PROGRESS IN PREDICTION AND CONTROL OF SCALE EXFOLIATION ON SUPERHEATER AND REHEATER ALLOYS

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ABSTRACT

Scale exfoliation from ferritic and austenitic steels used for superheater and reheater tubes has long been recognized as a major cause of tube blockages and steam turbine erosion. A methodology based on a format first suggested by Armitt et al. in 1978 has proved to be a useful tool for providing warning of exfoliation, and has been used to aid decisions on tube cleaning and the estimation of remaining tube life. That approach uses the concept of the need to exceed a minimum level of strain energy in the scale before separation and exfoliation can occur. Equating the strain energy stored in the scale with scale thickness, hence time at temperature, allowed the use of relatively simple measurements to estimate the potential for scale exfoliation. The trend to higher steam temperatures and longer periods of full-load operation increases the rate at which oxide thickening occurs, so that increased awareness of the factors involved in scale exfoliation is required. Also, there is a need to examine the reliability of the oxide growth and exfoliation characteristics used in the present lifetime approaches in terms of operation at higher temperatures and pressures, the effects of changes in the frequency of load cycling and black starts, and the applicability of the currently-accepted mode of scale separation and loss to the new ferritic and austenitic alloys. To this end, a review of research and field experience related to oxide growth and spallation in steam, with an emphasis on results obtained over the past twenty-five years, was conducted and used as a basis for setting forth the characteristics of a high-level model for prediction and control of scale exfoliation on superheater and reheater alloys. The proposed approach is based on the Armitt et al. format, but envisions incorporation of the latest scientific understanding and field observations into a multilayered set of mechanistic and database algorithms, linked to a damage-accumulation parameter as the key tracking factor. Such an overarching model would, of necessity, link fundamental microstructural, compositional, mechanical, kinetic, and environmental factors to parameters that can be controlled or monitored at the plant level. The research, database, testing, and modeling requirements to accomplish such have been defined, and will be discussed.

INTRODUCTION

Scale exfoliation from the steam side of superheater and reheater tubes has been a problem for over 30 years, initially gaining notice when scale exfoliated from small-bore, austenitic alloy tubing led to flow restriction and blocking of tube bends, and resulting boiler tube failures from overheating. In the U.S. in the same time period, there was some concern resulting from solid particle erosion (SPE) of the nozzle blocks and first stage blades of steam turbines, due to oxide particles exfoliated from low-Cr ferritic alloys, typically T11 and T22 [1]. These problems were mainly experienced in the intermediate pressure turbine, due to exfoliation from the reheaters, in plants where the configuration of the piping allowed the exfoliated scales to be transported to the turbine. Research efforts were initiated to determine the causes of scale exfoliation by the Central Electricity Generating Board (CEGB) in the United Kingdom, and subsequently by EPRI in the US, which published a report that incorporated much of the CEGB's findings [2]. Over approximately the last five years, scale exfoliation problems from austenitic alloys have been reported worldwide [3)]; likewise, SPE due to oxides from ferritic alloys has increased in

importance, and is experienced predominately, but not solely, in North America [4]. Further, changes in operating practices, with extended running at near to full load, longer periods between scheduled maintenance, and the trend to higher steam temperatures and pressures, have contributed to mounting concerns over the increasing thickness of steam-side oxide scales. It is notable that long-term overheating due to flow restriction from exfoliated oxide scale is the second most important cause of boiler tube failures worldwide [4], and that increasing attention is being paid to the measurement of steam-side oxide thickness as a way of estimating remaining life. A further development that tends to exacerbate scale exfoliation is cyclic operation, although correlations between scale thickness, cycle frequency, and temperature change are not available. The requirement for heat-recovery steam generators to endure very rapid rates of heating and cooling suggests that they may be particularly prone to scale exfoliation problems [5]. Obviously, there is a need for the development of a rational basis that can be used by plant operators to manage, and possibly control, scale exfoliation.

