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Life Assessment of Corroded Superheater Tubes in a Powerplant Steam Generator

Chamaiporn Sudasna Na Ayudhya[1], Ruangdaj Tongsri[1], Nuchthana Poolthong[2], Nakorn Srisukhumbowornchai[2], Veera Loha[3], Panya Srichandr[2], and Nandh Thavarungkul[2]

[1] National Metal and Materials Technology Center, 114 Paholyothin, Klong 1, Klong Luang, Pathumthani, 12120, Thailand

[2] School of Energy and Materials and [3] Department of Chemical Engineering, King Mongkut University of Technology Thonburi, 91 Pracha U-Thit Road, Bangmod, Thungkru, Bangkok, 10140, Thailand

Tel: 66 2564 6500 Ext. 4706 Fax: 66 2564 6403 E-mail: chamaips@mtec.or.th

Abstract

Remaining life of superheater tubes from a powerplant steam generator was evaluated using a tube thickness as an input parameter. The tube thickness has been decreased as a result of high temperature corrosion. The assessment revealed that the tubes at different locations exhibited different remaining lives. The tubes with shortest remaining lives usually located in severe environment. Damage of the tubes caused by high-temperature corrosion was examined using standard materials characterization techniques and chemical analysis methods. Corrosion was obviously observed at outer surfaces of the tubes located in high-temperature zones of the steam generator. Chemical analysis using inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD) of tube scales revealed the presence of sodium and vanadium elements in the scales. These two elements are important species causing oil-ash corrosion. Microstructural observation at the outer surfaces of the corroded tubes revealed the evidence of carbide coarsening and corrosion at grain boundaries. Using energy dispersive spectroscopy (EDS), depletion of chromium in the grains near the corroded surfaces was observed. The possible mechanism of high-temperature corrosion of the superheater tubes has been proposed in this report.

1. Introduction

There are several methods for generating electric power. Power generation using boiler-turbine generators or steam turbine generators is one of the most popular methods. In a steam turbine generator of a thermal powerplant, high temperature and high pressure steam is employed to turn a turbine, which in turn drives an electricity generator. Steam generators are used in both fossil- and nuclear-fuel electric-generating powerplants. Thus they represent by far the greatest energy source for powerplants in the world today [1]. A steam generator is a complex combination of waterwall, superheater, reheater, and economizer tubes, and air preheater.

In a fossil fired steam generator, rows of tubes or coils are heated by a fireball with temperatures of 530-1000 $^{\circ}$C. Exposure of tubes to high pressures, high temperatures, and flame contaminated with corrosive residues for a long period of time usually causes tube failures. Many failure modes associated with steam generator tubes have been reviewed in the literature [2-4].

Superheater tubes are usually located in the hottest zone of a steam generator. The steam with highest pressure and highest temperature is carried inside the tubes, which are exposed to heat generated by combustion of fuel in air. In general, the fuel used in combustion is relatively cheap and frequently contaminated with traces of corrosive impurities. Therefore, the superheater tubes are most susceptible to high-temperature creep and corrosion failures. Although the materials of superheater tubes are superior to those of other tubes, failures of the superheater tubes occur most frequently. To prevent tube failures, which cause temporary shut down of the powerplant, assessment of the tubes is always conducted according to powerplant preventive maintenance practices. Investigation on creep of the tubes is difficult, time consuming and costly. Assessment of tube remaining life, using information about changes of tube thickness, can be easily performed. The decreasing tube thickness, indicating the corrosion rate, is related to remaining life of the tube [5]. In this study, values of remaining life of tertiary superheater tubes at different positions were estimated. Evidence of high-temperature corrosion of the superheater tubes from a steam generator was also investigated.

2. Experimental

2.1 Positions Investigated

The tube investigated were taken from different sites of tertiary superheater coils at upper rows (position A, B, and C) and lower rows (position D and E) as shown in Fig. 1. Life assessment were estimated at the outer surfaces of the tubes. There was variation of thickness in an individual tube, thus wall thicknesses were usually observed at the positions marked by a, b, and c (Fig.1).

