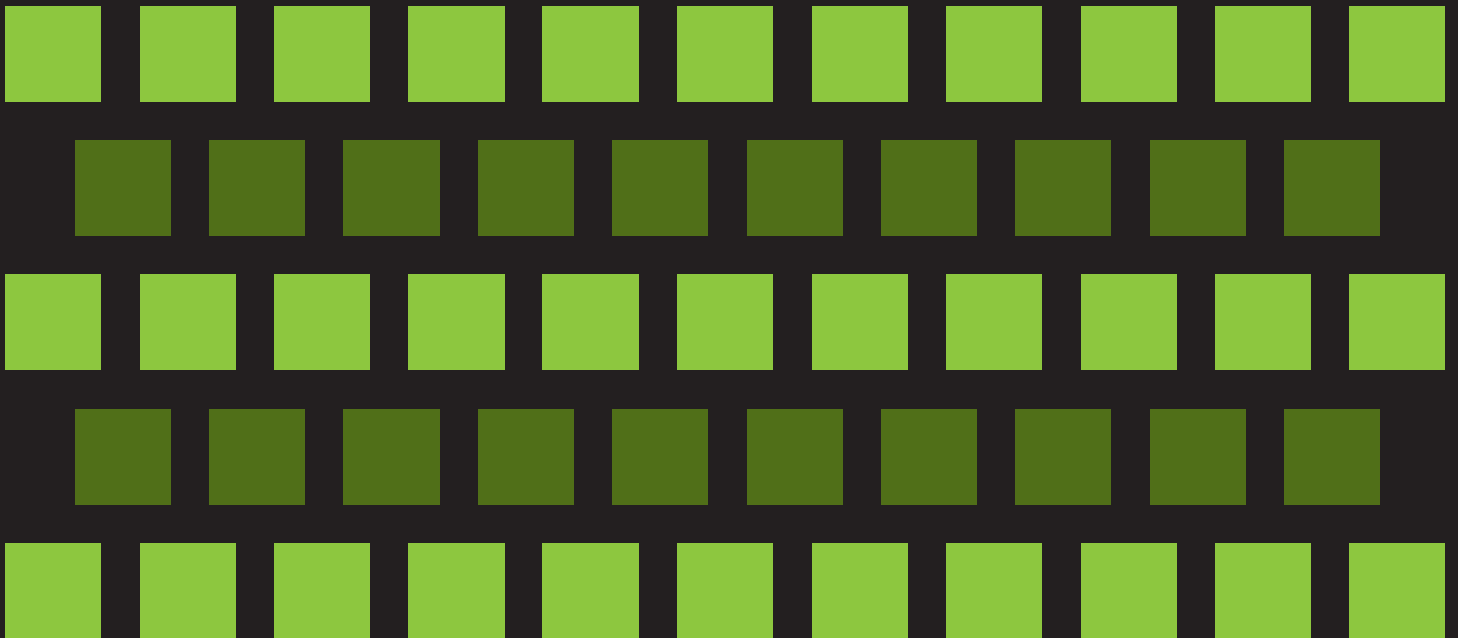


STP-PT-066

# DESIGN GUIDELINES FOR CORROSION, EROSION AND STEAM OXIDATION OF BOILER TUBES IN PULVERIZED COAL-FIRED BOILERS



STP-PT-066

# DESIGN GUIDELINES FOR CORROSION, EROSION AND STEAM OXIDATION OF BOILER TUBES IN PULVERIZED COAL-FIRED BOILERS

Prepared by:

W. R. Livingston  
Doosan Babcock Ltd.

Colin Davis  
E.ON New Build & Tehnology Ltd.

Tony Fry  
The National Physical Laboratory (NPL)

Ian Wright  
WrightHT, Inc.



Date of Issuance: March 26, 2014

This report was prepared as an account of work sponsored by ASME Pressure Technology Codes & Standards and the ASME Standards Technology, LLC (ASME ST-LLC).

Neither ASME, ASME ST-LLC, the authors, nor others involved in the preparation or review of this report, nor any of their respective employees, members or persons acting on their behalf, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe upon privately owned rights.

Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by ASME ST-LLC or others involved in the preparation or review of this report, or any agency thereof. The views and opinions of the authors, contributors and reviewers of the report expressed herein do not necessarily reflect those of ASME ST-LLC or others involved in the preparation or review of this report, or any agency thereof.

ASME ST-LLC does not take any position with respect to the validity of any patent rights asserted in connection with any items mentioned in this document, and does not undertake to insure anyone utilizing a publication against liability for infringement of any applicable Letters Patent, nor assumes any such liability. Users of a publication are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

Participation by federal agency representative(s) or person(s) affiliated with industry is not to be interpreted as government or industry endorsement of this publication.

ASME is the registered trademark of the American Society of Mechanical Engineers.

No part of this document may be reproduced in any form,  
in an electronic retrieval system or otherwise,  
without the prior written permission of the publisher.

ASME Standards Technology, LLC  
Two Park Avenue, New York, NY 10016-5990

ISBN No. 978-0-7918-6936-9  
Copyright © 2014 by  
ASME Standards Technology, LLC  
All Rights Reserved

## TABLE OF CONTENTS

|  |    |
|--|----|
| PART ONE - Design Guidelines for Pulverized Coal Boilers .....   | 2  |
| 1 GENERAL OVERVIEW .....   | 3  |
| 2 CORROSION - FIRESIDE OF BOILER TUBES .....   | 5  |
| 2.1 Technical Background.....  | 5  |
| 2.2 Furnace Wall Corrosion .....   | 5  |
| 2.2.1 Predictive Methods for Furnace Wall Corrosion .....  | 6  |
| 2.2.2 Remedial Measures for Furnace Wall Corrosion .....   | 6  |
| 2.2.3 Summary.....   | 8  |
| 2.3 Fireside Corrosion of Superheater and Reheater Tubes .....   | 8  |
| 2.3.1 Technical Background .....   | 8  |
| 2.3.2 Predictive Modeling.....   | 9  |
| 2.3.3 Remedial Measures .....  | 10 |
| 3 EROSION - ASH PARTICLE IMPACT EROSION .....  | 12 |
| 3.1 Technical Background.....  | 12 |
| 3.2 Predictive Modeling .....  | 13 |
| 3.3 Remedial Measures .....  | 15 |
| 4 OXIDATION - STEAM-SIDE OXIDATION .....   | 16 |
| 4.1 Technical Background.....  | 16 |
| 4.2 Predictive Methods.....  | 17 |
| 4.3 Remedial Measures .....  | 18 |
| 5 CONCLUDING REMARKS .....   | 20 |
| 6 REFERENCES.....  | 22 |
| <br>   |    |
| PART TWO - Investigation of Current State-of-the-Art Methods for Corrosion, Erosion and Steam Oxidation of<br>Boiler Tubes in Pulverized Coal-Fired Boilers..... | 23 |
| 1 INTRODUCTION.....  | 24 |
| 1.1 Fireside Corrosion.....  | 24 |
| 1.2 Particle Impact Erosion .....  | 25 |
| 1.3 Steam Oxidation .....  | 26 |
| 1.4 Materials and Temperatures .....   | 27 |
| 1.5 Content and Scope of the Design Guidelines .....   | 29 |
| 2 CORROSION- FIRESIDE .....  | 30 |
| 2.1 Introduction .....   | 30 |
| 2.2 Acid Dewpoint Corrosion .....  | 32 |
| 2.3 Furnace Wall Corrosion .....   | 34 |
| 2.3.1 Introduction.....  | 34 |
| 2.3.2 Furnace Wall Corrosion Rate Prediction .....   | 35 |
| 2.3.3 Influence of Chlorine on Furnace Wall Corrosion.....   | 39 |
| 2.3.4 Effect of NO <sub>x</sub> Emission Control Technology.....   | 43 |
| 2.3.5 Effect of Biomass Firing and Co-firing.....  | 45 |
| 2.3.6 Influence of Oxyfuel Firing .....  | 46 |
| 2.3.7 Effect of Boiler Pressure and Tube Temperatures .....  | 47 |
| 2.4 Furnace Wall Tube Corrosion Prevention.....  | 48 |