CURRENT UNDERSTANDING OF SCALE EXFOLIATION

It is well understood that the thickness of the steam-side oxide increases with time (usually according to a parabolic rate law), until some critical condition is reached at which scale exfoliation can occur; since exfoliation is not experienced typically until after many thousands of hours of service, the 'critical criterion' is thought to be related to scale thickness. Loss of protective scale not only leads to the problems indicated, but also results in an acceleration of the oxidation process in the affected locations, which increases the rate of alloy consumption, and may result in the formation of less adherent oxide scales. It is also well understood that there are major differences in the rate of oxidation between ferritic and austenitic steels, since the low-Cr ferritic steels tend to form iron oxide scales based on magnetite (Fe_3O_4), sometimes with a thin outer layer of haematite (Fe_2O_3) [6], which are less protective than the Cr-containing spinel oxides formed by the austenitic steels.

The rate of oxide thickening increases exponentially with increasing temperature [7]. Since the ferritic steels used in the relatively old fleet of U.S. steam boilers already are operated under conditions near their oxidation limits, increasing the main steam temperature by only 10 or 15°C could result in a significant increase in the rate to scale growth on those alloys. This relationship of scale thickening to temperature suggest that exfoliation conditions may be reached in shorter times at higher steam temperatures for both ferritic and austenitic steels, which also seems to match recent experience [3].

The general understanding from earlier research [2] is that the major criterion for scale exfoliation to occur is that the level of stored strain energy in the oxide must reach or exceed the energy needed to drive a crack along a plane of weakness in either the scale itself or between the scale and the metal substrate. Stress can accumulate in oxide scales from three main sources:

1. The increase in volume that occurs when the alloy is converted to oxide; for the low-Cr steels, the ratio of the volume of the oxide formed to that of the alloy consumed is of the order of 2. In the absence of other constraints, the growing oxide scale thus typically is in a state of compression. This stress can be exacerbated or relieved by shape effects: for instance, oxide growing on the inside of a tube will be more constrained than that growing on the outside. It is not clear to what extent these or other growth stresses may be relaxed during service by, for instance, creep or other deformation of the oxide itself or of the underlying metal.
2. Thermal stresses resulting from differences in coefficient of thermal expansion (CTE) between the oxide and the underlying metal. These differences can be significant, and so can provide a large driving force for creating differential stresses during thermal transients.
3. External stresses resulting from parasitic loads, vibrations, or impacts on the oxidizing component.

Figure 1 uses data from references [2,8] to show the relative CTEs of a ferritic steel (T22) and a type 300-series stainless steel, as well as data for the oxides likely to be formed, over the range of metal temperature of interest. Given the sparsity of CTE data as a function of temperature for the oxides of interest, it

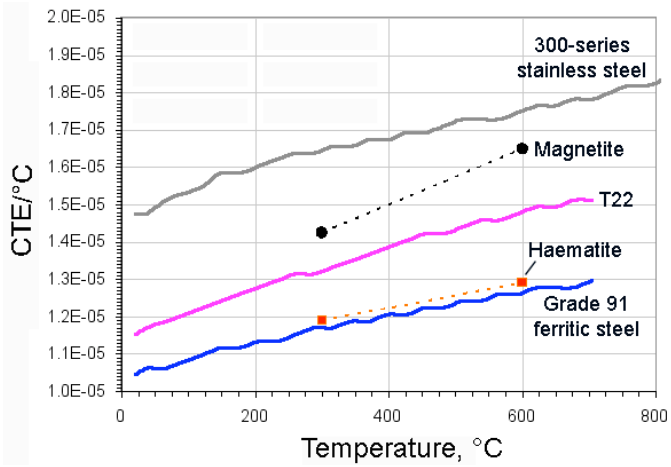

Figure 1. Temperature Dependence of the Coefficients of Thermal Expansion of Alloys and Oxides

would appear that magnetite growing on T22 will be put under compressive stress during heating, and under tensile stress during cooling cycles. In contrast, assuming that the CTE of the Fe-Cr spinel oxide that grows in contact with the austenitic steels is similar to that of magnetite (magnetite itself typically does not grow in contact with the austenitic steels, as it does on the ferritic steels), in heating-up cycles the scale on austenitic steels will be in tension, but in compression during cool down. Another way of visualizing these differences is shown in Fig. 2, which illustrates the decrease in the diameter of individual tubes made from T22, T91, a 300-series stainless steel, and the oxides magnetite and