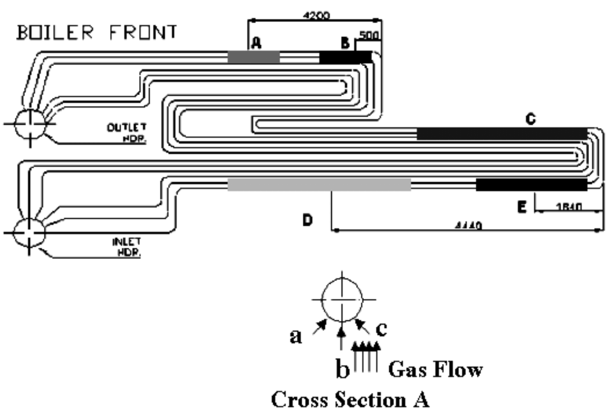

Fig. 1 Positions where the tubes were examined.

2.2 Method

Data including tube thickness, operating conditions, and tube materials were collected. The values of tube thickness, measured by using ultrasonic method, were used for calculating the corrosion rates, which were then used for estimating of the tube remaining life [5]. Microstructural observation was carried out using optical and scanning electron microscopy (SEM). Chemical analysis, using energy dispersive spectrometry (EDS), was performed near the outer surface of the corroded tube. Phase identification of the scales, taken from severely corroded tubes, was performed using X-ray diffraction (XRD). Quantitative chemical analysis of the scales is carried out using inductively coupled plasma-mass spectrometry (ICP-MS).

3. Results and discussion

3.1 Operating Condition and History of the Powerplant

The powerplant investigated in this study 15 years old and had been operated for 147,000 hours or 16 years old. It could produce power with maximum capacity of 550 megawatt (MW). The superheater tubes in this powerplant were consisted of austenitic stainless steel (SA213 TP347H). The composition of the tube materials is shown in Table 1. The tubes were used under conditions of internal pressure of 17 MPa, steam temperature of 520 ^{O}C, and flame temperature of 990-1500 ^{O}C.

Table 1 Composition of SA213 TP347H

Element	Content
C	0.04 - 0.1
Si	0.75 Max
Mn	2.0 Max
P	0.04 Max
S	0.03 Max
Ni	9 - 13
Cr	17 - 20
Mo	-
Others	Nb + Ta

3.2 Life Assessment of the Superheater Tubes

3.2.1 Tube Thickness

The tube thickness has been measured every two-years. Tube thickness data of several superheater tubes in 1985-2001 had been collected. It was found that the thickness of most tubes decreased with increasing time. Rust or scales were obviously observed on the tube surfaces. There was variation of thickness in an individual tube, for example, thinner walls were usually observed at the positions either marked by “a” or “c” rather than at the position marked by “b”, as shown in Fig. 1.

3.2.2 Remaining Life of the Superheater Tubes

The values of estimated remaining life (ERL) of the superheater tubes varied with positions on the tube. The positions A, B, C, D, and E showed ERL values of 41, 22, 15, 6, and 5 years, respectively. The tube at lower rows (positions D and E) showed little ERL as shown in Fig. 5 and 6 (Table 2). The tubes at upper rows (positions A, B and C) exhibited longer ERL as shown in Fig. 2, 3, and 4 and table 2. This is attributed to the fact that the tubes at positions D and E are exposed to severe environment (higher temperature and higher content of corrosive combustion residues). Combination effect of temperature and content of corrosive combustion residues in the deposit on the tube surfaces results in high-temperature corrosion, known as oil-ash corrosion, which in turn causes tube thickness reduction. The content of corrosive combustion residues deposited on the tube surfaces is a prime factor for corrosion rate determination. It is possibly that most corrosive combustion species in the flue are already deposited on the tube surfaces at lower rows. Thus less corrosive residues are deposited on the tube surfaces at upper rows. In order to confirm that damage of the tubes was caused by high temperature corrosion, investigation on the corroded tubes and the scales was performed.

