheating and creep damage. Degradation of tensile and hardness properties in premature cases has been mainly linked to microstructural variation. On other hand 13.5 years of service exposed tubes have been predicted to operate further 10.6 years at temperature of 1191 K and 15.4 MPa based on results of accelerated creep rupture tests. Accelerated creep rupture tests were carried out within the temperature range 1173–1248 K. Service exposed reformer tube achieved similar creep rupture behavior as that of the virgin alloy. There was no appearance of degradation behavior during creep rupture [7].

Johns et al. [8] have studied metal dusting behavior arisen from exceptionally high carburization rates from carbonaceous process gases with in 723–1073 K at low oxygen partial pressures. These process gases have carbon monoxides, hydrogen and other hydrocarbons. Metal dusting has produced carbon, metal particles, carbides and oxides. Degradations were due to pitting and general metal wastage. Syngas containing varying amounts of hydrogen, carbon monoxide, methane and water and down stream products e.g. methanol and ammonia is referred to make alloys susceptible to these types of degradations at elevated temperatures. Syngas has been typically produced within 1075–1148 K and transferred through refractory pipe lines. Even after periodic oxide coating and replacement, it has imposed economic impact by metal dusting. Similar impact from metal dusting have been appeared in (i) petroleum refineries-like hydro-dealkylation and catalyst re-generation processes, (ii) nuclear plants that employ carbon monoxide for cooling, (iii) recycle gas loop equipment of coal-gasification units, (iv) tubes of fired heaters handling hydrocarbons at elevated temperatures, (v) fuel cells using molten salts plus hydrocarbons to produce power, and (vi) plants for direct reduction of iron ore (DRI). However in any case metal dusting have elevated temperature effects from CO and H_2 gases. In this case, carburization of steel had led to formation of alloy elemental carbides at grain boundaries which loosened the grains of austenite. These loose grains escape as a burning particulate, leaving a pit at inner wall of tubes. This enhances effective surface area to promote similar degradation exponentially with passage of time [8].

3 Remaining life assessment of reformer tubes

Remaining life assessment studies in high temperature synthesis tubes of petrochemical and fertilizer plants have been made from creep rupture or stress rupture or accelerated creep tests and derivation of Larson-Miller plots to evaluate Larson-Miller constants. Welded tube joint performance on other hand has been studied for (i) microstructure, (ii) mechanical properties and (iii) impact energy performance. M.U. Long et al. [9] have suggested that life time performance has been improved by solution treatment. Post service tests in cracks at weld zones have been reported to be linked to anti-liquification capacity supposed to be recovered by change in welding technique [9]. S.A. Jenabali et al. [10] have reported a remaining life of 9 years after accelerated stress rupture tests and involvement of Larson-Miller parameter. Derived value of Larson-Miller constant (C) is 25.56 for a tube after service life of 12,350 hours. This equates to a further service life of seventy percent [10]. Tito Luiz da Silveira and Iain Le May [11] have described about severe requirements imposed on reformer tubes in radiation zones and hot reaction gas outlet zones. Increasing efficiency has been related to synthesis operations at increasing temperature and pressure. Suggestions have been to use better quality of catalyst, which has been operated at decreased temperature. Partition of elements through thickness of wall of column segment has been processing characteristics of centrifuge

Fig. 7: Macrograph of centrifugally cast structure of a column with yttrium addition, showing the duplex structure [11].

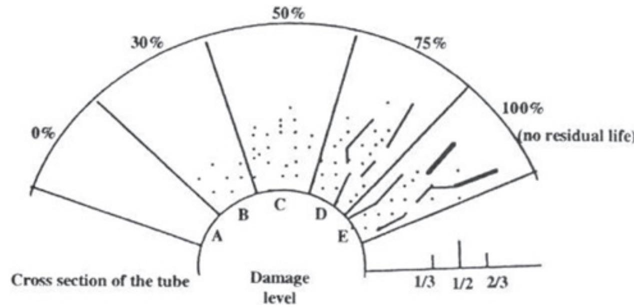

Fig. 8: Classification of damage in wall of a reformer tube, as indicated after metallographic preparation [11].

Table 4: Mechanisms for life Extinction of reformer columns [11].

