

GUIDE TO GRADE 91 USE TEMPERATURE LIMITS DUE TO STEAM OXIDATION AND EXFOLIATION

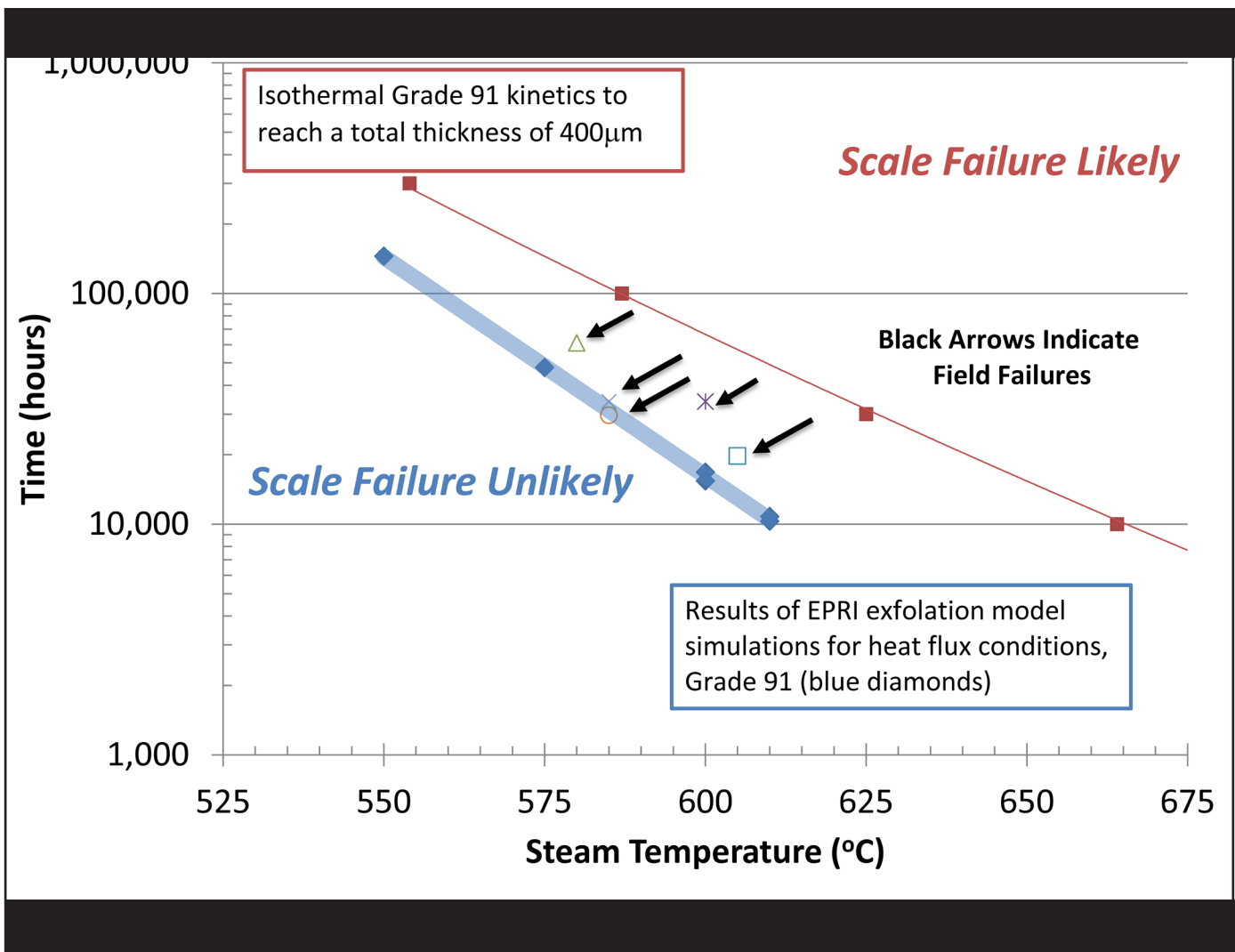


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Introduction

The ASME B&PV Code Section I allows ferritic-martensitic Grade 91 (Gr 91) steel to be used at metal temperatures up to 649°C (1200°F) [1]. In heat-flux components, this limit often refers to the tube mid-wall temperature. Many boiler OEMs and operators consider this temperature limit not conservative enough and therefore have further reduced it in boiler design. The reduced temperature limit for Gr 91 varies noticeably among the boiler OEMs, with the self-imposed value typically at or above 607°C (1125°F). This temperature limit is generally based only on the consideration of microstructural stability and creep strength of Gr 91, without taking into account materials losses from steam oxidation and potential collateral damage from excessive scale exfoliation. **This white paper focuses the temperature limits for Gr 91 on steam oxidation and exfoliation only. Other factors considered in design, procurement, and component fabrication, such as metallurgical risk, weld strength reduction factors (WSRFs), cyclic service (fatigue), and other design features are not addressed in this document, as they are the subject of many other EPRI research activities and reports.**

Steam oxidation of ferritic and austenitic steels typically leads to the formation of a multi-layered (duplex) scale morphology consisting of an inner spinel layer and outer magnetite layer [2–6]. Initially, the two layers in a duplex scale are of about equal thickness; however, a laminated structure forms subsequently in the inner layer adjacent to the outer layer [3, 7]. For Gr 91, the lamination in the inner

layer appears to be a series of pairs of dark wavy bands parallel to the alloy surface. The dark-appearing bands consist of fine-grained magnetite containing Cr, whereas the lighter-appearing bands are essentially fine-grained magnetite containing no Cr. In each pair, the Cr-rich band is always nearest to the scale-alloy interface, suggesting that these bands originate at this interface. The thickness of the laminations appears to decrease with increasing distance from the inner-layer/alloy interface. Eventually, the banded structure occupies the entire thickness of the inner layer.

The enrichment of Cr in the banded inner layer on Gr 91 helps reduce the growth rates of both the inner and outer layers, thus allowing the surface of the outer (magnetite) layer in direct contact with steam to further oxidize to hematite. Consequently, the conversion of magnetite to hematite in the outer layer promotes the formation of Kirkendall voids at the interface of the inner and outer layers, making this plane increasingly weaker over time and prone to delamination. Eventually, exfoliation of large sections of the outer layer (magnetite and hematite) can take place along the outer and inner layer interface during a high-stress event, such as unit shutdown and startup. Modeling and service experience have both confirmed that under normal operational conditions, scale failure occurs upon start-up in Gr 91 components. Figure 1 shows cross-sectional optical micrographs of partial exfoliation of the outer oxide layer from the internal diameter (ID) surface of a Gr 91 superheater tube. The exfoliates are typically present in the components as large oxide flakes (Figure 1b) that are relatively heavy and often cannot be easily removed by the flowing steam.