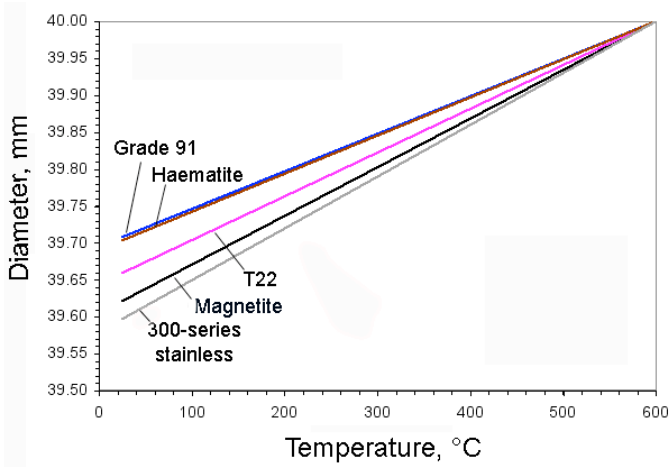

Figure 2. Decrease in Tube Diameter During Cooling, Showing Effects of Variations in CTE

haematite, due to contraction during cooling from 600 to 20°C, starting at 40 mm diameter. This clearly demonstrates the differences between the ferritic and austenitic steel tubes, with the 9Cr ferritic material (Grade T91) contracting significantly less than T22. This difference suggests that alloy T91 would be more prone than T22 to scale exfoliation. When magnetite is formed on T22, the oxide layer (in contact with the alloy) will experience a small tensile strain on cooling whereas, on a 300 series stainless steel, the magnetite would experience a compressive strain. Where a layer of hematite is grown on top of the magnetite (which typically is found more extensively on alloys which form scales that tend to increase in

protective behavior with time), the hematite will experience a compressive stress compared to the magnetite. Thus, the presence or absence of an outer hematite layer (that is, the specifics of the scale formed) can significantly influence the stress field in the main body of the scale, which is typically magnetite [9].

THE ARMITT APPROACH

Such considerations of the development and release of stress in growing oxide scales were used by Armitt et al. [2] to make estimations of the accumulated elastic strain as a function of scale thickness, and to relate these values to observed tendencies for scale damage and exfoliation. This overall approach was summarized very elegantly in the "Armitt diagram," shown in Fig. 3. The diagram deals with the conditions found on both ferritic (tensile cooling strains) and austenitic (compressive cooling strains) steels, and also shows the regimes where features such as through-scale cracking and the formation of

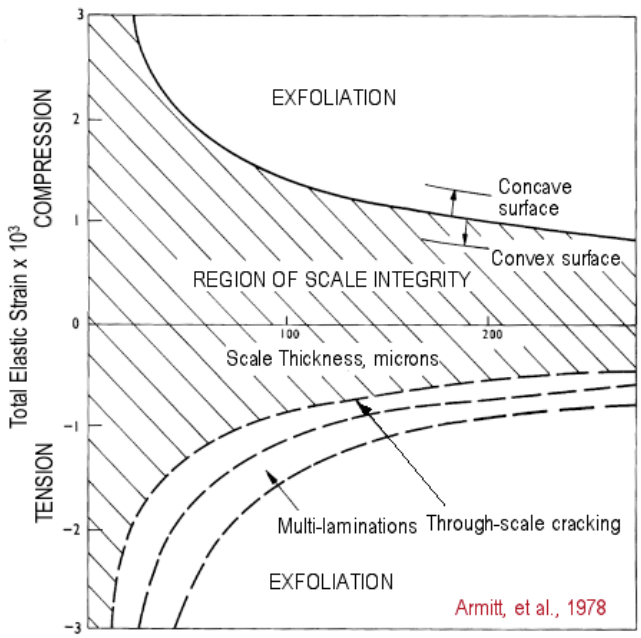

Figure 3. The Armitt Diagram

multi-laminated oxide layers are expected on ferritic steels. It is obvious that the regime of scale integrity (i.e., no exfoliation tendency) suggested by the diagram narrows rapidly with increasing scale thickness, which is a reflection of the decreasing amount of total elastic strain that can be accommodated as the scale thickness increases. The obvious practical drawback of this diagram is the need for values of scale thickness (which can be obtained from metallographic measurements on tube samples), and of the total elastic strain in the scale due to cooling. This latter value typically can be calculated from knowledge of the difference in temperature experienced by the tubes, using the simplified formulae shown in Table 1. Note that these calculations take account of the presence of haematite in the scale, with 20% haematite