Mechanism of damage	Damage	Site
Creep	Aligned creep voids and multiple cracks start in the inner third of wall, longitudinally oriented with respect to column	Sections in hotter segment of reformer column
Creep at weld	A main crack propagates at centre line of weld deposit starting in inner third of wall. Micro-cracks and aligned creep voids are distributed parallel to crack	Heat affected zone of butt welds between spindle cast segments. Hey appear in upper third of column.
Creep buckling	Offset may correspond to several column diameters. Offset may divert column towards its neighbors of furnace wall.	May be distributed over complete length of column or concentrated in one part.
Carburization	Scale formation, growth of interdendritic carbides and carbide precipitation in the austenite matrix	Internal surface of hotter segment of reformer column.

during solidifications. Small addition of yttrium has resulted in a duplex structure. Figure 7 has shown elongated grains near outer surface and finer grains at inner surface. Elongated grains are resistant to creep and fine grains are carburization resistant. Table 4 reveals representation mechanism of damage accumulation to dictate extinction of life in reformer column, outlet pigtails and outlet manifolds. Table 4 has also shown preferential sites of damage accumulation and damage morphology [11].

Figure 8 has illustrated form of creep damage within a section of a furnace tube and manner in which it can be classified. Five levels of damage were categorized by formation of isolated cavities to presence of macro-cracks. These have been (i) level A – having no detectable voids, (ii) level B – displaying isolated cavities, (iii) level C – having oriented cavities, (iv) level D – having micro-cracks and (v) level E – having macro-cracks. These features have been observed in specimen cross section after polish-etch steps in metallographic procedures [11].

Maharaj et al. [12] have illustrated evolution and progression of grain boundary cavity nucleation, coalescence, microcrack formation and eventual crack formation for long-term creep failure. Failures have been largely attributed to temperature. Random nature of failures indicates that defects have been independent of possible quality inconsistencies in tube manufacturing operations e.g. welding, bending and annealing. Creep failures were due to localized temperature heating beyond 1173 K. Therefore remaining life assessment where long term creep failure is concerned, has been done based on metallurgical evaluation of tube outer diameter, mid-wall and inner diameter wall of tube, in response to presence of percent creep cavities. Existence of creep cavities were more near the outer wall and inner wall compared to mid sections. Authors have suggested effects of stress, temperature and external environment have contributions to these failures. Effects of temperature and stress have been highest at inner wall of tubes while outer wall has been affected by oxidation from air weather. Outer wall has shown tertiary creep at a strain increment of 9.3%. Author has suggested that the benchmark of tube replacement should be after every seven years when tertiary creep based rejection criteria has been concerned. Prediction of on-line remaining life assessment has been suggested by (i) Installation of thermocouple at selected location of reformer furnace to assess variation in local heating effects and (ii) application of thermographs to observe temperature profile of tubes. Therefore based on on-line measurements life has been referred to be prolonged by reducing burner heating in local zones of over heating [12].

Swaminathan et al. [13] have reported failure analysis and remaining life assessment of catalyst filled process heater tubes for (natural gas + steam) and (naptha + steam) reforming reaction in petrochemical industries over HP alloy steel grades. Onset of embrittlement and over heating above 1173 K has seen incidences of premature failure of tubes [13–18]. Schematic of tube samples have been shown in Figure 9. Figure 10 has shown failed tube samples under investigation. Microstructures of specimens in polished and etched condition have been shown in Figure 11.

Creep damage of failed portion shows increased outer diameter of tube. Advanced aging of carbides has been observed in microstructure of failed tube. Reversion of NbC after dissolution into Ni-Nb-Si phase from NbC has been found. Longitudinal cracks have originated on surface side of tube. Poor creep strength and microcracks have appeared because of over heating from flame irregularities. Life assessment studies pertained to those tubes which have no outer diameter expansion [19–24].

Tables 5–7 has shown details of data after investigation of reformer tubes.

Microstructures of non failed portions of tube sample namely CD123-2 and AB49-2 have been presented in Figure 12 [24].