In addition to wall thinning from oxidation, a thick oxide scale formed on the tube ID surface and/or blistering of the outer layer can function as an insulator to impede heat transfer, resulting in elevated metal temperatures locally, as shown in Figure 1(b). A higher metal temperature can have several serious consequences: an increase in scale growth due to oxidation kinetics that vary exponentially with temperature not only leads to accelerated tube wall thinning but, together with reduction in alloy strength, also accelerates creep damage. Furthermore, as the scale thickens, the thermal gradient across the tube wall increases, thus further increasing the metal temperature. When sufficient oxide has exfoliated following a thermal-cycling event, steam flow can be impeded due to pluggage in the bottom bend of superheater and reheater pendants, as indicated in the radiograph shown in Figure 2(a), leading to catastrophic failures of the components from short-term overheating. Entrainment of exfoliated scale in the steam flow can lead to erosion damage in downstream components, such as turbines, stop valves and drain lines, as shown in Figure 2(b).

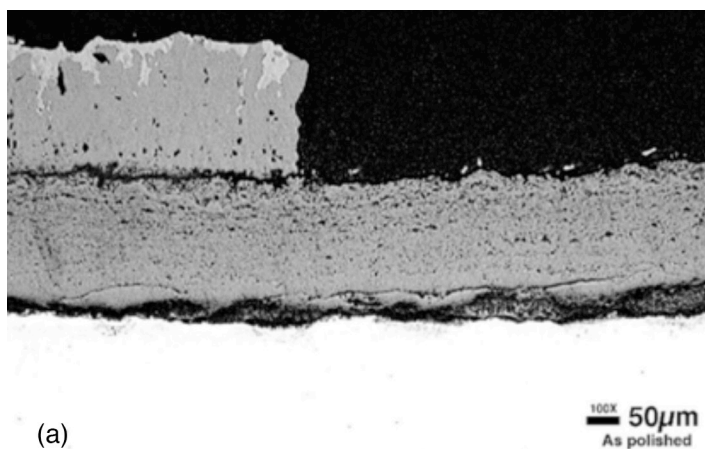


Figure 1 – Cross-sectional optical micrograph showing (a) partial exfoliation of the outer scale from the ID surface of a Gr 91 superheater tube and (b) scale lifting (or blistering) that can lead to local tube overheating due to a thermal insulating effect [3].

As a result of these issues, the impact of steam and metal temperatures on the performance of boiler components must be fully considered in boiler design. Because the current temperature limit of 649°C (1200°F) allowed by ASME B&PV Code Section I for Gr 91 is based solely on the consideration of microstructural stability and creep strength, a careful review of additional impact from steam

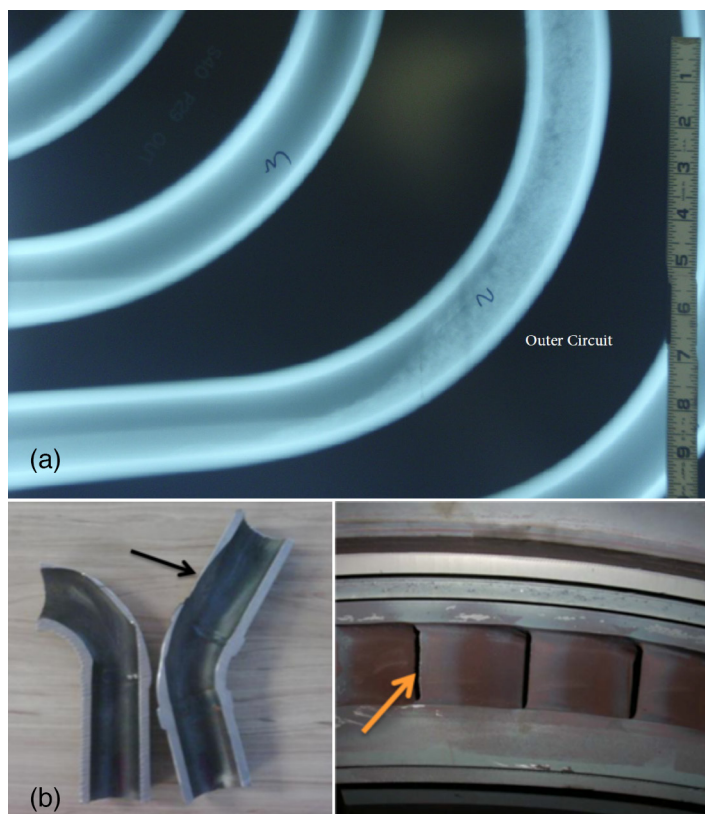


Figure 2 – Exfoliation of oxide scale from tube inner diameter surfaces leads to (a) pluggage in the lower tube bend of a superheater pendant and (b) erosion damages in the drain lines and steam turbine blades.

oxidation on the tube life is imperative. Such a review has been performed by EPRI and presented here to provide recommended temperature limits for Gr 91 steel on the basis of a well-engineered review of a decade of research regarding steam oxidation.

Needs for Reduction of Gr 91 Temperature Limit

Many utility boilers have experienced premature failures in Gr 91 components operated below the ASME Section I allowable temperature limit of 649°C. In many cases, steam oxidation was found to be a contributing or primary factor for premature failures in superheater and reheater tubing. Additional failures could have been linked to steam oxidation and exfoliation if quality tube samples had been obtained and adequate failure analyses performed. Most of the scale failures experienced with Gr 91 were in heat-transferring components, such as superheater and reheater pendants, in which tubes failed

catastrophically from short-term overheating due to excessive oxide exfoliation from the tube ID surfaces [3, 8–11]. Partial or complete blockage of a tube by exfoliated oxide scale, as shown in Figure 2(a), can impede the steam flow in a tube and cause tube rupture from overheating at locations either upstream or downstream of the steam circuit. In addition, erosion damage has been identified in steam turbines, stop valves, and drain lines due to exfoliated oxide, leading to unplanned outages and increased maintenance cost. The concern that such premature failures are associated with Gr 91 components typically operated within the ASME allowable temperature limit has been addressed by EPRI and other research organizations in many relevant studies, workshops, and publications [3, 8, 12–27]. However, despite these efforts, boiler Original Equipment Manufacturers (OEMs) continue to offer Gr 91 for applications at temperatures exceeding 600°C, with little consideration to the effect of steam oxidation and scale exfoliation. Therefore, stakeholders in the power generation industry need a consensus temperature limit for Gr 91 to ensure safe and reliable operation of power plant components fabricated from Gr 91 steel.