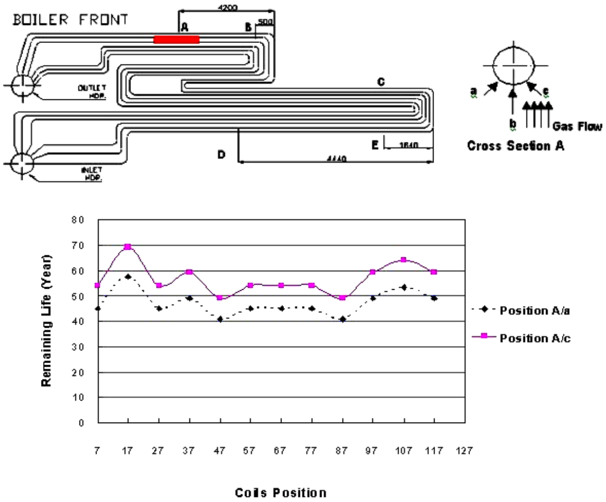

Fig. 2 Remaining life of the superheater tubes position A/a and A/c

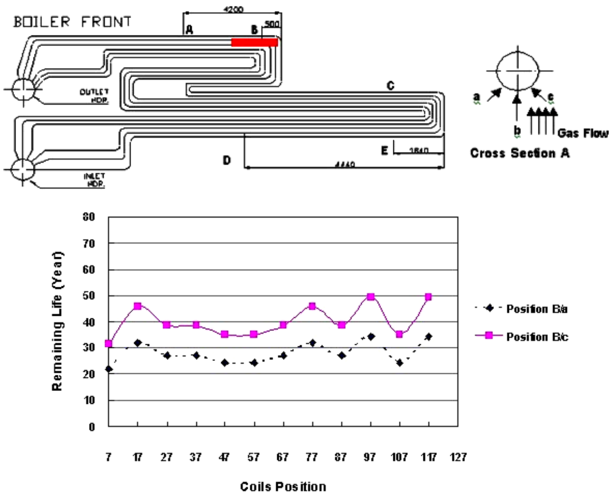

Fig. 3 Remaining life of the superheater tubes position B/a and B/c

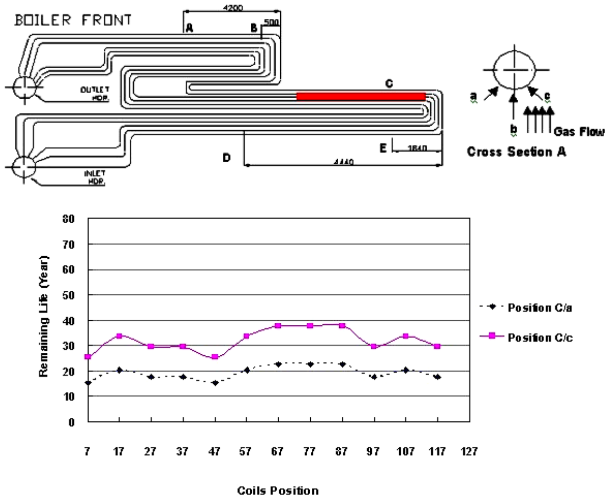

Fig. 4 Remaining life of the superheater tubes position C/a and C/c

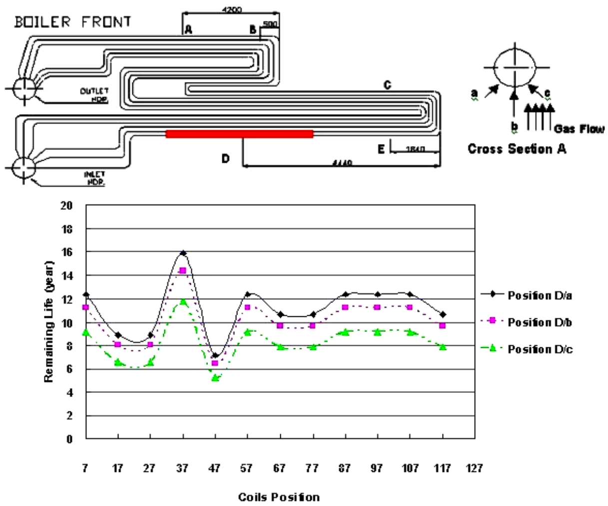

Fig. 5 Remaining life of the superheater tubes position D/a D/b and D/c

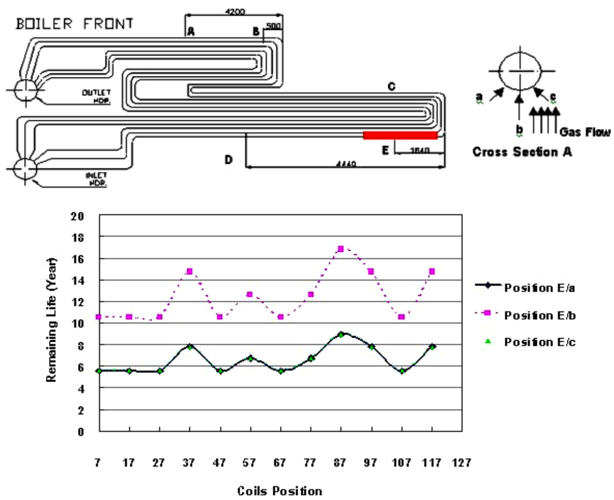

Fig. 6 Remaining life of the superheater tubes position E/a E/b and E/c

Table 2 Estimated remaining life of the superheater tubes

Tube Position	Estimated Remaining Life (year)		Critical Remaining Life (year)
	Range	Minimum	
A/a	41-60	41	41
A/c	48-70	48	
B/a	22-35	22	22
B/c	31-50	31	
C/a	15-23	15	15
C/c	25-38	25	
D/a	8-15	8	6
D/b	6-15	6	
D/c	6-12	6	
E/a	5-9	5	5
E/b	10-16	10	
E/c	5-9	5	

3.3 Analysis of the Scale from Superheater Tube Outer Surfaces

3.3.1 Analysis of the Scale using XRD

XRD patterns of the scales taken from severely corroded superheater tubes Nos. 20T and 80B are shown in Figs. 7 and 8, respectively. Interpretation of the patterns suggested that Na_2SO_4 compound was present in the scales from both tubes. During combustion of low-grade fuel oils, vapors of vanadium oxide (V_2O_5) and alkali metal sulfates (for, example Na_2SO_4 or $Na_2O{\cdot}SO_3$) are formed. These vapors, combine with other ash constituents, then deposit onto cooler component surfaces. Reactions between vanadium and sodium compounds result in formation of low-melting complex vanadates, which flux the protective oxide scale from the metal surfaces, accelerated corrosion attack [3].

The presence of Na_2SO_4 compound may confirms that corrosion on the superheater tube surfaces involves with molten salts. The low-melting point eutectic V_2O_5-Na_2SO_4 salts of may be formed with greater molar ratio than that V_2O_5:Na_2SO_4, so that some non-reacted Na_2SO_4 compound remains in the scales.

3.3.2 Analysis of Scales using ICP-MS

Analyses of the scales using ICP-MS revealed the presence of Na and V (Table 3). It was assumed that all vanadium atoms were present in the form of V_2O_5 compound whereas all sodium atoms were either in the forms of Na_2O or Na_2SO_4. The ratio of vanadium oxide (V_2O_5) to sodium oxide (Na_2O) in the scale from both tubes (Table 3) is less than 5:1. This may indicate that the complex salt of sodium-vanadium oxide in the scale is not severely corrosive.

Table 3 Chemical analyses of scales using ICP-MS

Tube	Concentration of Element (ppm)		Mole Ratio of V_2O_5:Na_2O	Mole Ratio of V_2O_5:Na_2SO_4
	Na	V		
20T	2.108	0.253	0.05:1	0.05:1
80B	0.128	0.163	0.57:1	0.57:1