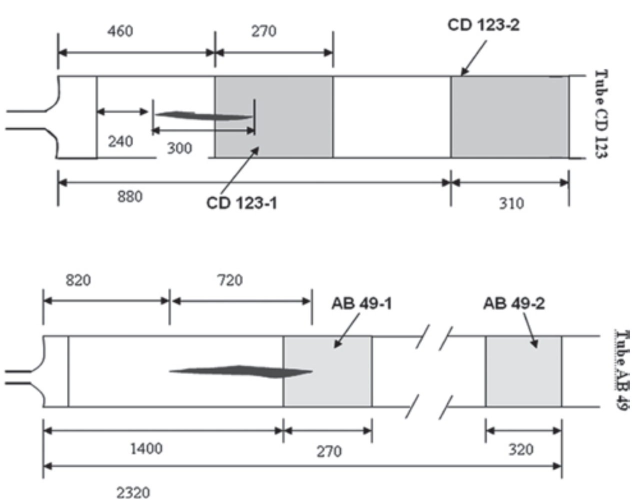

Fig. 9: Schematic of sampling cut for failure analysis and remaining life assessment (RLA). All dimensions are in mm [24].

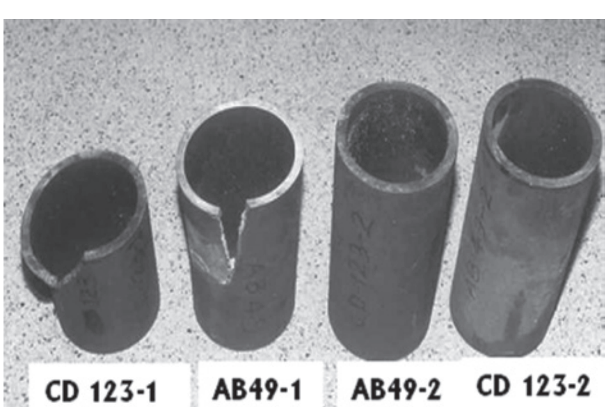

Fig. 10: Photographs of reformer tubes under investigation [24].

4 Refinery and chemical plants-syngas

Creep limits tube life due to combination of internal pressure and through-wall thermal stresses generated during start-up cycles and operating transients. Progressive grain boundary cavitations by influences of thermal stresses generation during operating transients have been initiated within tube wall towards bore. These are evidences as exhaustion of creep life in tubes. Pressure stresses, outside wall temperatures and factored lower-bound material rupture data are ordinarily the basis of tubular component design. However, they do not provide a realistic data as basis of remaining life assessment of reformer tubes. Optimistic estimation of future operational capability by inverse design procedure is to take account full range of operational behavior, transients as well as steady state, life limitations from actual service tube-wall loadings. Process gas and steam enter each reformer tube between 723 K and exit at 1123 K with slight pressure drop down the length of the tube. Process conditions, firing configuration and the design of the unit are influenced by variation in tube metal skin temperatures, which vary along the length of tube. Variation in temperature has been greatest, therefore tube life assessment is done with actual process conditions and material properties in response to effective creep assessment temperature (outlet) and local through-wall thermal gradients (inlet). Nature of distribution of cracks and pre-crack damage in reformer catalyst tube has been shown in Figure 13. Contributions from both mechanical and thermal loading derived from specific process configuration are responses of complex catalyst tubes in reformer services. Structural analysis is successful in predicting response of radiant catalyst tubes. Suitable method of addressing growth of crack arrays in these components has been made by damage front propagation methods. Properties of damaged material and