Reference Temperatures for Prediction of Scale Growth

The growth rate of oxide scale in high-temperature steam increases exponentially with increasing temperature. Because of the extreme sensitivity of the rate of oxide growth to temperature, the actual metal temperature at the ID surface of a given location and the thermal gradient through the scale thickness should be used to calculate the oxide growth kinetics. In practice, these temperatures cannot be measured directly. In the case of non-heat flux components, the metal and scale temperatures are reasonably assumed to be the same as the steam temperatures. However, the same assumption cannot be made for heat-absorption surfaces where a steep temperature gradient can exist across the pressure boundary.

To further complicate the oxide growth calculations, the metal and steam temperatures vary not only along a given steam circuit but also differ considerably from circuit to circuit due to temperature imbalance in boilers. To estimate the steam and metal temperatures for the purposes of boiler design and performance calculation, OEMs have developed proprietary software tools based on finite element analysis, computational fluid dynamics, and total heat balance. The tools can typically be used to generate temperature information at key locations of interest, such as steam, ID, mid-wall, and OD temperatures of various tube rows. Due to the complexity of boiler design, the predicted local temperatures can be somewhat different among boiler OEMs,

even for boiler components of similar configurations. In general, such differences in temperatures would not affect the boiler performance calculations noticeably. However, a small temperature variation can affect the results of scale growth kinetics significantly, especially over a longer period of boiler operation. Furthermore, changing operational conditions (fuel switching, low-load operation, boiler cycling, slagging and de-slagging, etc.) are generally not all considered by these tools in the design phase. Therefore, the use of local steam and metal temperatures derived from the OEM tools is not necessarily risk free for scale growth calculations.

While reliable temperature information is not easily attainable for oxide growth calculations, an alternative approach is perhaps to simply use the main steam temperature leaving the final superheater of a boiler. This temperature represents the normalized conditions of the oxide growth, qualitatively, throughout a boiler, and can be easily measured and monitored by power plant operators. By incorporating the boiler performance data and tube failure history, the main steam temperature may be used to set a temperature limit for Gr 91 in boilers. In other words, instead of setting a temperature limit based on local metal temperatures, it is proposed that the limit is correlated to the maximum main steam temperature under normal boiler operating conditions. A model analysis based on this approach has been performed and combined with experience to determine the temperature limit for Gr 91, and the results are presented in this document.

Calculations of Oxide Scale Growth Kinetics for Gr 91 (Modeling Approach to Inform Engineering Decision Making)

EPRI's Fossil Materials and Repair Program (Program 87) has investigated the steam oxidation and scale exfoliation of Gr 91 extensively, and a large amount of information has been documented in various publications and EPRI reports [3, 7–17, 19, 24]. In addition, a computational model on oxidation and exfoliation has been developed, capable of predicting the time to scale failures for Gr 91 as well as several other superheater and reheater alloys [28–30]. This knowledge and model have been applied in the current analyses of oxide growth kinetics.

The oxide growth kinetics of Gr 91 in high-temperature steam are assumed to follow a parabolic rate law, which can be described in Equation 1:

$$d_{sp}^2 = 2Ae^{Q/(RT_{met-sp})}t \text{ and } d_{mag}^2 = 2Ae^{Q/(RT_{mag})}t \quad \text{Equation 1}$$

in which d is the oxide thickness for the respective spinel and magnetite layers, t exposure time in hours, $A=2.5 \times 10^{11} \mu\text{m}^2/\text{hour}$ (the Arrhenius constant), $Q=199 \text{ kJ/mole}$ (the activation energy for the rate-controlling process), and R the Universal Gas Constant. The values of A , Q and R are the same for the growth of both oxide layers [7]. The oxide growth temperatures for the spinel and magnetite layers are represented by the variables of $T_{\text{met-sp}}$ and $T_{\text{mag-st}}$, respectively. A typical superheater fabricated from Gr 91 with a tube dimension of 1.75" OD x 0.34" wall thickness (44.45 mm OD x 8.64 mm wall) is used here as an example for the calculations. It is assumed in the model that the outer magnetite layer grows outward from the alloy (i.e., new oxide forms at the scale-steam interface), and the inner spinel layer grows inward (i.e., new oxide is formed at the scale-metal interface).

Consequently, the temperatures that govern the growth of these layers would be those at the magnetite-steam and the metal-spinel interfaces, respectively [3, 7]. For non-heat transferring components, the temperatures of $T_{\text{met-sp}}$ and $T_{\text{mag-st}}$ are the same as that of the steam, thus remaining constant with time in the calculations. However, for heat-flux applications, such as superheater and reheater pendants, these temperatures are determined by the thermal gradient existing from the fireside (OD) surface of the tube to the steam side. Since this temperature gradient increases with time due to the growth of steam-side scale, the value of $T_{\text{met-sp}}$ at the metal-spinel interface also increases with time (faster than the $T_{\text{mag-st}}$ at the magnetite-steam interface). Therefore, the change of growth temperatures for spinel and magnetite with time would result in a change in the ratio of the calculated scale thicknesses.

To illustrate the effects of various parameters on steam oxidation and exfoliation, a number of simulations were performed representing ranges of average oxidation behaviors in boiler tubing. Clearly, boiler components differ in tube diameters, flow rates, specific locations in boilers, etc. Therefore, the results of the simulations may deviate from the actual experiences. For heat-transferring components, two values of heat fluxes at 10,000 and 15,000 BTU/sq.ft-hr (31,500 and 47,500 W/m²) were assumed in these calculations, which are within the range of typical heat fluxes in boiler superheaters. Both the gas-side and steam-side heat transfer coefficients were held constant at 100 and 3,000 W/m²K, respectively. Three steam temperatures were investigated, i.e., 550, 600, and 620°C (1022, 1112, and 1148°F), and the corresponding gas temperatures were allowed to vary to attain the desired heat fluxes, as shown in Table 1.