|       |  |     |
|-------|--|-----|
| 2.4.1 | Combustion Environment Solutions .....                                 | 48  |
| 2.4.2 | Material Solutions .....   | 49  |
| 2.4.3 | Furnace Wall Corrosion Models .....                                    | 51  |
| 2.4.4 | Corrosion Monitoring .....   | 51  |
| 2.5   | Superheater/Reheater Corrosion.....                                    | 52  |
| 2.5.1 | Technical Background .....   | 52  |
| 2.5.2 | Effects of the Combustion Environment.....                             | 53  |
| 2.5.3 | Effects of the Tube Material and the Steam Temperature.....            | 54  |
| 2.5.4 | Effects of Biomass Co-firing .....                                     | 56  |
| 2.5.5 | Effect of Oxyfuel Firing.....  | 65  |
| 2.5.6 | Prevention of Corrosion in Superheaters and Reheaters .....            | 67  |
| 2.6   | Self-Learning Corrosion Models.....                                    | 68  |
| 2.6.1 | Genetic Algorithms .....   | 68  |
| 2.6.2 | Neural Network Modelling .....   | 70  |
| 2.7   | Corrosion Monitoring.....  | 74  |
| 2.8   | Implications for Boiler Tube Design Codes.....                         | 75  |
| 2.9   | References .....   | 76  |
| 3     | EROSION - THE PARTICLE IMPACT EROSION WEAR OF BOILER TUBES .....       | 82  |
| 3.1   | Introduction .....   | 82  |
| 3.2   | Nature of Particle Impact Erosive Wear.....                            | 84  |
| 3.3   | Measurement of Erosive Wear Rates .....                                | 85  |
| 3.4   | Particle Impact Erosion Wear of Boiler Tubes.....                      | 86  |
| 3.5   | Assessment of the Erosion Potential of Pulverized Coals and Ashes..... | 87  |
| 3.6   | Predictive Modelling of the Erosion Wear Rates of Boiler Tubes .....   | 91  |
| 3.6.1 | Erosion Models .....   | 91  |
| 3.6.2 | Erosion-Corrosion Models.....  | 93  |
| 3.7   | Boiler Design Methods and Design Features to Minimized Erosion .....   | 96  |
| 3.8   | Diagnostic Methods.....  | 99  |
| 3.9   | Conclusions and Summary.....   | 101 |
| 3.10  | References .....   | 103 |
| 4     | OXIDATION - THE STEAM-SIDE OXIDATION OF BOILER TUBES.....              | 104 |
| 4.1   | Introduction .....   | 104 |
| 4.2   | Basic Concepts of High-Temperature Oxidation in Steam .....            | 105 |
| 4.2.1 | Oxide Stabilities.....   | 105 |
| 4.2.2 | Oxidation in Oxygen.....   | 105 |
| 4.2.3 | Oxidation in steam .....   | 106 |
| 4.2.4 | Application to Fe-Cr-Based Alloys.....                                 | 107 |
| 4.2.5 | Development of an Oxide Scale.....                                     | 109 |
| 4.2.6 | Oxidation Kinetics .....   | 111 |
| 4.2.7 | Effects of Steam Pressure on Oxidation Kinetics .....                  | 113 |
| 4.3   | Oxide Scale Morphologies .....   | 113 |
| 4.3.1 | Oxide Scale Morphologies on Ferritic Steels.....                       | 114 |
| 4.3.2 | Oxide Scale Morphologies on T91.....                                   | 117 |
| 4.3.3 | Oxide Scale Morphologies on Austenitic Steels .....                    | 118 |