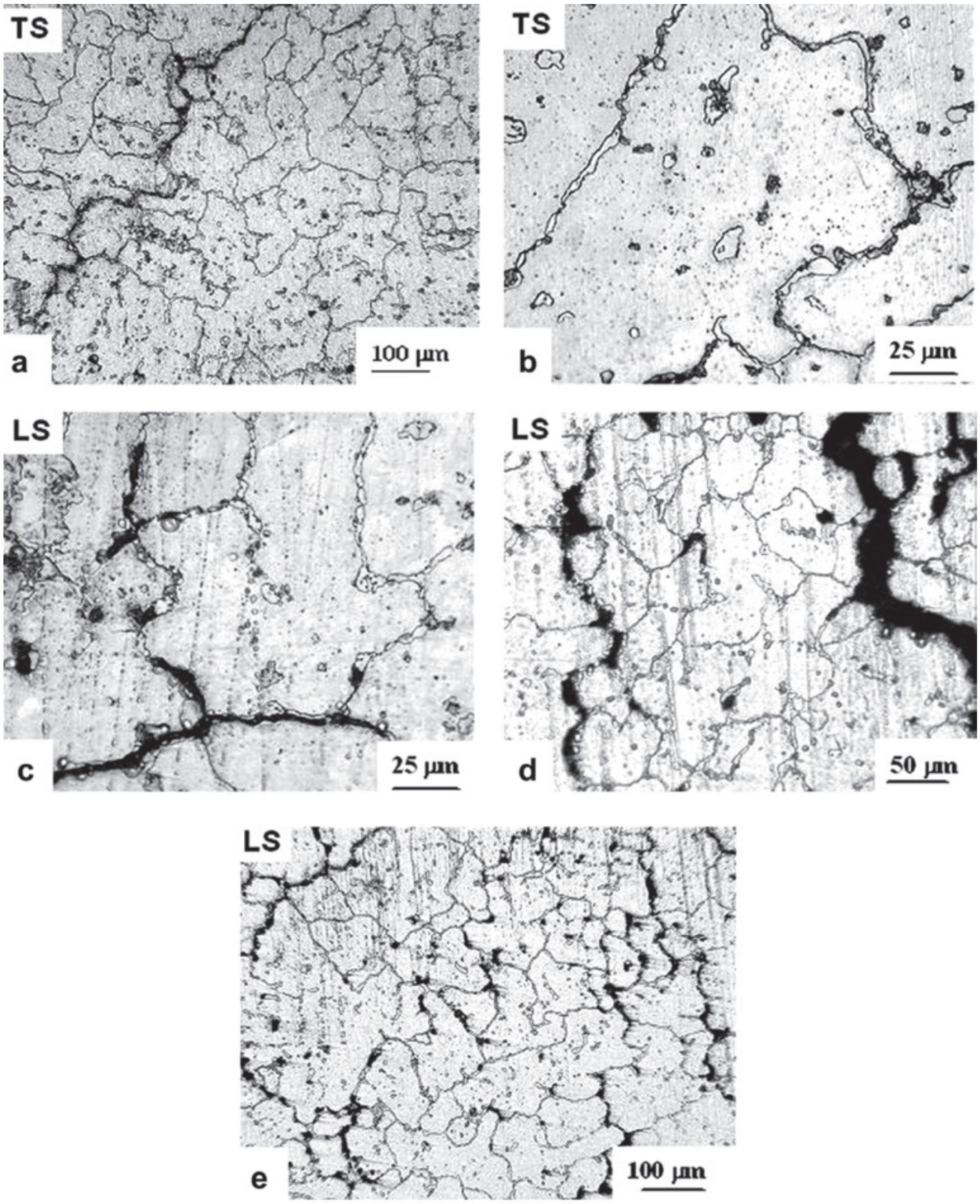

Fig. 11: Photomicrographs of etched specimens from failed tube portion. Interdendritic cracks with carbide phases halved at many places. Creep voids have been found only on outer wall side. TS = transverse section, LS = longitudinal section [24].

calculation of load, heat and displacement transmission which has controlled primary and secondary stress evolution, have been defined by application of Kachanov's postulate of 'continuity' [25].

5 Steam methane reformer

Knowles et al. [26] have optimized tube life management from consideration of measured approach without replacement as follows: (i) Prior to first use tubes have been base lined in response to dendritic growth, (ii) selection of worst tube for strain based accelerated creep test as a routine prevention, (iii) estimation of comparative life in exposed tubes to that of microstructure-creep conditions of actual tube, (iv) regular measurement of temperature and strain monitoring, (v) estimation on basis of primary creep as a lower bound. Complements of common technique are the ability to monitor early stages of creep evolution strain measurement in form of diametric growth. Perception of accurate and regular strain measurement in low ductility failure of cast alloys has been experienced from microstructure understanding and generation of creep strain related data. Life management of tubes were

Table 5: Vickers hardness values of reformer tube samples [24].