Table 1 – Flue gas temperature used to attain the targeted initial heat fluxes

Run	Steam Temperature [°C]	Initial Heat Flux [W/m ²]	Gas Temperature [°C]
1a	550	31,500	888
1b	550	47,500	1,065
2a	600	31,500	944
2b	600	47,500	1,114
3a	620	31,500	961.5
3b	620	47,500	1,135

The effect of heat fluxes on the temperatures of tube OD and metal-spinel interface as a function of the scale thickness is illustrated in Figure 3 at the steam temperatures of 550 and 600°C. Both the temperatures at the tube OD and metal-spinel interface increase steadily with scale thickness (or time). For Gr 91, a critical total scale thickness of 250–400 μm is typically required for the magnetite layer to generate sufficient strain and cause delamination and/or exfoliation. Using the condition of 31,500 W/m² heat flux and 550°C steam in Figure 3(a) as an example, an increase in the tube OD temperature from approximately 578 to 589°C is expected during the growth of oxide scale during a 100,000-hour exposure, while the temperature at the metal-spinel interface ($T_{\text{met-sp}}$) that governs the inner-oxide growth increases from 568 to 580°C on a Gr 91 tube during the same period of time. In contrast, the temperature at the magnetite-steam interface ($T_{\text{mag-st}}$) that controls the outer-layer growth remains relatively constant compared to that of the steam.

In addition to growth temperature rise, the average tube temperature also increases. To illustrate the effects of tube temperature and loss of load-carrying capacity due to oxide scale growth, Table 2 shows the result of a series of simulations on Gr 91 tube life using the EPRI Gr 91 Life Calculator [35]. At the steam temperature of 600°C, yearly temperature rises of 2°C and 4°C in Gr 91 with and without stress increases of 0.5 and 1.0% were calculated. The table compares the results in terms of reduction in creep life, which shows that, while a 2°C increase per year has a modest effect on creep life consumption, a 4°C rise or any temperature rise combined with additional stress increase can significantly impact on the long-term creep life of Gr 91. If these effects are not accounted for in design, premature creep failures will likely occur.

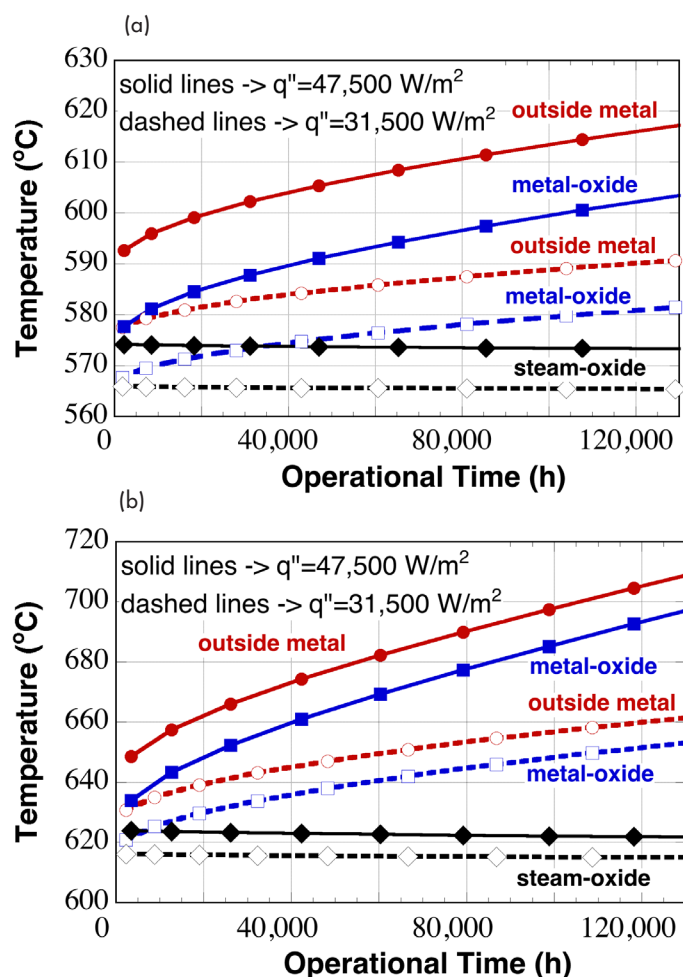


Figure 3 – Change of temperatures at tube OD, metal-spinel interface (T_{met-sp}), magnetite-steam interface (T_{mag-st}) for Gr 91 at the steam temperature (T_{st}) of (a) 550°C and (b) 600°C and heat fluxes of 31,500 and 47,500 W/m² (data with diamond symbols indicate the isothermal condition, i.e., no thermal gradient through the tube thickness).

Table 2 – Reduction in Creep Life for Gr 91 Steel (Simulations using EPRI Life Calculator at the steam temperature of 600°C)

Calculations for 10 years	
2°C Increase/year	2–12%
4°C Increase/year	27–32%
2°C+0.5%Stress Increase/year	12–25%
4°C+1%Stress Increase/year	64–99%

Figure 4 shows the results of total oxide thicknesses calculated for Gr 91 under the isothermal and heat-flux conditions as a function of time at the three steam temperatures investigated. The calculations did not take into account for any thermal-cycling events that would result in delamination or exfoliation of the outer magnetite layer. The results in Figure 4 indicate that the oxide growth rates are significantly higher for Gr 91 under the heat-flux conditions than those of isothermal. The steam temperature also plays an important role in the oxide growth kinetics for Gr 91. While the exposure time to scale failure due to oxide exfoliation of Gr 91 in 550°C steam may be acceptable for the operation of some plants, the oxide scale is expected to reach the critical thickness quickly in steam at 600 and 620°C (even using the ‘most optimistic’ upper bound scenario of 400 μ m), regardless of the presence of heat fluxes or not. Furthermore, the growth rate of oxide formed on Gr 91 under all heat-flux conditions exhibits an effectively linear relationship with time shortly after the initial transient period due to increasing growth temperature with scale thickness. Oxidation growth behavior following a linear rate law are highly undesirable compared to a parabolic behavior.

The impact of steam temperature on oxidation is further demonstrated in Figure 5 where the total oxide thicknesses formed on Gr 91 are plotted against operating time. The heat fluxes assumed for Figure 5 (a and b) are 31,500 and 47,500 W/m², respectively. For each steam temperature, the solid symbols represent the oxide thicknesses calculated under an isothermal condition, whereas the open symbols are for the heat-flux conditions. The results clearly indicate that the scale growth of Gr 91 is a strong function of both steam temperature and heat flux. The results also show that the scale thickness of Gr 91 formed under the heat-flux conditions is greater than that of the corresponding isothermal condition. Furthermore, the differences in total scale thickness for Gr 91 between the heat-flux and isothermal conditions increase with increasing operating time. Conversely, at a given steam temperature, the differences in oxide growth kinetics increase with increasing heat flux. Assuming 400 μ m is the critical total thickness for the outer oxide layer formed on Gr 91 to exfoliate, the results show that a steam temperature of 600°C is approaching the use limit for isothermal conditions after 100,000 hours but is clearly too high for heat-flux conditions. These plots also show that a higher heat flux further reduces the time to scale failure quite significantly due to the thermal insulating effect and a temperature gradient through the tube wall.