Table 1. Estimation of Cooling Strains

Oxide	300-series Austenitic Steel	T22 Ferritic Steel
With 0% Fe_2O_3	$+ 1.8 \times 10^{-3} (T_s-T_a)/ (600^\circ C-T_a)$	$- 1 \times 10^{-3} (T_s-T_a)/ (600^\circ C-T_a)$
With 20% Fe_2O_3	$+ 2.0 \times 10^{-3} (T_s-T_a)/ (600^\circ C-T_a)$	$- 0.5 \times 10^{-3} (T_s-T_a)/ (600^\circ C-T_a)$

where: T_s = service temperature, $^\circ C$
T_a = temperature to which the component is cooled, $^\circ C$
-ve is tensile, +ve is compressive

in the scales on a 300-series stainless steel producing a slight increase in the compressive strain, but a decrease in the scale formed on T22. Note also that the convention used on the Armitt diagram assigns a negative sign to tensile strains.

Figure 4 shows data points superimposed on the Armitt diagram for measurements from scales of different thicknesses that were taken from superheater and reheater tubes that exhibited moderate to severe exfoliation [10]. The total elastic strains calculated for the scales formed on the austenitic steel tubes placed them in the zone of expected exfoliation, for scale thicknesses as low as 70 µm. The much thicker scales formed on the ferritic steels had reached the point of damage through cracking and delamination, but only those with thin, outer hematite layers had accumulated sufficient elastic strain to cause exfoliation.

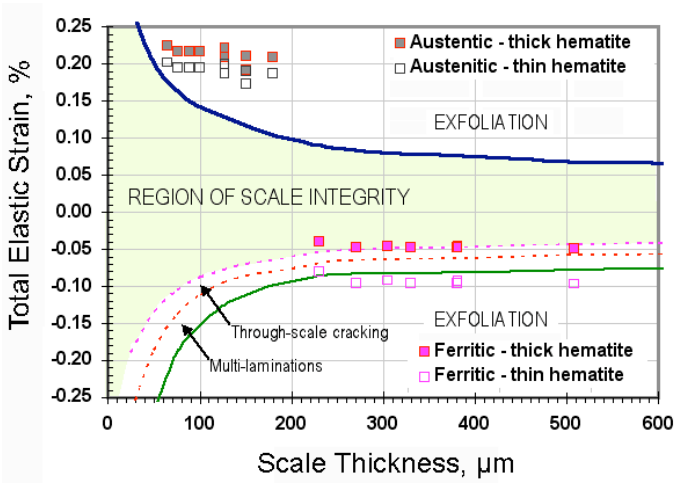

Figure 4. Data for Superheater and Reheater Tubes with Moderate-to-Severe Exfoliation

The relatively limited use in the US of the Armitt diagram approach mostly has been to supplement failure analyses to explain why exfoliation was experienced only after many years of service. Occasionally, however, the diagram has been used to predict when exfoliation is likely to occur, so that preventive actions could be completed to prevent exfoliation, and consequent damage for tube failures. The types of corrective actions that can be used include inspection of the lower bends of the superheater and reheater platens during normal outages, for which X-ray imaging can provide a very useful, graphic, nondestructive tool. Tube bends found to have significant deposits can be cleaned, or cut out and replaced. In some cases, it has been found possible to clean out blocked bends by blowing down the exfoliated oxide, using an auxiliary forced air system. Where the oxide is approaching a thickness at which, under the anticipated operating conditions (temperature cycles) the Armitt diagram suggests that exfoliation will be likely, chemical cleaning has been used to remove the oxide from the components.

The differences that exist among alloys in terms of CTE (Fig. 1 and 2) and in rate of oxide growth as a function of time and temperature could provide a rational basis for the selection of replacement materials for use in components where exfoliation has been a particular problem. Further, since the tendency for exfoliated scale to accrete into blocking deposits can be strongly affected by the hydrodynamics in the tubes, some local redesign, such as changes in tube bend radius, could be considered. The predictive qualities of the Armitt diagram also can be used to determine the most effective location for the installation of an online oxide exfoliation detection system.