Specimen ID (Fig. 10)	Hardness, HV_{30}
123-1	181
	187
	188
	178
123-2	174
	175
	180
	177
49-1	184
	186
	187
	196
49-2	198
	194
	185
	185

Table 6: Tensile strength results for tube samples [24].

Test temperature (K)	Specimen ID	0.2% P.S. (MPa)	U.T.S. (MPa)	% RA	% EL
RT	AB 49-1	275	472	3	5
	AB 49-2	301	464	3	4
	CD 123-1	295	507	6	8
	CD 123-2	242	487	120	8
1108	AB 49-1	135	157	50	26
	AB 49-2	139	166	43	21
	CD 123-1	139	167	40	28
	CD 123-2	140	166	39	31
1158	AB 49-1	99	121	58	18
	AB 49-2	126	140	39	23
	CD 123-1	103	126	43	37
	CD 123-2	102	124	45	40
1208	AB 49-1	84	99	60	26
	AB 49-2	82	97	56	28
	CD 123-1	83	103	49	39
	CD 123-2	100	107	41	30

AB & CD are reference names of two radiant chamber

done by using combination of inspection technique, accurate temperature measurement and sample removal and creep test [26].

Swaminathan et al. [24] have described mechanical properties and microstructural observation for remaining life assessment of service exposed 24Ni-24Cr-1.5Nb cast austenitic steel reformer tube. Evaluation of remnant life is supposed to be difficult by several non-destructive tests and non-monotonous appearance under microstructure. Therefore accelerated creep rupture, hot tension and hot hardness tests are accepted as limiting destructive tests [27–34].

Table 7: Accelerated creep rupture test results for tube samples [24].

Test temperature (K)	Applied stress (MPa)	Specimen ID	Rupture time (h)	% EL	% RA
1173	46	AB 49-2	353	20	48
		AB 49-1	326	15	35
		CD 123-2	319	8	12.3
		CD 123-1	276	18	32
1193	42	AB 49-2	429	17	40
		AB 49-1	306	14	42
		CD 123-2	233	23	36
		CD 123-1	192	23	34
1213	37	AB 49-2	331	18	42
		AB 49-1	205	11	51
		CD 123-2	344	13	32
		CD 123-1	276	19	35
1233	32	AB 49-2	442	12	29
		AB 49-1	283	16	38
		CD 123-2	260	19	32
		CD 123-1	300	23	35
1253	28	AB 49-2	575	9	23
		CD 123-2	283	13	35
1273	25	AB 49-2	435	7	10
		CD 123-2	400	12	21

Metallographic examination was carried out to observe difference of precipitation between virgin and service exposed specimens [34]. SEM observation on 1,31,400 hours service exposed tube sample has shown coarsening of lamellar primary carbides (dark in contrast) at inter-dendritic boundaries to semi-lamellar network. Secondary carbides (light in contrast) at intra-dendritic region have been blocky types and effected by coarsening. EDAX analysis of precipitates for light grey and darker precipitate phases have been shown in Table 8 [34]. Bone skeleton structures are primary carbides of composition $Cr_{23}C$ and (Nb, Ti)C and fine indigenous secondary precipitates are compositions of NbC [34].

Table 9 reproduces compositions of sigma phases in matrix.

Analysis of tensile and stress rupture strength for cast 24Cr-24Ni-1.5Nb reformer tube alloy served for 96,000; 105,120; and 131,400 hours, reported reliability of