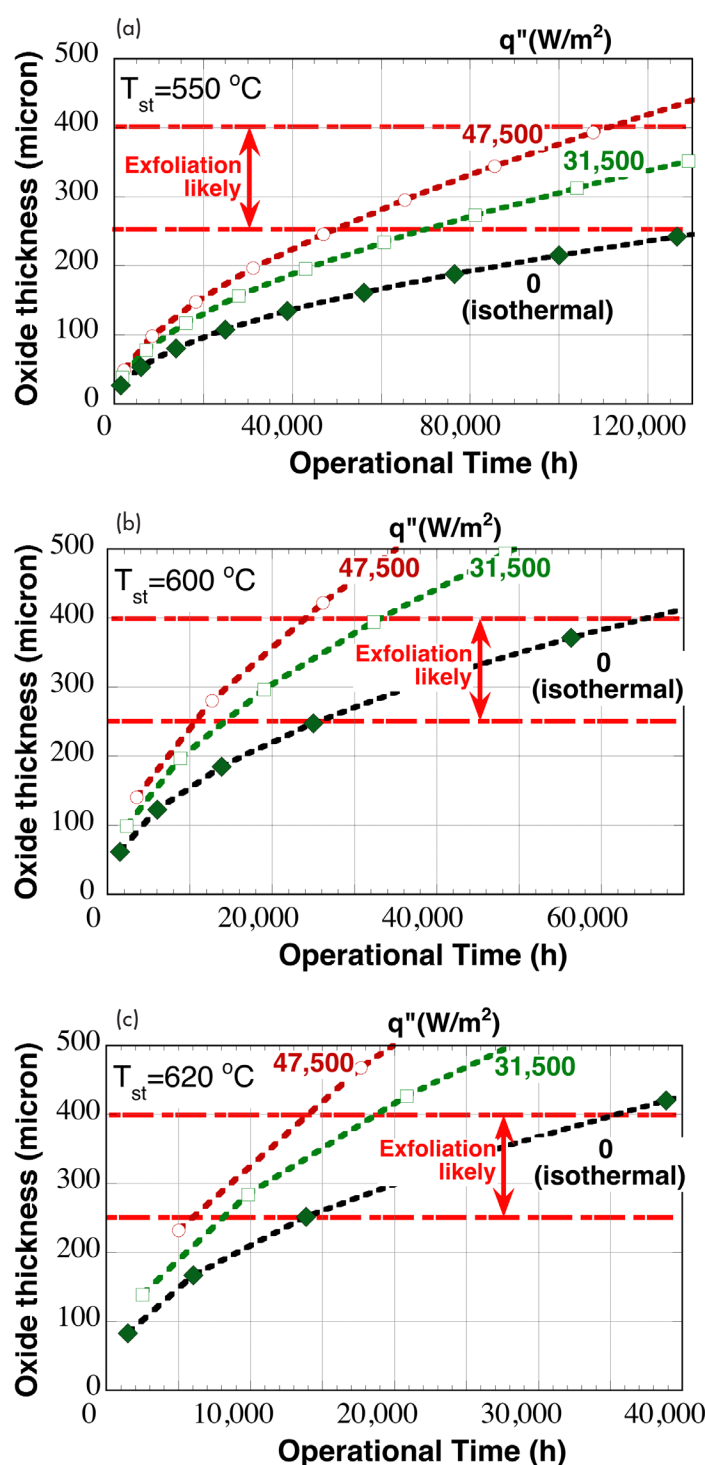


Figure 4 – Total scale thickness on Gr 91 for steam temperatures, T_{st} , of: (a) 550°C, (b) 600°C, and (c) 620°C at heat fluxes of 31,500 and 47,500 W/m² (data with diamond symbols indicate the isothermal condition, i.e., no thermal gradient through the tube thickness).

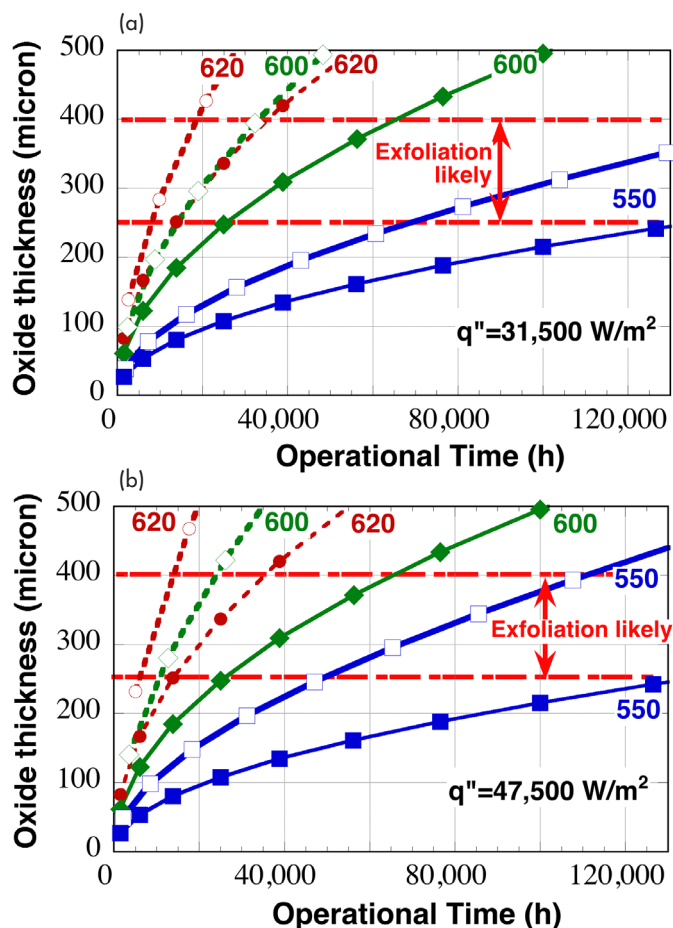


Figure 5 – Comparison of total scale thickness on Gr 91 with and without heat flux at (a) 31,500 W/m² and (b) 47,500 W/m² for steam temperatures of: 550, 600, and 620°C. Solid symbols represent oxide thickness variation under isothermal conditions, and open symbols represent heat-flux conditions.

