Managing Steam-Side Oxidation and Exfoliation in USC Boiler Tubes

Superheaters (SH) and reheaters (RH) in modern supercritical (SC) and ultrasupercritical (USC) coal-fired steam power plants operate with maximum steam temperatures between 580 and 620°C and pressures up to 28 MPa. A single unit can contain miles of tubing, therefore the formation (growth) of steam-grown oxide scales on the inside of this tubing and the potential for these scales to exfoliate during operation can have a significant impact on plant operations. In 2012, National Physical Laboratory (NPL) and Electric Power Research Institute (EPRI) held a joint workshop to review recent experience in the practical management of exfoliation, progress in understanding the phenomenon, and development of models intended to provide the basis for improved approaches. This article briefly describes some of the characteristics of oxide growth and exfoliation, the impact of these oxides in modern power plants, and highlights findings from the workshop and requirements for additional research.

Oxide growth

The growth and exfoliation of thermally grown oxides, or scales, in steam is a complex phenomenon that depends on alloy composition, microstructure (including surface condition), temperature, pressure, and plant operation. Steels and stainless steels used in SH and RH tubing have varying chemical compositions with 2 to 25 wt% chromium and 0 to 25% nickel, and can be austenitic, bainitic, or martensitic.

Figure 1 shows the difference in oxide scale morphology between martensitic T91 alloy steel (9Cr-1Mo-V) and austenitic TP347H stainless steel (18Cr-8Ni-Nb) after service in the superheaters of utility steam boilers. Scale on T91 forms as layers of uniform thickness, and separation occurs between the main inner and outer layers (with the outer layer lifting off). The inner layer of the essentially double-layer scale formed on TP347H has a very irregular thickness, and while separation also occurs between the two main layers, the outer layer exfoliates completely. Figure 2 shows the complexity in the types of oxides and defects that can form in a 9% Cr martensitic steel.

Results of exfoliation

When oxide scales fail (crack), separate, and are lost (exfoliate) from tube surfaces, there is potential for tube overheating (thermal insulation from a lifted scale), tube blockage from accumulation of oxides, and erosion damage to downstream components. Figure 3a shows a tube blocked from oxides that accumulated in the lower loop of a superheater after a plant shutdown. The blockage severely restricted steam flow and caused a short-term overheat tube failure during the unit restart. The figure...

Fig. 1 — Structures of oxide scales (polished cross sections) observed on T91 alloy steel after about eight years of service at a steam temperature of approximately 541°C, and on TP347H stainless steel after about six months service in steam at a temperature of approximately 580°C. Alloy composition plays an important role in the structure/morphology of the oxide scale.

Fig. 2 — Cross section of 9% Cr steel after laboratory exposure for 10,000 hours in dry steam at a temperature of 625°C showing the complexity of the oxide scale.
also shows erosion damage to a valve stem due to exfoliated oxides. A 2011 EPRI survey of U.S. utilities showed that over 50% of respondents experienced exfoliation-related damage in their power plants including tube failures, erosion of drain lines, reduced steam turbine performance due to erosion of blading, and increased maintenance of valve components.

**Modeling the process**

To minimize the likelihood of tube failures, manage exfoliation, and select suitable materials for different operating conditions, EPRI conducted modeling work on the process of oxide growth and exfoliation taking into consideration the accumulation of strain in the oxide or oxide layers\(^1\). Strain accumulates during operational transients, and is a function of many factors including scale chemistry and structure, physical properties of the scale, oxide growth stresses, creep, and physical tube dimensions. One major driver for strain accumulation and eventual scale failure is the mismatch in coefficient of thermal expansion (CTE) between oxide layers and substrate alloys. Figure 4 shows the CTE as a function of temperature for various iron oxides compared with TP347 stainless steel.

![Coefficient of thermal expansion of various iron oxides compared with that of TP347 stainless steel\(^4\).](image)

Modeling oxide growth and strain accumulation (which is particularly high during unit start-up and shutdown events) enables identification of the point when oxide exfoliation is expected to occur. Applying this methodology to the operation of a superheater (including temperature and heat-flux gradients) can provide guidance on the amount of scale lost by exfoliation and the potential for tube blockage. Figure 5 shows modeling results for a stainless steel superheater. Tube blockage is predicted during the first two to three years of operation (8000 to 20,000 hours), and the likelihood of further blockages decreases with time assuming that exfoliated scale is removed after each shutdown event (i.e., the scale is blown through the system), which is consistent with field experience.

**EPRI-NPL workshop findings**

Challenges with steam-side oxide growth and exfoliation management are being experienced worldwide, and an “experts workshop” was held at NPL in January 2012\(^2\) to bring together practical experience and current research to identify key knowledge gaps and research needs. A number of issues were identified including:

- Boilers with nominally the same materials and operating conditions had vastly different experiences with exfoliation, and the role of boiler design has not been clearly identified.
In the case of modeling, the failure criteria for exfoliation need further refinement, and scale defect sizes that are key to developing failure criteria are currently unknown. Many discrepancies exist between laboratory test results and those obtained from field experience. This is partly due to difficulties in simulating some key aspects of plant operation in laboratory testing, and to the fact that mass gain and not oxide thickness are often reported from laboratory examinations. This is critical because laboratory testing is currently being used to validate materials for future higher-temperature advanced USC steam designs. There may be a need to define temperature use limits for alloys based not only on high-temperature strength, but also on exfoliation considerations.

Based on this feedback, a major outcome of the workshop was the need for development of an atlas of steam-grown oxide structures containing the necessary details to provide practical diagnostic guidance to power-plant operators dealing with oxide exfoliation, a consistent set of data to use for modeling activities, and accepted field microstructures for laboratory researchers to validate their experimental approaches. EPRI and Oak Ridge National Laboratory have started this effort[3].

New research

Work also continues through the use of advanced characterization techniques to further clarify mechanisms and long-term stability of steam-grown oxides scales. Figure 6 shows an electron probe secondary electron image and a color compilation of Fe, Cr, and O x-ray maps from the inner scale formed on a stainless steel superheater after ~3.5 years of service in a SC steam boiler. The formation of a chromium rich scale is expected to slow the oxide growth rate significantly, but the x-ray map clearly indicates regions of oxide where no Cr-rich oxide layer has formed adjacent to the metal and regions in the metal with chromium depletion. Typically, a uniform Cr-rich layer is present at the reaction front, and this result suggests there is nonuniform growth, perhaps initiated by Cr depletion. Measurements of these various layers with time will provide a more detailed picture of the reaction mechanism during long-term service in supercritical steam.

References


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