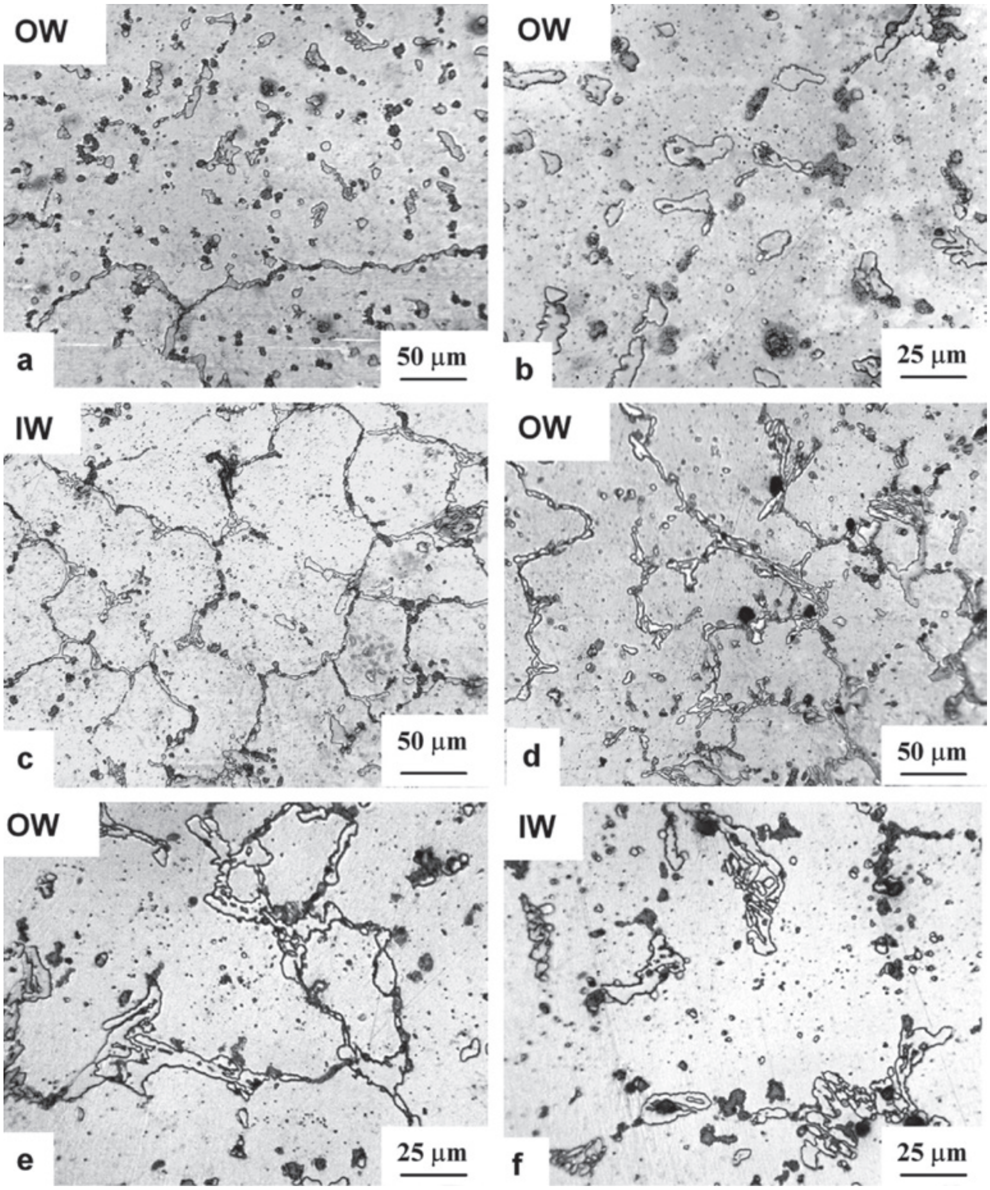

Fig. 12: Photomicrographs of transverse sections of etched specimens from unfailed tube portions: (a–c) CD123-2; (d–f) AB49-2. No microcracks and creep cavities were observed. IW, near inner wall; OW, near outer wall region [24].

destructive tests, e.g. stress rupture tests, which is dependent on selection of sample location. This has been referred to be detrimental because of inadequacy in results of stress rupture life and ultrasonic scam method of nondestructive life evaluation [34].

Thomas et al. [35] have described hypothetical life assessment using ductility exhaustion approach. Results generated have been listed in Table 10.

Distribution of values is assigned to variables as opposed to a single value. Thus probabilistic technique data refers to the time to produce a 1% chance of failure, i.e. predicted time to failure of first tube in a 100 tube furnace. This describes high influence of cycling to life of low ductility as cast tubes while more influence by temperature to high ductility ex-service material. Service exposure of cast tubes has been considered as in-situ formation of aged condition. This has increased ductility of cast tubes. Ductility exhaustion is consumption of ductility per thermal cycle of exposure. Therefore failure by cracking is loss of strength by effects of temperature on material with a threshold of optimum ductility of tubes; however consequence has been resistant to stress cycling [35].