Results of the above exfoliation analyses provide a clear argument for the need to reduce the use temperature limit for Gr 91 from what ASME B&PV Code Section I allows. Separate limits corresponding to the isothermal and heat-flux conditions should also be differentiated.

Industry Experience with Scale Failures of Gr 91

EPRI has been provided information and tube samples from more than 20 cases of failures associated with short-term and long-term overheating in Gr 91 components, which were attributed to steam oxidation and scale exfoliation. Most of the scale failures have been documented in several EPRI publications [8, 10, 11, 16, 33] as well

Table 3 – Examples of Gr. 91 Oxide Exfoliation Challenges (partial list)

Type of Unit	Estimated Steam Temperature (Average/Tube)	Estimated Time (hours)	Damage and Notes	Reference
Subcritical – Superheater	540°C/600°C	30,000–34,000	Excessive oxidation (350–700mm thick), severe thermal degradation, and creep damage observed (tubing replacements)	EPRI 1018151 [35]
Subcritical – Superheater	565°C/580°C	61,000	A long-term overhear creep (LTO-C) failure prompted a detailed life assessment of the superheater; assessment showed thermal insulating effect of thickening oxide would cause additional LTO-C failures before end of design life	EPRI 1019328 [8]
Supercritical – Superheater	582°C/605°C	19,720	5 short-term overhear failures after superheater failures from oxide exfoliation blocking bends (life management challenge leading to replacement with shot-peened Super 304H stainless steel)	[24]
HRSG – Superheater	577°C	25,000	Utility experienced significant exfoliation (no tube failures). During one shut-down 28kg of oxides were removed from the system; concerns over wall thinning, long-term tube life, and turbine erosion	[10]

as through EPRI-hosted workshops throughout the U.S., Europe and Asia [9, 24]. These failures were experienced in utility boilers around the world, typically operating with steam temperatures near or above 600°C for supercritical, ultra-supercritical and state-of-the-art HRSG operating parameters. Table 3 provides a brief description of a few of these observations. The experiences cover short-term overheating due to tube blockages from exfoliated oxides, long-term overheating due to insulating effect of the oxide and tube metal temperature rises, and excessive oxidation leading to wall loss and downstream damage.

Additionally, a recent study summarized the exfoliation experiences of Gr 91 in the superheaters of five Japanese power plants operating in the range of steam temperatures from 510 to 617°C for 72,500–168,000 hours [34]. The tube temperatures associated with the cases studied were estimated to be 571–609°C. Scenarios experienced are summarized in Figure 6, which include: (1) oxide exfoliation and accelerated creep life consumption due to high scale thicknesses, (2) oxide cracking and some exfoliation, and (3) the outer layer was still intact. The ‘better performing’ scenarios of (2) and (3) exhibited an inner oxide thickness of 200 µm or less (approximately 400 µm total thickness). Such results are reasonably consistent with the EPRI Oxidation and Exfoliation Model [28–30] that predicts a critical total scale thickness of 250–400 µm for the magnetite layer to begin failure or cracking. It should be mentioned that a portion of the inner oxide scale might have been lost in prior exfoliation events along with the outer oxide layer.

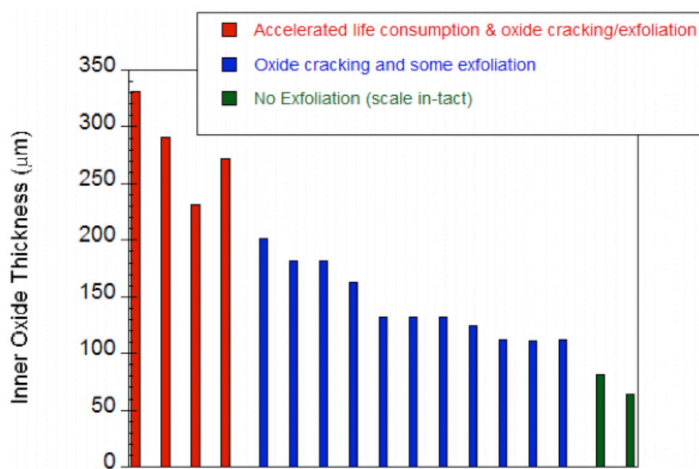


Figure 6 – Comparison of inner oxide scale thickness formed on Gr 91 in superheaters of five Japanese power plants operating at steam temperatures of 510–617°C for 72,500–168,000 hours. The data are segmented by oxide scale behavior and creep life consumption. At the highest inner oxide thickness, the tubes experienced oxide exfoliation and accelerated creep life consumption (red). At intermediate thicknesses, scale cracking and exfoliation was observed (blue). Below 100 µm inner thickness, no exfoliation or cracking was observed (green).

Comparison of Gr 91 Experience and Modeling

Based on recent industry experiences and EPRI's current knowledge in steam oxidation and scale exfoliation, plant data and modeling simulations are summarized in Figure 7 to illustrate the relationship between time-to-scale failure and the main steam temperature in utility boilers. The time-to-scale failure was calculated using the EPRI Oxidation and Exfoliation Model [28–30] based on the steam temperatures and heat-flux conditions of the specific applications considered. As mentioned, depending on the boiler operating parameters, a critical total scale thickness of 250–400 μm is required for the magnetite layer to fail and potentially exfoliate from the Gr 91 surface. A thickness of 400 μm was used in this plot for isothermal conditions. The red line in Figure 7 represents the time for the oxide layer to reach a critical total thickness of 400 μm on Gr 91 under isothermal conditions. Without heat flux, the metal and scale temperatures of the components are identical to the steam temperature. Examples of isothermal components include superheater headers, high-energy steam piping, and connection tubing. A design life of 100,000 hours is usually expected for major boiler components. The results shown in Figure 7 suggest that, for non-heat flux applications (red line), such a lifetime could be obtained for Gr 91 components only if the temperature is limited to approximately 600°C, beyond which scale failures may result in potential damage or management issues.

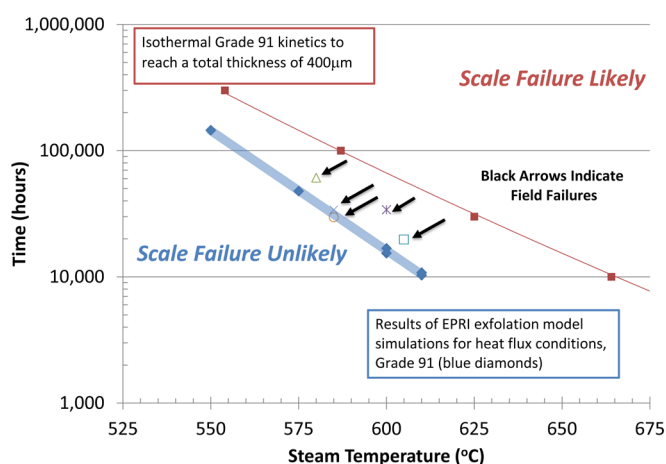


Figure 7 – Comparison of time to scale failure for Gr 91 as a function of main steam temperature under isothermal and heat-flux conditions in utility boilers.