BEYOND THE ARMITT DIAGRAM

Overall, the Armitt approach has demonstrated merit, even though the parameters required by the diagram currently are not readily available to plant operators. Ideally, however, an all-encompassing model is needed that will allow quantitative prediction of the size and amount of exfoliated scale debris as a function of plant operating parameters, such as time, temperature, steam conditions, and cycling parameters. An ongoing, EPRI-funded program is addressing these issues [11]. The approach being taken is to develop a coded suite of simplified algorithms that can be used to guide plant operators. These will use scale failure criteria that can be referred directly to plant operating parameters, as well as a common base parameter that includes the operating history experienced by the scale, and the effects of scale properties. The need for measurements by plant personnel will be minimized by the use of sophisticated models to calculate the parameters required. Of course, some measurements from samples collected from the boiler will be required to confirm and periodically update the models.

In the intervening time since the Armitt diagram was devised, advances have been made on a number of fronts that should allow these design improvements to be made. In particular, significant progress has been made in the detailed, quantitative description of the failure strains in oxides, and failure models now involve physical defects that can be approximated to those found in real scales. These models can now quantitatively treat fracture in tension, as experienced by ferritic steels, and account for the role of microcrack networks that develop in such scales. Models that address fracture in compression, as experienced by the austenitic steels, include treatments for the role of scale porosity, voids, surface roughness, as well as the creep behavior of the substrate [12]. One qualifying factor is that many of these advances have been made for oxide scales grown in air, not in steam. Thus there are questions concerning the extent to which air-grown and steam-grown oxide scales differ, particularly in terms of oxide composition and structure, scale porosity, and differences in the depletion of elements such as Cr from the alloy substrate.

The proposed approach for developing a successor to the Armitt diagram is summarized in Fig. 5, which is intended to indicate the continuity with the Armitt approach. In this, the scale thickness in the original Armitt diagram is replaced by a parameter (ω) that incorporates all of the various oxide property-related

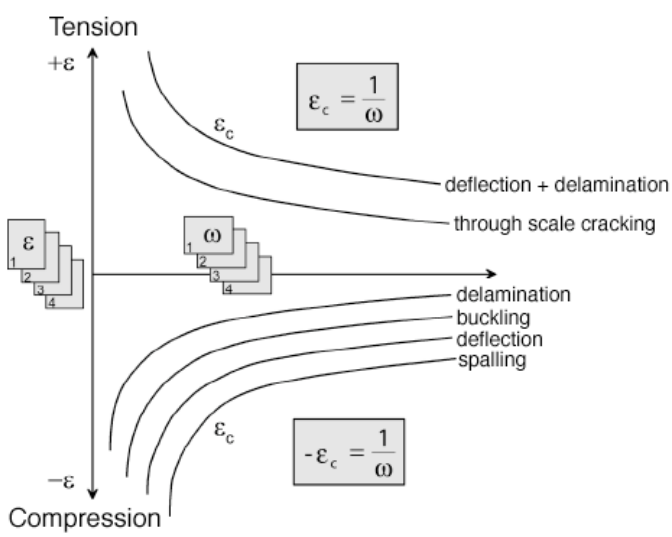

Figure 5. The Next-Generation 'Armitt Diagram'

parameters, and which essentially is the criterion for scale failure. Stored strain energy in the scale (ε) is retained as the other main parameter, but the models and equations needed to calculate this, as well as the new oxide scale property parameter, are included in the background behind the classic Armitt approach.

The different levels (1, 2, 3...) indicated in Fig. 5 contain increasing detail. As an example, for calculating the accumulated strain (ε) in the oxide:

Level 1: will represent the residual elastic strain from plant operation, which will be the sum of the strains imposed by growth of the oxide ($\varepsilon_{grow,int}$); by geometric factors that affect the oxide growth ($\varepsilon_{grow,geo}$); the stresses from thermal excursions (ε_{therm}); and strains from external loading (ε_{ext}); minus the strain relief due to creep of the oxide and/or alloy (ε_{creep}); and from other forms of deformation such as pseudo plasticity ($\varepsilon_{pseudo\text{-}pl}$). That is: $\varepsilon = (\varepsilon_{grow,int} + \varepsilon_{grow,geo} + \varepsilon_{therm} + \varepsilon_{ext}) - (\varepsilon_{creep} + \varepsilon_{pseudo\text{-}pl})$

Level 2: will include models that will allow the calculation of strain from each of these causes;

Level 3: will incorporate models that calculate specific parameters used in the Level 2 models; these will include, for instance, the temperature dependence of particular parameters. This level, or further sublevels will accept plant data as input.