|   |     |
|---|-----|
| 4.4 Data Selection for Modeling .....   | 120 |
| 4.5 Compilation of Oxidation Kinetic Data.....  | 121 |
| 4.6 Modeled Kinetic Curves.....   | 122 |
| 4.7 Use of the Model to Calculate Tube Metal Losses.....  | 125 |
| 4.7.1 Examples of Model Predictions .....   | 125 |
| 4.7.2 Comparison of the model predictions with plant data.....  | 130 |
| 4.8 Reference Data for Metal Thickness Loss.....  | 135 |
| 4.8.1 Oxidation Curves .....  | 135 |
| 4.8.2 Contour Plots .....   | 135 |
| 4.9 References.....   | 136 |
| <br>  |     |
| APPENDIX A – The Original Oxide Scale Thickness Data .....  | 140 |
| APPENDIX B – The Laboratory Scale Thickness Data Used to Supplement Plant Data for Training the Model ... | 154 |
| APPENDIX C – Chemical Compositions of Alloys Used .....   | 160 |
| APPENDIX D – Reference Data for Metal Thickness Loss – Oxidation Kinetic Curves.....                      | 164 |
| APPENDIX E – Reference Data for Metal Thickness Loss: Contour Plots .....                                 | 181 |

## LIST OF FIGURES

### PART ONE

|   |    |
|---|----|
| Figure 4-1: A Comparison of the Predicted Values of Inner Oxide Layer Thickness for Alloy Super 304H at 1202°F (650°C) Over a range of Pressures: 725, 2175, 2900, and 3610 psi (50, 150, 200, and 250 bar) ..... | 18 |
|---|----|

### PART TWO

|   |     |
|---|-----|
| Figure 2-1: Sulfuric Acid Dewpoint Temperature Variation Due to Combustion Gas Water Vapor and SO <sub>3</sub> Variation According to the Equation Defined by Verhoff and Banchero .....                                    | 33  |
| Figure 2-2: Hydrochloric Acid Dewpoint Temperature Variation Due to Combustion Gas Water Vapor and HCl Variation According to the Equation Defined by Kiang [17]. .....   | 33  |
| Figure 2-3: Measured Corrosion Rates for Austenitic TP347HFG When Firing and Co-Firing Straw [76] .....   | 59  |
| Figure 2-4: An Example of a Genetic Programming Tree Structure Representing a Simple Equation .....   | 69  |
| Figure 2-5: An Example of Two Parent Trees Being Bred to Create the Child Expression .....  | 70  |
| Figure 2-6: Change in Predicted Probability of “Pass” With Temperature and H <sub>2</sub> S, After Zhou et al .....   | 72  |
| Figure 2-7: Predicted Metal Loss Compared With Actual Metal Loss Showing the Results from the Training Data and Those from the Test Data .....  | 72  |
| Figure 2-8: Predicted Corrosion Rate as a Function of Temperature and Fuel.....   | 73  |
| Figure 2-9: Predicted Corrosion Rate as a Function of Temperature and Alloy.....  | 74  |
| Figure 3-1: Moh Hardness Values for the Major Mineral Species Found in Coals .....  | 88  |
| Figure 3-2: The Measured Pulverized Fuel Erosion Rate Plotted Against the Hard Mineral Content of the Coals, Excluded Mineral Particles In Excess of 25 µm In Diameter. (After Wells et al. 2005) .....                     | 89  |
| Figure 3-3: The Major Mineral Transformations in A Pulverized Coal Flame .....  | 90  |
| Figure 3-4: Relative Erosion Rate Data At An Impact Velocity of 40 m s <sup>-1</sup> , for Two Bituminous Coals and Their Corresponding Fly Ashes, Generated In A 1 MWth Combustion Test Rig. (After Wells et al. 2005) ... | 91  |
| Figure 3-5: A Sketch of the Part of the Convective Section of the Boiler and Illustrations of a Number of Erosion Protection Features .....   | 100 |
| Figure 4-1: Partial Pressures of Oxygen from the Dissociation of Steam .....  | 107 |