Moss et al. [36] have discussed risk based planned replacement program of reformer tube which have been op-

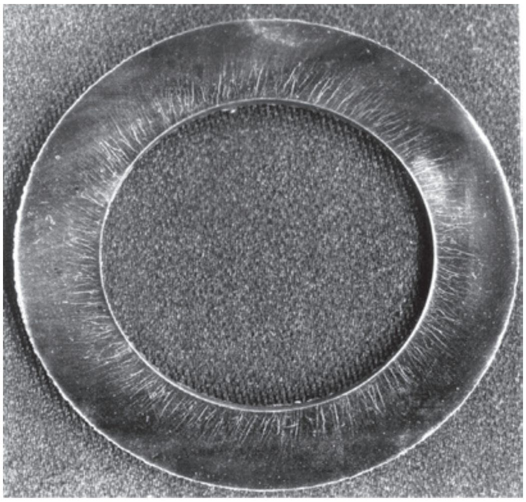

Fig. 13: Typical damage distribution in a reformer catalyst tube, HK40 material [25].

Table 8: SEM-EDAX results of composition in precipitate phases present [34].

Element	Light grey precipitates		Darker precipitates	
	Wt.%	At.%	Wt.%	At.%
Cr	8.83	16.02	76.57	78.09
Fe	15.46	21.23	15.96	15.16
Ni	6.80	8.88	7.47	6.75
Nb	69.91	56.87	–	–
Cr	7.85	11.55	51.83	55.98
Fe	14.80	20.26	25.47	25.61
Ni	6.98	9.09	11.70	11.19
Nb	69.73	57.38	10.59	6.40
Si	0.63	1.72	0.41	0.83

Table 9: SEM-EDAX results of composition for sigma precipitates [34].

Element	Sigma precipitate 1		Sigma precipitate 2		Sigma precipitate 3	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Fe	57.23	57.78	51.68	51.60	49.69	51.79
Cr	13.21	14.33	25.59	27.45	17.18	19.23
Ni	19.39	18.63	20.90	19.85	22.56	22.36
Nb	6.31	3.83	1.84	1.10	10.57	6.62
Ca	3.86	5.43	–	–	–	–

Table 10: Predicted time (hours) to produce a 1% chance of tube failure [35]

Cycles per year	As cast material		Aged material	
	1173 K	1223 K	1173 K	1223 K
12	88,000	80,000	190,000	48,200
6	167,000	140,000	300,000	51,500
4	240,000	185,000	380,000	52,500
2	450,000	270,000	460,000	53,600
1	830,000	350,000	510,000	54,300
Steady state	625,000	500,000	580,000	55,000
Mean rupture elongation	2%		10%	

erated for twenty years. Existing complications for assessment are (i) tested tubes may not be exposed to maximum temperature for life of furnace and (ii) test stress is different from service stresses because pressure and wall thickness combinations exist. It is found that there has been sufficient remaining life for tubes in furnace and no replacements are required prior to next normal outage. However it was found that if high temperatures are experienced in furnace, failure may occur early. Information from life assessment study is that set temperature limits to allow planned replacements of tubing. Temperature is accepted to impose critical influence on remaining life (Table 11). Continued on-line monitoring of process temperatures backed up by thermographic imaging is required by operators to ensure furnace temperature not to be excessive and tube life is inline with requirement. It is suggested to install thermocouples at critical sites to monitor tube skin temperatures [36].

Strategies of reforming furnace rejuvenation, Zhang et al. [37] have described life assessment by microstructure ranking, hardness measurement and Larson-Miller parameter. This synthetic evaluation has been done for weld joint between new and serviced tubes. This has been in response of rejuvenation by replacing one locally failed tube within service exposed tubes. Residual life of such tubes has been evaluated to be 4.5×10^{-4} hours. Accelerated creep rupture test failure was observed at side of service exposed tube in shaped specimen [37].