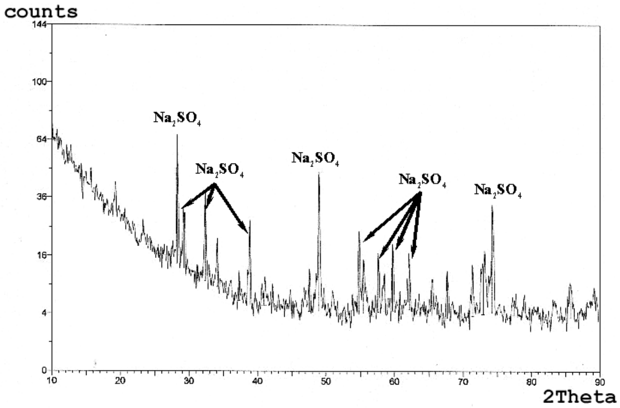

Fig. 7 XRD Pattern of a tertiary superheater tube No. 20T (Phase identification using JCPDS 74-1738 card for Na_2SO_4).

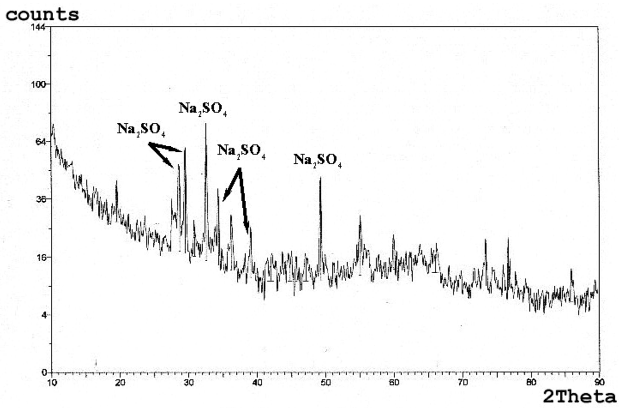

Fig. 8 XRD Pattern of a tertiary superheater tube No. 80B (Phase identification using JCPDS 74-1738 card for Na_2SO_4).

3.4 Chemical Analysis of the Corroded Superheater Tubes using EDS

Chemical analyses using EDS, performed on the scale (Fig. 9), revealed that high chromium contents were observed in the scale inner layers Nos. 2 and 3. Depletion of chromium in matrix (region No. 1) near the scale inner layers was observed. The scale outer layers Nos. 4 and 5 and the attacked surfaces of the scale (regions Nos. 6 and 7) showed low contents of chromium but high contents of vanadium. Porosity in the scales was also observed.

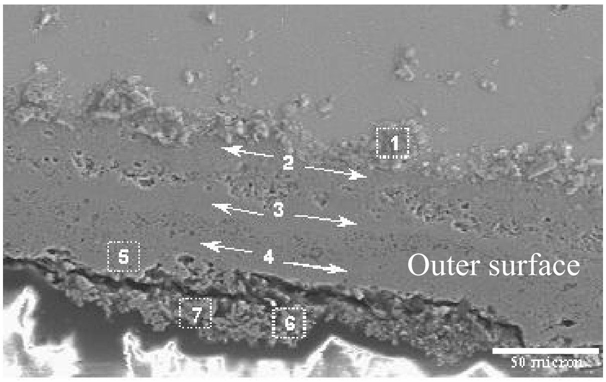

Fig. 9 Regions for chemical analyses of the tube No. 80B using EDS.

This indicates that the scale inner layers may still have capability to protect the metal matrix from corrosion attack whereas the scale outer layers loss some chromium due to corrosion attack. High vanadium contents in the outer layers and the attacked surfaces of the scales may indicate deposition of complex vanadates. Fluxing of protective chromium oxide film by low melting point vanadates results on loss of scale mass.

3.5 Mechanism for corrosion attack at tube Surfaces

From the series of micrographs (Fig. 10) taken from different superheater tubes at different locations investigated, possible mechanism for high-temperature corrosion may be purposed as follows. In new superheater tubes, microstructures exhibit fine austenitic grains with few precipitates (Fig. 10(a)). After the tubes have been in service at high temperatures and under high pressures for a certain time, grain growth and precipitation of fine carbide particles either in grains or at grain boundaries will occur (Fig. 10(b)). Exposure to elevated temperatures and high pressures for longer times will cause abundant carbide precipitation at grain boundaries (Fig. 10(c)). Coarsening of carbide particles will be assisted thermally by diffusion of carbon and chromium, along grain boundaries or through the matrix of the grain, to the growing particles (Fig. 10(d)).