|   |     |
|---|-----|
| Figure 4-2: The Stability of the Oxides of Interest as a Function of the Oxygen Partial Pressure (pO <sub>2</sub> ) and Temperature .....   | 108 |
| Figure 4-3: A Simplified Schematic Diagram Indicating That Scale Growth in an Oxidizing Gas Results in the Location of the Oxide-Metal Interface Near the Original Metal Surface [13] .....                                       | 110 |
| Figure 4-4: A Simplified Schematic Diagram to Illustrate That Oxide Growth in Steam Results in the Original Alloy Surface Being Located at the Interface Between the Main Inner and Outer Oxide Layers. ....                      | 111 |
| Figure 4-5: Expected Effect on Oxidation Kinetics of Increasing Steam Pressure.....   | 113 |
| Figure 4-6: Typical Duplex Scale Formed on the 1-2% Cr Ferritic Steels .....  | 115 |
| Figure 4-7: A Typical Scale with a Multi-Laminated Inner Layer on Ferritic Steels .....   | 116 |
| Figure 4-8: A Scanning Electron Micrographs of a Cross Section of the Oxide Scale Formed On T91 in Steam After 63kh at 1050°F (566°C).....  | 118 |
| Figure 4-9: The Typical Scale Formed in Steam on the 300-Series Stainless Steels.....   | 119 |
| Figure 4-10: Optical Cross-Section of a Typical Area of a Superheater Tube From Which the Outer Layer of Scale Has Exfoliated, i.e. TP304H After 22kh Service in Steam At 1000°F and 2,400 psi (538°C and 165 bar).....           | 120 |
| Figure 4-11: A Comparison of the Final Model Prediction of Inner Oxide Thickness Plotted Against the Measured Values .....  | 123 |
| Figure 4-12: A Comparison of the Model Prediction (Red Line) of Inner Oxide Thickness and the Measured (Black Line) Value for Inner Oxide Thickness for the Neural Network Model Developed.....                                   | 124 |
| Figure 4-13: The Scatter in the Total Oxide Thickness Measurements from the Laboratory Test Data for P92.....   | 125 |
| Figure 4-14: Comparison of the Predicted Inner Oxide Thickness of Alloy T22 at 1022°F (550°C) for a Range of Pressures .....  | 126 |
| Figure 4-15: Comparison of the Predicted Inner Oxide Thickness of Alloy T22 at 1112°F (600°C) for a Range of Pressures .....  | 126 |
| Figure 4-16: Comparison of the Predicted Values of Inner Oxide Thickness for Alloy T22 at 2,120 psi (146 bar) Over a Range of Temperatures; Also Shown Are Plant Data From the Literature .....                                   | 127 |
| Figure 4-17: Comparison of the Predicted Values of Inner Oxide Thickness for Alloys T22, T23, T91, T91 and T122 at 725, 1,450, and 2,120 psi at 1022°F (50, 100, and 146 bar at 550°C) .....                                      | 128 |
| Figure 4-18: Comparison of the Predicted Values of Inner Oxide Thickness for Alloys T22, T23, T91, T91 and T122 at 725, 1,450, and 2,120 psi for 1112°F (50, 100 and 146 bar for 600°C) .....                                     | 129 |
| Figure 4-19: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for Alloy T23 at 192 Bar Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [37].....         | 130 |
| Figure 4-20: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for T91 at 3,630 psi (250 bar) Over a Range of Temperatures. Also shown, As Individual Points, Are Plant Data from the Literature [38].....   | 131 |
| Figure 4-21: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for T92 2,800 psi (192 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [39].....      | 131 |
| Figure 4-22: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) For E911 at 2,700 psi (186 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [40].....  | 132 |
| Figure 4-23: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for HCM9M at 2,785 psi (192 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [37]..... | 132 |
| Figure 4-24: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for HCM12 at 2,785 psi (192 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [37]..... | 133 |

Figure 4-25: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for T122 at 2,785 psi (192 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [37] ..... 133

Figure 4-26: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for 1714CuMo at 4,496 psi (310 bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [41] ..... 134

Figure 4-27: A Comparison of the Predicted Values of Inner Oxide Thickness (Curves) for X3CrNiMoBN 17-13-3 at 2,700 psi (186 Bar) Over a Range of Temperatures. Also Shown, As Individual Points, Are Plant Data from the Literature [40] ..... 134

Figure 4-28: Contour Plot Example for Alloy T22 at 1022°F (550°C) Showing the Predicted Inner Oxide Thickness as a Function of Time and Pressure ..... 135

## FOREWORD

This report provides a development of design rules for advanced power plant boilers that pertain to fireside corrosion, erosion and steam oxidation of boiler tubes. These boilers will operate at advanced steam conditions, include discussion of CO<sub>2</sub> capture and contain co-firing of biomass or waste materials.