Zhu et al. [38] have been studied creep crack growth behavior of HK40 reformer tube within temperature ranges of 1103–1273 K and stress intensity factor range of 3.3–7.8 MPa $m^{1/2}$ that has been serviced for 81,000 hours. Proposed residual life has been derived from relation between initial stress intensity factor and Larson-Miller parameter (P) [38].

Jaske et al. [39] have derived remaining life of Nb modified and microalloyed HP reformer tubes by multi-parameter inspection technique. Controlling important operating parameters are (i) tube temperature, (ii) heat

Table 11: Comparison of time to rupture for service exposed material and data base predictions and remaining life fraction [36].

	Temperature				
	853 K	863 K	873 K	883 K	893 K
Tube 26, 26M (PTR2)					
Extrapolated life (h)	2.0×10^5	1.1×10^5	7.5×10^4	5.0×10^4	3.0×10^4
Database life	1.3×10^6	8.7×10^5	4.8×10^5	2.8×10^5	1.7×10^5
Remaining life fraction	0.15	0.13	0.16	0.18	0.17
Tube 5 (PTR3)					
Extrapolated life (h)	3.8×10^5	2.1×10^5	1.3×10^5	8.0×10^4	5.0×10^4
Database life	8.5×10^5	5.0×10^5	3.1×10^5	2.0×10^5	1.2×10^5
Remaining life fraction	0.45	0.42	0.42	0.40	0.42

flux, (iii) start up / shut down frequency and (iv) operating trip frequency. Variables under evaluation are material selection, tube wall thickness and internal pressure. This procedure has also been employed to demonstrate which combination of parameters have been important to measure during inspection of tubes. These have been (i) creep strain at tube interior and exterior, (ii) tube wall thickness, (iii) early stages of creep damage as evidenced by void formation and growth, (iv) later stages of creep damage as evidenced by formation of fissures or linked voids and (v) cracking at tube interior or exterior surface. Authors have referred to that single parameter inspection e.g. tube diameter has low effectiveness than multi-parameter inspection [39].

Determination of service life by Jaske [40] include (i) modeling operating conditions, (ii) characterizing creep behavior, (iii) modeling evolution of creep damage in tubes, (iv) accounting for metallurgical aging, (v) influence of material defects and (vi) evaluation of effects from high-temperature corrosion [40].

Lu [41] has predicted remnant life of reformer tubes made of HK40 alloys by method of regression analysis based on data of quantitative metallography and endurance tests. Evaluation has considered confidence level within 95% [41].

6 Infrared thermography and non-destructive tests

James [42] has described inspection of steam reformers and catalyst tubes with infrared thermography. This technique of inspection of reformer temperature has been online and under fired condition. Proper and regular thermographic inspection has been suggested to increase efficiency from planned shutdown and rejuvenation. Furnace is usually a large refractory lined box with gas burners heating many catalyst filled tubes that carry natural gas (feed) and steam. Reformer fire box contains a single row of tubes or multiple rows. Inspection of overheating problems by infrared thermography has been described in response to (i) flame impingement, (ii) gas flow restriction, (iii) burner associated issues, (iv) external tube scaling, (v) after burning gas from burner or tube leaks, etc. [42].

7 Conclusions

Design and plant level inspection for safety causes is very important during reforming natural gas in fertilizer industries and petrochemicals. Deterioration of mechanical properties are mainly due to the following factors: (i) greater temperature and pressure involved during period of decoking, (ii) composition variation in natural gas, (iii) difference in coefficient of thermal expansion between steel tube and nickel catalyst, (iv) presence of blow holes and pin holes in centrifuged as-solidified tubes within inner wall to mid section of tube thickness which has been stipulated for removal by machining, (v) application of in-situ thermocouples or infrared radiation pyrometers to control temperature variation by on-line inspection. Temperature variation above 1223 K has been found to be most reaction rate limiting, provided mechanical damages e.g. effects on tube from shuttering of nickel catalyst or carbon deposition to reduce effective heat absorption tendency to form hot spot zones, have not been accounted for. Role of overheating by catalyst poisoning were studied with respect to different types of overheating, namely Tiger tailing, Hot bands and Giraffe Necking.

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