Chromium depletion in grains may due to dissolution of chromium carbide particles in the matrix and diffusion of chromium and carbon atoms to grain boundaries. Coarsening of chromium carbide particles at grain boundaries will reduce corrosion resistance of the grain boundaries themselves and/or of the matrix adjacent to grain boundaries. When the protective chromium oxide film is destroyed, corrosion attack will occur according to two modes. In the first mode, the metal matrix is fluxed by molten salts causing two wastage plats at about 2-o'clock and 10-o'clock positions (3). In the second mode, the broken chromium oxide film cannot be repaired thus oxidation of iron along grain boundaries are accelerate (Fig. 10(e)).

The possible mechanism for elevated-temperature corrosion of the superheater tubes is purposed as follows:

Fine austenitic grains $\rightarrow$ Grain growth and carbide precipitation $\rightarrow$ Abundant precipitation of carbide at grain boundaries $\rightarrow$ Dissolution of chromium carbide particles in the grains $\rightarrow$ Diffusion of chromium and carbon atoms to grain boundaries $\rightarrow$ Coarsening of carbide at grain boundaries $\rightarrow$ Depletion of chromium at grain boundaries and/or in the matrix adjacent to grain boundaries $\rightarrow$ Fluxing of protective chromium oxide films $\rightarrow$ Corrosion attack by molten salts and/or oxidation of iron at grain boundaries

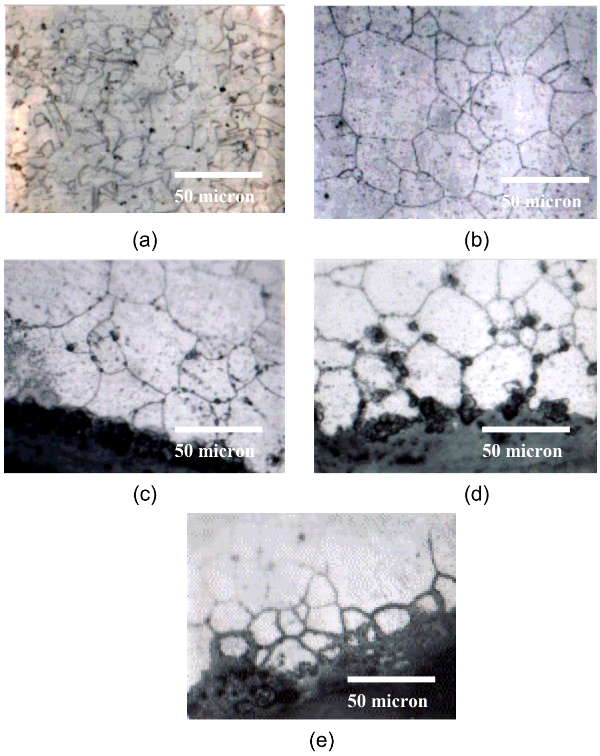

Fig. 10 Series of microstructural changes according to the mechanism for high-temperature corrosion of the superheater tubes (x500).

4. Conclusions

Life assessment of the tertiary superheater tubes in a powerplant steam generator were conducted using tube thickness as a parameter for calculating the tube remaining life. The tubes at different positions showed different remaining life values. The variation in these values is due to different levels of tube damage caused by high-temperature corrosion. Corrosion was obviously observed at the tube outer surfaces locating in high-temperature zones of the steam generator. Chemical analysis using ICP-MS and phase identification using XRD of scales revealed the presence of sodium and vanadium elements in the scales. These two elements are important species causing oil-ash corrosion. Microstructural observation at the outer surfaces of the corroded tubes revealed the evidence of precipitate coarsening and corrosion at grain boundaries. The mechanism for corrosion attack at tube surfaces involves with grain growth, carbide precipitation, carbide dissolution in the matrix, diffusion of chromium and carbon atoms to grain boundaries, chromium depletion in the matrix, carbide coarsening at grain boundaries, fluxing of protective chromium oxide films, and corrosion attack by molten salts and/or oxidation of iron at grain boundaries.

5. Acknowledgments

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