For heat-flux applications, however, the temperatures at the metal-scale and scale-steam interfaces, which govern the growth of inner and outer oxide layers, respectively, are higher than that of the steam due to the presence of a temperature gradient across the pressure boundary. Consequently, the higher metal and scale temperatures resulting

from the heat flux lead to faster scale growth compared to that of the corresponding isothermal condition at the same steam temperature. As described previously, EPRI's Oxidation and Exfoliation Model [28–30] is capable of taking into account the increased temperatures from the heat fluxes in scale growth kinetics. The blue line in Figure 7 shows the operating time calculated for the scale layer formed on Gr 91 to reach a thickness of 250–400 μm from a variety of simulations. As expected, the blue line for the heat-flux conditions has shifted noticeably downward from that of the red line for isothermal conditions. To validate such a shift, several plant data with confirmed steam temperatures and times to scale failure in boiler superheaters are also included in Figure 7 (indicated by black arrows). These plant data are in excellent agreement with the predicted times to scale failure under the heat-flux conditions. Clearly, if the red line for the isothermal condition is used to predict the time to scale failure, the performance of the superheaters would be severely over-estimated, leading to 'premature' component failures and forced outages. However, if the temperature limit is set by the blue line for heat-flux condition, scale failures can likely be averted. Note that the maximum steam temperature for Gr 91 components with heat flux to meet a 100,000-hour design life is now reduced to approximately 560°C, an approximately 40°C drop from that of the isothermal conditions.

Proposed Guidelines for Gr 91 Use Temperature Limit in Boilers

As demonstrated above, the impact of heat flux on oxide growth kinetics is quite significant. As a result, the temperature limit for Gr 91 used in isothermal and heat-flux applications must be specified separately. The steam temperature of 600 and 560°C shown in Figure 7 would allow Gr 91 components to service for 100,000 hours under isothermal and heat-flux conditions, respectively, before the oxide scale reaches the critical thickness. Because the critical oxide thickness for Gr 91 to cause scale failure with the potential to exfoliate lies in the range of 250 to 400 μm , the use of 400 μm is reasonable for the isothermal condition. The plant data in Figure 7 appear to support the use of the model predictions in heat-flux applications.

If the main steam temperature is raised to the range of 600–620°C for Gr 91 components, design reviews and contingency plans are recommended to account for the increased potential of scale failures prior to reaching the 100,000-hour design life. In addition, design modifications should be considered, if possible, to minimize the risk of tube failures, including an increase in the bend and elbow radii, upgrade of materials at critical locations, and installation of screens

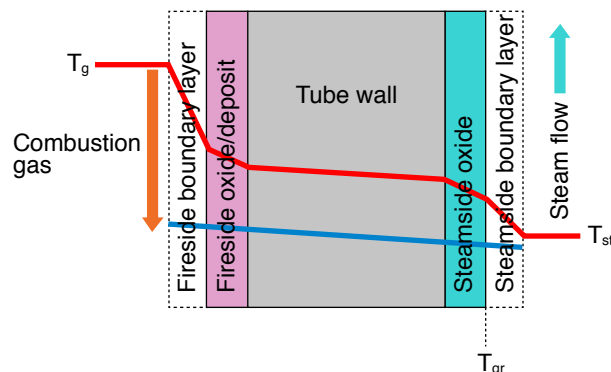
to protect downstream components from solid particle erosion and blockage. EPRI recommends against the use of Gr 91 at main steam temperature above 620°C for any isothermal applications in boilers.

For heat-flux applications in boilers, additional risks of creep damage and catastrophic failures from overheating need to be considered. The failure modes consist of (1) short-term overheating in superheater and reheater pendants that typically occurs within the first 40,000 hours of boiler operation due to tube blockage by oxide exfoliates and (2) long-term overheating that occurs after 40,000–150,000 hours of operation from excessive scale formation. In boilers with main steam temperatures below 560°C, the operation of Gr 91 heat-flux components would avoid creep damage associated with a significant temperature rise from oxide thickening and scale failures during the 100,000-hour design life. When the steam temperature is increased to 560–580°C, design reviews and contingency plans are recommended to account for increased metal temperatures and thus increased potential for long-term overheating on Gr 91 from excessive scale growth. Additional measures are recommended in design modifications for extreme locations in boilers, including an increase of bend radii, elimination of tight (180°) bends in the superheater and reheater pendants, materials upgrade, reduction of temperature imbalance, coatings, and addition of heat-absorption surfaces. For main steam temperatures exceeding 580°C in boilers, the use of Gr 91 is inadvisable for any high heat-flux applications.

Proposed Guidelines for Gr 91 Use Temperature Limit in HRSGs

The flue gas temperatures in heat recovery steam generators (HRSGs) are considerably lower than those in conventional boilers, typically ranging from 610 to 650°C, while the hot reheat outlet steam temperatures of HRSGs are similar to those of the main steam temperatures of boilers, varying in the range of 560 to 590°C. Recent advancement in HRSGs has increased the hot reheat steam temperatures to above 600°C. Because the temperature difference across the heat-absorbing tubing in HRSGs is relatively small compared to utility boilers, the wall thickness of HRSG tubing is reduced, typically in the proximity of 0.100–0.125" (2.54–3.18 mm), to achieve optimal heat transfer.

Figure 8 illustrates the temperature profiles of a boiler tube and a HRSG tube across the pressure boundary, which are represented by the red and blue lines, respectively. Note that the two types of tubing, although shown overlapped in the figure for ease of comparison, are quite different in both outside diameter (OD) and wall



T_g , T_{st} : Temperatures of combustion gas and steam, respectively
 T_{gr} : Growth temperature of oxide scale

Figure 8 – Comparison of temperature profiles across heat-transferring tube wall in boilers (red) and HRSGs (blue).

thickness. Given the relatively low gas temperatures, the difference between T_g and T_{st} for HRSG tubing is typically only 30–60°C, with the high end being observed in tubes close to the duct burners. Due to this relatively small difference, the temperature gradient across a HRSG tube wall can be assumed to be linear between T_g and T_{st} .