For the scale property parameter (ω):

Level 1: will represent a critical strain for scale failure (ε_{crit}), where $\varepsilon_{crit} = 1/\omega$.

Level 2: will address the modes of scale cracking.

Level 3: will incorporate other models as needed. For instance, there is a need for improved models to describe the details of oxide scale failure, including delamination, cracking, and local spalling.

Level 4: will contain models for calculating the parameters required, including: oxide thickness; the elastic modulus and fracture toughness of the scale; surface energies; pore sizes; and geometric parameters. These are related to plant data through algorithms.

A more detailed description is given in, for example, references 13-14.

The input required from the plant operator will consist of data that are typically logged or are available from records, including such information as alloy type, steam temperature, time at temperature, number of cooling cycles, and magnitude of the temperature drop associated with the cooling cycles. Some form of integrated thermal history of the components of interest is needed, ideally, and suitable algorithms to extract this from typical plant records will have to be developed. These plant data will be used by the models embedded in the new approach, which will also contain alloy and oxide properties, oxidation kinetics and morphological data needed in the equations, to calculate all of the parameters required to redraw the Armitt Diagram for the specific cases considered. It is expected that it should be possible to incorporate this approach into a menu-driven, software-based tool that would be easily accessible to the plant engineer for use in determining when spallation events can be expected, for understanding the influence of plant operational parameters on tendencies for scale exfoliation, and for providing guidance for planning.

Obviously, the usefulness of this approach depends on the availability of acceptable values for the parameters used. While there exists a comprehensive, quantitative database for the oxidation in steam of a few alloys, there is a continuing need for an oxidation model that can account for the effects of steam on the oxide composition and structure, scale porosity, and subsurface zone depletion. There is also a need to extend the current knowledge base to the higher temperatures and pressures associated with advanced steam conditions. Further, the move to ultra-supercritical (USC) steam conditions will require the introduction of new alloys [15], for which there are few data available for behavior in steam. A particular characteristic of new plant designs is the intention to make more extensive use of the high Cr (9-12 Cr) ferritic steels which, by analogy to the remarks made earlier for the T91 material, may exhibit tendencies to earlier or more extensive scale spallation than do currently-used alloys. The projected final stage

superheater and steam piping materials required in the USC steam plants are Ni-based alloys, such as Inconel 617, HR6W, and Inconel 740. Research on the oxidation behavior on alloys of this type is critically needed, and several research programs are under way [16-18].

SUMMARY

Scale exfoliation is now recognized as a problem worldwide, and is expected to become even more widespread as plants are run for increased times at maximum load (that is, maximum temperature), and as steam temperatures increase with new plant designs. The Armitt diagram developed and published in 1978 provides a sound basis for predicting the tendency for scale exfoliation, but it involves parameters such as oxide thickness and stored strain energy, that are not readily accessible to plant operators. Work is in progress to build on the Armitt diagram approach, and the direction taken is to incorporate current analytical understanding of the exfoliation process to improve the representation of features found in real, exfoliating scales. The new approach is intended for incorporation into a menu-driven, software-based tool, and will be capable of using available data bases to calculate the parameters required, so greatly reducing the amount of data input required by the user. It is intended that this approach will result in a tool that can be used to provide guidance to plant operators to allow them to manage the exfoliation problem, as defined by the materials of construction and the mode of operation of each particular plant. The analytical models needed in this approach are, in principle, available now, but they need to be brought together and linked to work in the manner described. Data for testing the ability of the new system also are available for the low Cr ferritic steels, and possibly for the 300-series austenitic steels. However, new data will be required for extension of this approach to advanced steam conditions, and for the new alloys required for use in them.

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