The authors acknowledge, with deep appreciation, the activities of ASME ST-LLC and ASME staff and volunteers who have provided valuable technical input, advice and assistance with review of, commenting on, and editing of, this document.

Established in 1880, the American Society of Mechanical Engineers (ASME) is a professional not-for-profit organization with more than 135000 members and volunteers promoting the art, science and practice of mechanical and multidisciplinary engineering and allied sciences. ASME develops codes and standards that enhance public safety, and provides lifelong learning and technical exchange opportunities benefiting the engineering and technology community. Visit [www.asme.org](http://www.asme.org) for more information.

The ASME Standards Technology, LLC (ASME ST-LLC) is a not-for-profit Limited Liability Company, with ASME as the sole member, formed in 2004 to carry out work related to new and developing technology. The ASME ST-LLC mission includes meeting the needs of industry and government by providing new standards-related products and services, which advance the application of emerging and newly commercialized science and technology and providing the research and technology development needed to establish and maintain the technical relevance of codes and standards. Visit [www.stllc.asme.org](http://www.stllc.asme.org) for more information.

# **PART ONE - DESIGN GUIDELINES FOR PULVERIZED COAL BOILERS**

## 1 GENERAL OVERVIEW

The purpose of this document is to provide a set of Design Guidelines for boiler design engineers and others aimed at the minimization of the effects of fireside corrosion, particle impact erosion and steam-side oxidation on boiler tubing and other components of large, pulverized coal-fired boilers. Particular emphasis is placed on the boiler components considered to be at highest risk in advanced supercritical and ultra-supercritical boilers, i.e. the superheater and reheater tubing operating at metal surface temperatures up to approximately 1350°F (730°C).

Modern coal-fired steam power plants are required to incorporate the relevant advances in technology to improve efficiency and maximize power generated per unit of coal burned, and hence reduce the overall emissions of CO<sub>2</sub>. They should also be fitted with advanced combustion technologies and environmental control equipment to comply with mandated limits on the release levels of the prescribed pollutant species to air, land and water.

The pressure part materials are required to have the relevant high-temperature strength capabilities, and the heat transfer surfaces are exposed to increasingly aggressive hot flue gases. The available alloys are increasingly required to operate near to the limits of their capabilities. The boilers are also expected to have the capability of cyclic operation, and pressure parts are required to have the minimum possible wall thickness, to minimize thermal fatigue.

It is increasingly important, therefore, that the minimum tube dimensions, calculated according to the ASME Boiler & Pressure Vessel Code, are not overly conservative. This has implications for the accuracy of the input data used in the calculations and, for the first time, there is a requirement to provide estimates of the alloy thickness losses expected over the lifetime of the component, due to environmental factors, both on the fluid side and the fire side of the tubes.

In this report, the knowledge currently available on the modes of environmental degradation expected for pressure parts in advanced coal-fired boilers, and the expected metal loss rates have been examined. The available approaches for the quantification and mitigation of the associated metal loss have been analyzed to provide a set of guidelines for incorporation into ASME B&PV Code calculations.

The major factors considered are:

- Increasing final steam temperatures lead to increased rates of oxide growth on the internal surfaces of the pressure parts, and this can result in increased risks of premature component failure. The modes of failure include delamination and blistering of the oxide layers, and/or exfoliation with loss of oxide fragments capable of causing tube blockage. These can result in rapid local overheating. More generally, the increases in tube metal temperatures, associated with oxide growth, can have a significant effect on the overall rate of steam-side oxidation, and a negative impact on plant integrity.
- Fireside corrosion of the furnace wall tubes, superheater and reheater tubes, and other high-temperature components can be responsible for excessive rates of metal wastage and premature failure of boiler components. Conditions leading to acceleration of such wastage are directly related to the increased operating temperatures and to the changes to the fuels and combustion conditions and hence to the flue gas chemistry, which can combine to create increasingly corrosive environments.
- Erosive wear from ash particle impact wear of the fireside surfaces of the boiler tubes and other components can be a significant cause of metal loss. In addition to direct removal of metal, the erosion process may act to modify or accelerate fireside corrosion by removing ash deposit layers