In the EPRI Exfoliation Model [28–30], the temperature at the spinel/metal interface dictates the growth of the inner oxide layer, and the temperature at the magnetite/steam interface governs the growth of the outer layer. Both of these temperatures must be determined through calculations based on scientific understanding of oxide growth kinetics, heat transfers, and materials properties [3, 7]. Such calculations have been applied extensively to predict the oxidation and exfoliation behaviors of boiler tubes. Figure 7 serves as an example of the modeling output for Gr 91 used in utility boilers. However, unlike boilers, extensive modeling and calculations have not been performed for HRSGs.

Nevertheless, due to the presence of a relatively small temperature difference and an essentially linear temperature gradient across the HRSG tube wall, a simplified approach is attempted here to quantify the oxidation behaviors of Gr 91 in HRSGs without the need for extensive modeling. This approach assumes that the mid-wall temperature, approximately $T_{st} + \text{half of } (T_g - T_{st})$ [or $T_{st} + (T_g - T_{st})/2$], is the equivalent temperature at the spinel/metal interface and therefore governs the scale growth of the inner oxide layer formed on the ID surfaces of HRSG tubing. The value of $(T_g - T_{st})/2$ is approximately 20°C, thus making the mid-wall temperature about $T_{st} + 20^\circ\text{C}$. Obviously, the use of the mid-wall temperature for oxide growth

calculations would be overly conservative for utility boiler tubes but likely reasonable for HRSGs. Similar to boilers, the growth of the outer oxide layer on HRSG tubes is dominated by the temperature at the magnetite/steam interface.

A small difference in temperature between T_{met-sp} and T_{st} suggests that T_{met-sp} , which governs the kinetics of inner oxide growth, but ultimately also the outer oxide growth, can be used to set the temperature limits for HRSG tubing without going through extensive modeling and calculations. In this case, the temperature limits for Gr 91 in HRSGs would simply be assumed to be 20°C higher than those in utility boilers under equivalent heat-flux conditions. This 20°C allowable margin is proposed in Table 4 below. Obviously, for non-heat flux components, the temperature limits for Gr 91 components in HRSGs are the same as those in utility boilers.

Summary of Proposed Use Temperature Limits for Gr 91

The proposed temperature limits for Gr 91 are summarized in Table 4, which are noticeably lower than those allowed by ASME B&PV Code Section I. These lower use temperatures would ensure safe and reliable operation of Gr 91 components in boilers and HRSGs where steam oxidation and oxide exfoliation leading to scale failures from overheating are of concern. Again, this white paper focuses the temperature limits for Gr 91 only on its behaviors of

steam oxidation and exfoliation. Other factors for considerations in procurement and fabrication, such as metallurgical risks, weld strength reduction factors, and cyclic services, are not addressed in this document, as they are covered elsewhere in many EPRI research and reports.

Conclusions

The growth rate of oxide scale formed on Gr 91 surfaces from exposure to high-temperature steam increases exponentially with temperature. In heat-flux components, the metal temperature is further increased due to a temperature gradient existing across the pressure boundary. Therefore, the impact of steam and metal temperatures on the performance of boiler components must be fully considered in boiler and HRSG design. The current temperature limit of 649°C (1200°F) allowed by ASME B&PV Code Section I for Gr 91 was determined based primarily on microstructural stability and creep strength. There have been a number of failures of Gr 91 components operated at temperatures significantly lower than the ASME limit. Causes for many of these failures were closely associated with steam oxidation and scale exfoliation. A careful review of the impact of steam oxidation on the design life of Gr 91 components has been performed by EPRI. Results of this review, along with extensive engineering calculations and model predictions for boilers, led to the recommendations of reduced use temperatures for Gr 91.

Table 4 – Comparison of Proposed Use Temperature Limits for Gr 91 in Boilers and HRSG

* Design reviews and contingency plans recommended to include materials upgrade, design modifications, operation optimizations, and unplanned outages.

Steam Temperature*	Grade 91 – (Non Heat-Flux)	Gr 91 (Heat-Flux) – High Heat Flux and High Gas Temperature	Gr 91 (Heat-Flux) – Low Gas Temperature
Component	Boilers and HRSGs	Boilers	HRSGs
Recommended Use Temperature	<600°C Relatively small scale thickness expected at 100,000 hours	<560°C Exfoliation not expected in first 150,000 hours of operation	<580°C Minimal exfoliation expected for entire system
Maximum Recommended Use with a Design Review*	600-620°C Exfoliation likely after ~50,000 hours: will need to manage effects on equipment	560-580°C Exfoliation expected after ~40,000 hours: Increased tube temperatures must be accounted for in design	580-600°C Exfoliation is expected to occur, as more tubing approaches 600°C, more exfoliation will require management
Not Recommended	>620°C Exfoliation likely at less than 50,000 hours	>580°C Short-term overhear failures from exfoliation and tube blockages plus accelerating oxidation rates likely	>600°C Exfoliation will occur with potential for extensive I.D. and O.D. wall loss
ASME B&PV Sec I Code	649°C	649°C	649°C

* Steam temperature refers to main steam temperature for boilers and hot reheat outlet temperature for HRSGs.

For isothermal components in utility boilers, a maximum main steam temperature of 600°C is recommended for Gr 91 with essentially no concern for scale failures within a typical design lifetime. If the main steam temperature is raised to the range of 600–620°C, engineering reviews should be conducted and design modifications be considered to account for the potential of premature scale failures within the design lifetime. The use of Gr 91 for non-heat flux components in boilers with the main steam temperature higher than 620°C is not recommended. However, additional concerns for creep damage and failure from overheating are present in heat-flux components. To address these concerns, the maximum main steam temperature for the safe and reliable operation of heat-transferring Gr 91 components in boilers is reduced to 560°C. When the main steam temperature is increased to the range of 560 to 580°C, design reviews should be performed to account for the potential of short and long-term overheating from excessive scale growth on Gr 91. If the main steam temperature is higher than 580°C, the use of Gr 91 is not recommended for any heat-flux components in boilers.

Due to relatively low gas temperatures, a small temperature difference and an essentially linear temperature gradient exists across the tube wall in HRSGs. Based on simplified analyses, the mid-wall temperature of HRSG tubing is only about 20°C higher than the steam temperature. Such a relatively small difference allows the mid-wall temperature to be used in determining the temperature limits for HRSG tubing without requiring extensive modeling and calculations. As a result, the temperature limits for Gr 91 components in HRSGs are given a 20°C allowable from those in utility boilers under equivalent heat-flux conditions. For non-heat flux components, the temperature limits for Gr 91 in HRSGs are the same as those in utility boilers.

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